

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

Method	Range of Applicability	Number of Atoms	Obtainable Properties	Methodological Characteristics
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

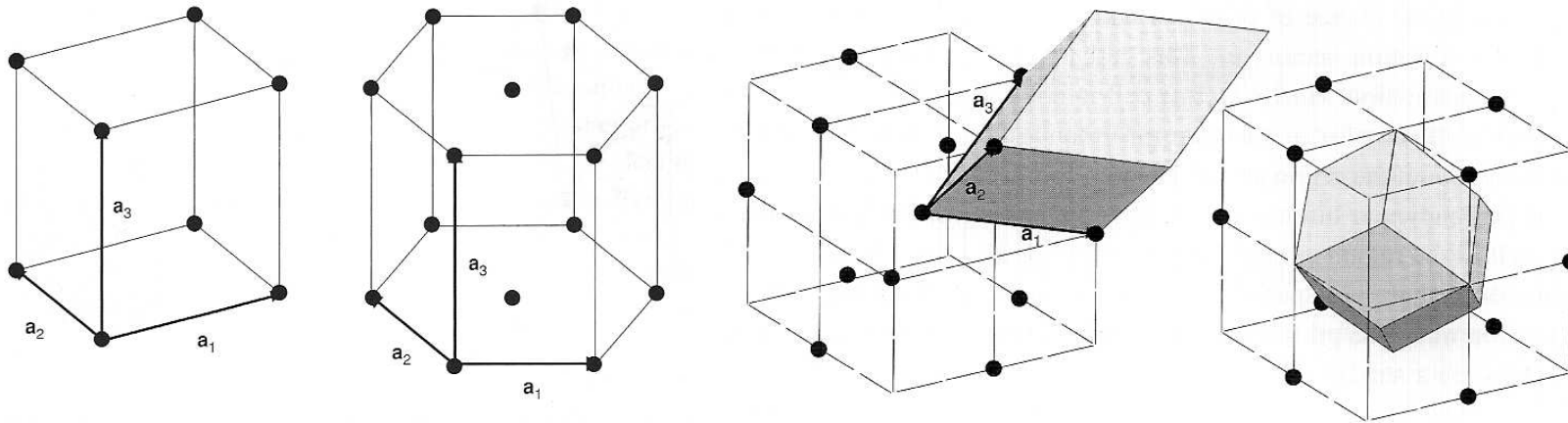
Method	Acronym	Systems	Atom types	Obtainable Properties	Methodological Characteristics
Pseudopotential plane wave		Periodic structures, metals, semi-conductors, insulators	All main group elements and transition metals; not well tested for rare-earth and actinides	Crystallographic structures, binding 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:

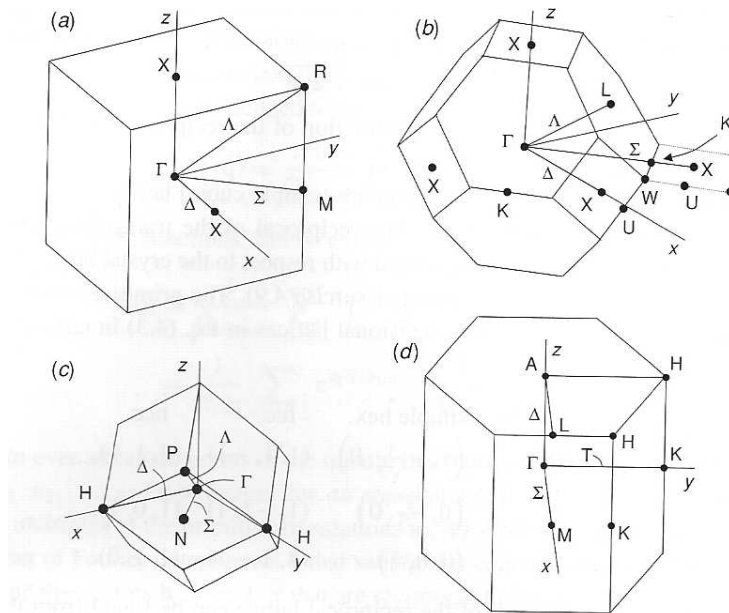
- Any translation of a Bravais lattice can be written as an integral multiple of primitive vectors

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

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

$$\mathbf{k} = \frac{n_1}{N_1} \mathbf{b}_1 + \frac{n_2}{N_2} \mathbf{b}_2 + \frac{n_3}{N_3} \mathbf{b}_3 \text{ and reciprocal lattice vector } \mathbf{K}, \text{ i.e. } \mathbf{q} = \mathbf{k} + \mathbf{K}. \text{ Here}$$

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 basis 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

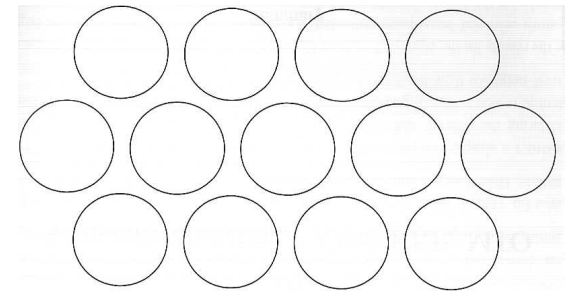
$$\left(-\tilde{\nabla}^2 - \frac{2Z}{\tilde{r}}\right)\psi = \tilde{\varepsilon}\psi. \quad (8)$$

Augmented Plane Wave Method (APW)

Is today probably most precise method in its full potential linearize form (Wien2k, Elk, etc.). It is hard to do Car-Parinelo molecular dynamics. Structural optimization is possible, but much more involved. While forces are implemented in most codes, the strain fields are mostly still missing. In plane wave codes all these extensions exists.

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

$$\chi_{\mathbf{k}+\mathbf{K}}^{APW}(\mathbf{r}) = \frac{1}{\sqrt{V}} \begin{cases} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}} & r > S \\ \sum_L C_L(\mathbf{k} + \mathbf{K}) \psi_L(\varepsilon, \mathbf{r}) & r < S \end{cases} \quad (10)$$

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

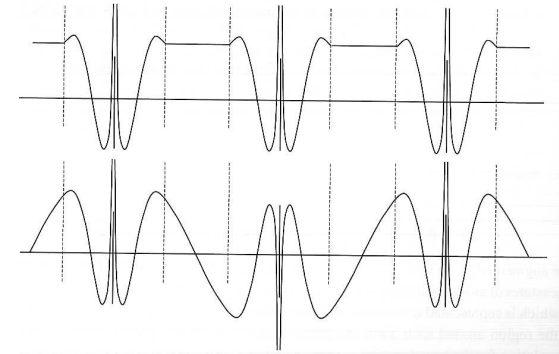
$$\psi_L(\varepsilon, \mathbf{r}) = i^L Y_L(\hat{\mathbf{r}}) \psi_l(\varepsilon, r)$$

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

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

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

The secular equation in APW basis takes the form

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

$$\sum_{\mathbf{K}} (H_{\mathbf{K}'\mathbf{K}} - \varepsilon_{\mathbf{k}} O_{\mathbf{K}'\mathbf{K}}) A_{\mathbf{K}} = 0. \quad (15)$$

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 basis functions are already solutions of the Schroedinger equation.

The interstitial region contributes

$$P_{\mathbf{K}'\mathbf{K}}^I = \int_I d\mathbf{r} e^{-i(\mathbf{k}+\mathbf{K}')\mathbf{r}} (H - \varepsilon_{\mathbf{k}}) e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} = \int_{V_{cell}} d\mathbf{r} e^{-i(\mathbf{k}+\mathbf{K}')\mathbf{r}} (H - \varepsilon_{\mathbf{k}}) e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} - \int_{r < S} d\mathbf{r} e^{-i(\mathbf{k}+\mathbf{K}')\mathbf{r}} (H - \varepsilon_{\mathbf{k}}) e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} \quad (16)$$

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

$$P_{\mathbf{K}'\mathbf{K}}^{I,1} = V_{cell} \left(\frac{1}{2} (\mathbf{k} + \mathbf{K})^2 + V_{KS}^I (\mathbf{K} - \mathbf{K}') - \varepsilon_{\mathbf{k}} \right) \delta_{\mathbf{K}\mathbf{K}'} \quad (17)$$

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

$$P_{\mathbf{K}'\mathbf{K}}^{I,2} = \left(\frac{1}{2} (\mathbf{k} + \mathbf{K})^2 + V_{KS}^I (\mathbf{K} - \mathbf{K}') - \varepsilon_{\mathbf{k}} \right) 4\pi \int_0^S j_0(|\mathbf{K} - \mathbf{K}'|r) r^2 dr \quad (18)$$

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

The interstitial contribution is therefore

$$P_{\mathbf{K}'\mathbf{K}}^I = \left(\frac{1}{2}(\mathbf{k} + \mathbf{K})^2 + V_{KS}^I(\mathbf{K} - \mathbf{K}') - \varepsilon_{\mathbf{k}} \right) \left(\delta_{\mathbf{K}\mathbf{K}'} - \frac{4\pi S^2 j_1(|\mathbf{K} - \mathbf{K}'|S)}{V_{cell}|\mathbf{K} - \mathbf{K}'|} \right) \quad (20)$$

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

$$\int_V \nabla[\chi_i^* \nabla \chi_j] d\mathbf{r} = \oint_{S_V} \chi_i^* \nabla \chi_j d\mathbf{S} = \int_V \nabla \chi_i^* \nabla \chi_j d\mathbf{r} + \int_V \chi_i^* \nabla^2 \chi_j d\mathbf{r} \quad (21)$$

Because the derivative of the wave function jumps, the second derivative at the MT-sphere is not well defined. Using Green's identity, we can turn the second derivative into the first derivative, which jumps, but is finite. By defining the kinetic energy as

$$T \equiv \frac{1}{2} \int_V \nabla \psi_{\mathbf{k}}^* \cdot \nabla \psi_{\mathbf{k}} = -\frac{1}{2} \int_V \psi_{\mathbf{k}}^* \nabla^2 \psi_{\mathbf{k}} + \frac{1}{2} \oint_{S_V} \psi_{\mathbf{k}}^* \nabla \psi_{\mathbf{k}} d\mathbf{S} \quad (22)$$

we remove the term with infinite second derivative. We can now divide the space into MT part and the interstitials. We can use ∇^2 form in each volume, but then we need to add the surface term at the muffin-tin sphere. Hence, we get an additional contribution to the

kinetic energy

$$P_{\mathbf{K}'\mathbf{K}}^{DDT} = \frac{1}{2}S^2 \int d\Omega \chi_{\mathbf{k}+\mathbf{K}'}^*(r=S, \hat{\mathbf{r}}) \left[\frac{\partial}{\partial r} \chi_{\mathbf{k}+\mathbf{K}}(r=S^-, \hat{\mathbf{r}}) - \frac{\partial}{\partial r} \chi_{\mathbf{k}+\mathbf{K}}(r=S^+, \hat{\mathbf{r}}) \right] \quad (23)$$

To evaluate this term, we first expand $\chi_{\mathbf{k}+\mathbf{K}'}^*(r=S, \hat{\mathbf{r}}) = \exp(-i(\mathbf{k} + \mathbf{K}')\mathbf{r})$ in spherical harmonics, as shown in Eq.12. An equivalent expansion over the spherical harmonics exists also for the terms in the square brackets. Next, because of the integral over the angle $\int d\Omega$ only the terms with $L = L'$ give nonvanishing contribution. This gives

$$P_{\mathbf{K}'\mathbf{K}}^{DDT} = \frac{1}{2}S^2 \sum_L 4\pi i^{-l} j_l(|\mathbf{k} + \mathbf{K}'|S) Y_L(\mathbf{k} + \mathbf{K}') \times \left[C_L(\mathbf{k} + \mathbf{K}) i^l \frac{\partial}{\partial r} \psi_l(\varepsilon, r) - \right. \quad (24)$$

$$\left. -4\pi i^l j_l(|\mathbf{k} + \mathbf{K}|S) Y_L^*(\mathbf{k} + \mathbf{K}) \frac{\partial}{\partial r} j_l(|\mathbf{k} + \mathbf{K}|r) \right]_{r=S} \quad (25)$$

We then also substitute the value of coefficients $C_L(\mathbf{k} + \mathbf{K})$, to obtain

$$P_{\mathbf{K}'\mathbf{K}}^{DDT} = \sum_L \frac{1}{2}S^2 (4\pi)^2 j_l(|\mathbf{k} + \mathbf{K}'|S) j_l(|\mathbf{k} + \mathbf{K}|S) Y_L(\hat{\mathbf{k}} + \hat{\mathbf{K}}') Y_L^*(\hat{\mathbf{k}} + \hat{\mathbf{K}}) \Delta D_{l,\mathbf{K}}/S \quad (26)$$

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

$$\Delta D_{l,\mathbf{K}} = S \left(\frac{\psi'_l(S)}{\psi_l(S)} - \frac{j'_l(|\mathbf{k} + \mathbf{K}|S)}{j_l(|\mathbf{k} + \mathbf{K}|S)} \right). \quad (27)$$

Using another well known relation

$$\sum_m Y_{lm}(\hat{\mathbf{q}}) Y_{lm}(\hat{\mathbf{q}}') = \frac{2l+1}{4\pi} P_l(\hat{\mathbf{q}} \cdot \hat{\mathbf{q}}') \quad (28)$$

we finally get

$$P_{\mathbf{K}'\mathbf{K}}^{DDT} = \frac{2\pi S}{V_{cell}} \sum_l (2l+1) j_l(|\mathbf{k} + \mathbf{K}'|S) j_l(|\mathbf{k} + \mathbf{K}|S) P_l((\hat{\mathbf{k}} + \hat{\mathbf{K}}') \cdot (\hat{\mathbf{k}} + \hat{\mathbf{K}})) \Delta D_{l,\mathbf{K}}. \quad (29)$$

Lets repeat the final set of equations:

$$P_{\mathbf{K}'\mathbf{K}}^{DDT} = \frac{2\pi S}{V_{cell}} \sum_l (2l+1) j_l(|\mathbf{k} + \mathbf{K}'|S) j_l(|\mathbf{k} + \mathbf{K}|S) P_l((\hat{\mathbf{k}} + \hat{\mathbf{K}}') \cdot (\hat{\mathbf{k}} + \hat{\mathbf{K}})) \Delta D_{l,\mathbf{K}}. \quad (30)$$

The secular equation of APW method reads

$$\sum_{\mathbf{K}} (H_{\mathbf{K}'\mathbf{K}} - \varepsilon_{\mathbf{k}} O_{\mathbf{K}'\mathbf{K}}) A_{\mathbf{K}} = 0 \quad (31)$$

where

$$O_{\mathbf{K}'\mathbf{K}} = \delta_{\mathbf{K}\mathbf{K}'} - \frac{4\pi S^2 j_1(|\mathbf{K} - \mathbf{K}'|S)}{V_{cell} |\mathbf{K} - \mathbf{K}'|} \quad (32)$$

$$H_{\mathbf{K}'\mathbf{K}} = \left(\frac{1}{2} (\mathbf{k} + \mathbf{K})^2 + V_{KS}^I (\mathbf{K} - \mathbf{K}') \right) O_{\mathbf{K}'\mathbf{K}} + P_{\mathbf{K}'\mathbf{K}}^{DDT} \quad (33)$$

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.,

$$\psi_l(\varepsilon, r) = \psi_l(E_\nu) + (\varepsilon - E_\nu) \frac{\partial}{\partial \varepsilon} \psi_l(E_\nu, r) \equiv \psi_l(E_\nu) + (\varepsilon - E_\nu) \dot{\psi}_l(E_\nu, r) \quad (34)$$

This energy derivative has very nice properties

- Since the 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 $\rightarrow \langle \dot{\psi}_l | \psi_l \rangle = 0$. (hint: $\frac{d}{d\varepsilon} (\langle \psi_l | \psi_l \rangle - 1) = 0$),

- The energy derivative $\dot{\psi}_l$ is clearly orthogonal to all core states, because

$$\langle \psi_c | H - \varepsilon | \dot{\psi}_l \rangle = \langle \psi_c | \dot{\psi}_l \rangle = 0 \quad (35)$$

$$(\varepsilon_c - \varepsilon) \langle \psi_c | \dot{\psi}_l \rangle = 0, \quad (36)$$

which is essential for the construction of correct basis.

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

$$\chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}} = \sum_L \frac{4\pi i^l}{\sqrt{V}} j_l(|\mathbf{k} + \mathbf{K}|r) Y_L^*(\hat{\mathbf{k}} + \hat{\mathbf{K}}) Y_L(\hat{\mathbf{r}}) & r > S \\ \sum_L Y_L(\hat{\mathbf{r}}) [a_L(\mathbf{k} + \mathbf{K}) \psi_l(r) + b_L(\mathbf{k} + \mathbf{K}) \dot{\psi}_l(r)] & r < S \end{cases} \quad (37)$$

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

energy E_ν

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_{KS}(r) - E_\nu\right) r \psi_l(r) = 0 \quad (38)$$

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_{KS}(r) - E_\nu\right) r \dot{\psi}_l(r) = r \psi_l(r) \quad (39)$$

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

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

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

$$\dot{\psi}_l(S) \frac{d}{dr} \psi_l(S) - \psi_l(S) \frac{d}{dr} \dot{\psi}_l(S) = \frac{2}{S^2} \quad (41)$$

To derive this, multiply the first equation by $r \dot{\psi}_l$ and the second by $r \psi_l$, subtract them, and integrate in the MT-sphere. Then use integration by parts, and you should obtain the above result.

This leads to the simplified expression

$$\begin{pmatrix} a_L \\ b_L \end{pmatrix} = \frac{2\pi i^l S^2}{\sqrt{V}} Y_{lm}^*(\hat{\mathbf{k}} + \hat{\mathbf{K}}) \begin{pmatrix} \dot{\psi}_l(S) \frac{d}{dr} j_l(|\mathbf{k} + \mathbf{K}|S) - \frac{d}{dr} \dot{\psi}_l(S) j_l(|\mathbf{k} + \mathbf{K}|S) \\ \frac{d}{dr} \psi_l(S) j_l(|\mathbf{k} + \mathbf{K}|S) - \psi_l(S) \frac{d}{dr} j_l(|\mathbf{k} + \mathbf{K}|S) \end{pmatrix} \quad (42)$$

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

$$\psi_{\mathbf{k}} = \sum_{\mathbf{K}} \chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) A_{\mathbf{K}}(\mathbf{k}) \quad (43)$$

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

$$\sum_{\mathbf{K}} \langle \chi_{\mathbf{K}'+\mathbf{k}} | H - \varepsilon_{\mathbf{k}} | \chi_{\mathbf{K}+\mathbf{k}} \rangle A_{\mathbf{K}}(\mathbf{k}) = 0. \quad (44)$$

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

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

$$\sum_{\mathbf{K}} (\langle \chi_{\mathbf{K}'+\mathbf{k}} | H - E_{\nu} | \chi_{\mathbf{K}+\mathbf{k}} \rangle - \varepsilon'_{\mathbf{k}} \langle \chi_{\mathbf{K}'+\mathbf{k}} | \chi_{\mathbf{K}+\mathbf{k}} \rangle) A_{\mathbf{K}}(\mathbf{k}) = 0. \quad (45)$$

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

$$\begin{aligned}
 H_{\mathbf{K}'\mathbf{K}}^{MT} &= \sum_L \langle a_L(\mathbf{k} + \mathbf{K}')\psi_l + b_L(\mathbf{k} + \mathbf{K}')\dot{\psi}_l | H - E_\nu | a_L(\mathbf{k} + \mathbf{K})\psi_l + b_L(\mathbf{k} + \mathbf{K})\dot{\psi}_l \rangle \\
 &= \sum_L a_L^*(\mathbf{k} + \mathbf{K}')b_L(\mathbf{k} + \mathbf{K}) \\
 \Rightarrow &\frac{1}{2} \sum_L a_L^*(\mathbf{k} + \mathbf{K}')b_L(\mathbf{k} + \mathbf{K}) + b_L^*(\mathbf{k} + \mathbf{K}')a_L(\mathbf{k} + \mathbf{K}) \quad (46)
 \end{aligned}$$

Here we symmetrized the Hamiltonian, because it must be Hermitian. Using relation Eq. (28), we can further simplify

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

where

$$a_{l,\mathbf{K}} = \dot{\psi}_l(S) \frac{d}{dr} j_l(|\mathbf{k} + \mathbf{K}|S) - \frac{d}{dr} \dot{\psi}_l(S) j_l(|\mathbf{k} + \mathbf{K}|S) \quad (47)$$

$$b_{l,\mathbf{K}} = \frac{d}{dr} \psi_l(S) j_l(|\mathbf{k} + \mathbf{K}|S) - \psi_l(S) \frac{d}{dr} j_l(|\mathbf{k} + \mathbf{K}|S) \quad (48)$$

For the overlap we similarly obtain

$$O_{\mathbf{K}'\mathbf{K}}^{MT} = \frac{\pi S^4 (2l + 1)}{V} \sum_l P_l((\hat{\mathbf{K}}' + \hat{\mathbf{k}}) \cdot (\hat{\mathbf{K}} + \hat{\mathbf{k}})) (a_{l,\mathbf{K}'} a_{l,\mathbf{K}} + b_{l,\mathbf{K}} b_{l,\mathbf{K}'} \langle \dot{\psi} | \dot{\psi} \rangle) \quad (49)$$

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

$$\begin{aligned}
 H_{\mathbf{K}'\mathbf{K}}^I &= \frac{1}{V} \int d\mathbf{r} e^{-i(\mathbf{k}+\mathbf{K}')\mathbf{r}} \left(-\frac{1}{2} \nabla^2 + V^I(\mathbf{r}) - E_\nu \right) e^{i(\mathbf{K}+\mathbf{k})\mathbf{r}} & (50) \\
 &= \left(\frac{1}{2} (\mathbf{k} + \mathbf{K})^2 - E_\nu \right) \int \frac{d\mathbf{r}}{V} e^{i(\mathbf{K}-\mathbf{K}')\mathbf{r}} + \sum_{\mathbf{Q}} V_{\mathbf{Q}}^I \int \frac{d\mathbf{r}}{V} e^{i(\mathbf{K}-\mathbf{K}'-\mathbf{Q})\mathbf{r}} = \\
 &= \left(\frac{1}{2} (\mathbf{k} + \mathbf{K})^2 - E_\nu \right) \left(\delta_{\mathbf{K}\mathbf{K}'} - \frac{4\pi S^2 j_1(|\mathbf{K} - \mathbf{K}'|S)}{V_{cell} |\mathbf{K} - \mathbf{K}'|} \right) & (51) \\
 &+ \sum_{\mathbf{Q}} V_{\mathbf{Q}}^I \left(\delta_{\mathbf{K}-\mathbf{K}'-\mathbf{Q}} - \frac{4\pi S^2 j_1(|\mathbf{K} - \mathbf{K}' - \mathbf{Q}|S)}{V_{cell} |\mathbf{K} - \mathbf{K}' - \mathbf{Q}|} \right)
 \end{aligned}$$

The overlap in the interstitials is simply

$$O_{\mathbf{K}'\mathbf{K}}^I = \left(\delta_{\mathbf{K}\mathbf{K}'} - \frac{4\pi S^2 j_1(|\mathbf{K} - \mathbf{K}'|S)}{V_{cell} |\mathbf{K} - \mathbf{K}'|} \right) \quad (52)$$

Notice that the second part of the $H_{\mathbf{K}'\mathbf{K}}^I$ is a convolution of the KS-potential $V_{\mathbf{Q}}^I$ and the

overlap, i.e.,

$$\sum_{\mathbf{Q}} V_{\mathbf{Q}}^I \left(\delta_{\mathbf{K}-\mathbf{K}'-\mathbf{Q}} - \frac{4\pi S^2 j_1(|\mathbf{K}-\mathbf{K}'-\mathbf{Q}|S)}{V_{cell} |\mathbf{K}-\mathbf{K}'-\mathbf{Q}|} \right) = \sum_{\mathbf{Q}} V_{\mathbf{Q}}^I O_{\mathbf{K}-\mathbf{K}'-\mathbf{Q}} \quad (53)$$

and can be computed by the fast-Fourier technique.

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

$$\sum_{\mathbf{K}} (H_{\mathbf{K}'\mathbf{K}} - \varepsilon'_{\mathbf{K}} O_{\mathbf{K}'\mathbf{K}}) A_{\mathbf{K}} = 0 \quad (54)$$

$$O_{\mathbf{K}'\mathbf{K}} = O_{\mathbf{K}'\mathbf{K}}^I + \sum_l \mathcal{P}_l^{\mathbf{k}}(\mathbf{K}', \mathbf{K}) (\mathbf{a}_{l,\mathbf{K}'} \mathbf{a}_{l,\mathbf{K}} + \mathbf{b}_{l,\mathbf{K}'} \mathbf{b}_{l,\mathbf{K}} \langle \dot{\psi}_l | \dot{\psi}_l \rangle) \quad (55)$$

$$H_{\mathbf{K}'\mathbf{K}} = H_{\mathbf{K}'\mathbf{K}}^I + \sum_l \mathcal{P}_l^{\mathbf{k}}(\mathbf{K}', \mathbf{K}) \frac{1}{2} (\mathbf{a}_{l,\mathbf{K}'} \mathbf{b}_{l,\mathbf{K}} + \mathbf{a}_{l,\mathbf{K}} \mathbf{b}_{l,\mathbf{K}'}) \quad (56)$$

$$O_{\mathbf{K}'\mathbf{K}}^I = \delta_{\mathbf{K}\mathbf{K}'} - \frac{4\pi S^2 j_1(|\mathbf{K} - \mathbf{K}'|S)}{V_{cell} |\mathbf{K} - \mathbf{K}'|} \quad (57)$$

$$H_{\mathbf{K}'\mathbf{K}}^I = \left\{ \frac{1}{4} [(\mathbf{k} + \mathbf{K})^2 + (\mathbf{k} + \mathbf{K}')^2] - E_{\nu} \right\} O_{\mathbf{K}'\mathbf{K}}^I + [V^I * O^I]_{\mathbf{K}'\mathbf{K}} \quad (58)$$

$$\mathcal{P}_l^{\mathbf{k}}(\mathbf{K}', \mathbf{K}) = \frac{\pi(2l+1)S^4}{V_{cell}} P_l((\hat{\mathbf{K}}' + \hat{\mathbf{k}}) \cdot (\hat{\mathbf{K}} + \hat{\mathbf{k}})) \quad (59)$$

$$\mathbf{a}_{l,\mathbf{K}} = \dot{\psi}_l(S) \frac{d}{dr} j_l(|\mathbf{k} + \mathbf{K}|S) - \frac{d}{dr} \dot{\psi}_l(S) j_l(|\mathbf{k} + \mathbf{K}|S) \quad (60)$$

$$\mathbf{b}_{l,\mathbf{K}} = \frac{d}{dr} \psi_l(S) j_l(|\mathbf{k} + \mathbf{K}|S) - \psi_l(S) \frac{d}{dr} j_l(|\mathbf{k} + \mathbf{K}|S) \quad (61)$$

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. We know that the Hamiltonian must eventually appear Hermitian, but rather than relying on numerics, we explicitly symmetrized the equations.

Chemical potential

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

$$N/2 = \sum_{\mathbf{k},p} f(\varepsilon_{\mathbf{k}p} - \mu) \quad (62)$$

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

$$\psi_{\mathbf{k}p}(\mathbf{r}) = \sum_{\mathbf{K}} A_{\mathbf{K}}^p(\mathbf{k}) \chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) \quad (63)$$

the electron density takes the form

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}p} f(\varepsilon_{\mathbf{k}p} - \mu) |\psi_{\mathbf{k}p}|^2 = \sum_{\mathbf{k}p} f(\varepsilon_{\mathbf{k}p} - \mu) \sum_{\mathbf{K}\mathbf{K}'} A_{\mathbf{K}'}^{p*}(\mathbf{k}) A_{\mathbf{K}}^p(\mathbf{k}) \chi_{\mathbf{k}+\mathbf{K}'}^*(\mathbf{r}) \chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r})$$

$$\equiv \sum_L Y_L(\mathbf{r}) \sum_{\mathbf{k}p} f(\varepsilon_{\mathbf{k}p} - \mu) \sum_{\mathbf{K}\mathbf{K}'} A_{\mathbf{K}'}^{p*}(\mathbf{k}) w_{\mathbf{K}\mathbf{K}'}(\mathbf{k}, L, r) A_{\mathbf{K}}^p(\mathbf{k}) \quad (64)$$

Inside the MT sphere, we can expand the charge in terms of spherical harmonics

$$w_{\mathbf{K}\mathbf{K}'}^{MT}(\mathbf{k}, L, r) = \int \frac{d\Omega}{4\pi} \chi_{\mathbf{k}+\mathbf{K}'}^*(\mathbf{r}) Y_L^*(\mathbf{r}) \chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) \quad (65)$$

resulting in

$$w_{\mathbf{K}\mathbf{K}'}^{MT}(\mathbf{k}, r, L) = \int \frac{d\Omega}{4\pi} \langle (a_{L_1}^{\mathbf{K}'} \psi_{l_1} + b_{L_1}^{\mathbf{K}'} \dot{\psi}_{l_1}) Y_{L_1} | Y_L | (a_{L_2}^{\mathbf{K}} \psi_{l_2} + b_{L_2}^{\mathbf{K}} \dot{\psi}_{l_2}) Y_{L_2} \rangle \quad (66)$$

This can be conveniently expressed in terms of Gaunt-coefficients $\langle Y_{L_1} | Y_L | Y_{L_2} \rangle$ and corresponding matrix elements.

Here we will concentrate only on the spherical symmetric part, because we will make an approximation that the charge inside MT-sphere is spherically symmetric (this is not very good approximation in general, but is quite OK for simple metals like Cu). In the simplified spherical approximation we get:

$$w_{\mathbf{K}\mathbf{K}'}^{MT}(\mathbf{k}, r, 0) = \frac{1}{4\pi} \mathcal{P}_l^{\mathbf{k}}(\mathbf{K}', \mathbf{K}) [a_{l, \mathbf{K}'} \psi_l(r) + b_{l, \mathbf{K}'} \dot{\psi}_l(r)] [a_{l, \mathbf{K}} \psi_l(r) + b_{l, \mathbf{K}} \dot{\psi}_l(r)] \quad (67)$$

The interstitial region contributes

$$w_{\mathbf{K}\mathbf{K}'}^I(\mathbf{k}, \mathbf{r}) = \frac{1}{V} e^{i(\mathbf{K}-\mathbf{K}')\mathbf{r}} \quad (68)$$

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

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}p, \mathbf{K}\mathbf{K}'} f(\varepsilon_{\mathbf{k}p} - \mu) A_{\mathbf{K}'}^{p*}(\mathbf{k}) w_{\mathbf{K}\mathbf{K}'}(\mathbf{k}, \mathbf{r}) A_{\mathbf{K}}^p(\mathbf{k}) \quad (69)$$

which can also be written as

$$\rho(\mathbf{r}) = -\frac{1}{\pi} \text{Im} \int d\omega f(\omega) \sum_{\mathbf{k}p, \mathbf{K}\mathbf{K}'} \frac{\sum_{\mathbf{K}\mathbf{K}'} A_{\mathbf{K}'}^{p*}(\mathbf{k}) w_{\mathbf{K}\mathbf{K}'}(\mathbf{k}, \mathbf{r}) A_{\mathbf{K}}^p(\mathbf{k})}{\omega + \mu - \varepsilon_{\mathbf{k}p}} \quad (70)$$

For actual calculation, it is good idea to separate radial loop from the 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

$$w_{\mathbf{k}pl}^{(0)} = \sum_{\mathbf{K}\mathbf{K}'} A_{\mathbf{K}'}^{*p}(\mathbf{k}) a_{l, \mathbf{K}'} \mathcal{P}_l^{\mathbf{k}}(\mathbf{K}', \mathbf{K}) a_{l, \mathbf{K}} A_{\mathbf{K}}^p(\mathbf{k}) \quad (71)$$

$$w_{\mathbf{k}pl}^{(1)} = \sum_{\mathbf{K}\mathbf{K}'} A_{\mathbf{K}'}^{*p}(\mathbf{k}) a_{l, \mathbf{K}'} \mathcal{P}_l^{\mathbf{k}}(\mathbf{K}', \mathbf{K}) b_{l, \mathbf{K}} A_{\mathbf{K}}^p(\mathbf{k}) + \sum_{\mathbf{K}\mathbf{K}'} A_{\mathbf{K}'}^{*p}(\mathbf{k}) b_{l, \mathbf{K}'} \mathcal{P}_l^{\mathbf{k}}(\mathbf{K}', \mathbf{K}) a_{l, \mathbf{K}} A_{\mathbf{K}}^p(\mathbf{k}) \quad (72)$$

$$w_{\mathbf{k}pl}^{(2)} = \sum_{\mathbf{K}\mathbf{K}'} A_{\mathbf{K}'}^{*p}(\mathbf{k}) b_{l, \mathbf{K}'} \mathcal{P}_l^{\mathbf{k}}(\mathbf{K}', \mathbf{K}) b_{l, \mathbf{K}} A_{\mathbf{K}}^p(\mathbf{k}) \quad (73)$$

$$w_{\mathbf{k}p}^{(I)} = \sum_{\mathbf{K}\mathbf{K}'} A_{\mathbf{K}'}^{*p}(\mathbf{k}) O_{\mathbf{K}'\mathbf{K}}^I A_{\mathbf{K}}^p(\mathbf{k}) \quad (74)$$

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

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

$$w_l^{(x)} = \sum_{\mathbf{k}p} f(\varepsilon_{\mathbf{k}p} - \mu) w_{\mathbf{k}pl}^{(x)} \quad (75)$$

and the electron charge can finally be obtained by

$$\rho^{MT}(r) = \frac{2}{4\pi} \sum_l w_l^{(0)} \psi_l(r) \psi_l(r) + w_l^{(1)} \psi_l(r) \dot{\psi}_l(r) + w_l^{(2)} \dot{\psi}_l(r) \dot{\psi}_l(r) \quad (76)$$

$$\rho^I(r) = \frac{1}{V_{interstitial}} w^{(I)} \quad (77)$$

Here 2 is due to spin.

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

$$(a, b, c) \rightarrow (-a, b, c), (a, -b, c), \dots (b, a, c), (-c, -b, a) \quad (78)$$

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

$$\text{Im} \sum_{\mathbf{k}} \int_{-\infty}^{\mu} d\omega \frac{C_{\mathbf{k}}}{\omega - \varepsilon_{\mathbf{k}}} \quad (79)$$

and for density of states the form is

$$\text{Im} \sum_{\mathbf{k}} \frac{C_{\mathbf{k}}}{\omega - \varepsilon_{\mathbf{k}}} \quad (80)$$

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

$$\text{Im} \sum_{\mathbf{k}} \frac{C_{\mathbf{k}}}{\omega - \varepsilon_{\mathbf{k}}} = \sum_{\text{tetrahedra}} \int_{\text{tetrahedra}} d^3\mathbf{k} \frac{C_{\mathbf{k}}}{\omega - \varepsilon_{\mathbf{k}}} \quad (81)$$

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

$$\int_{\text{tetrahedra}} d^3\mathbf{k} \frac{C_{\mathbf{k}}}{\omega - \varepsilon_{\mathbf{k}}} \quad (82)$$

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

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

$$r_i = 6 \int_0^1 dc \int_0^{1-c} db \int_0^{1-b-c} da \frac{(1 - a - b - c)\delta_{i,1} + a\delta_{i,2} + b\delta_{i,3} + c\delta_{i,4}}{\omega - E_1 - a(E_2 - E_1) - b(E_3 - E_1) - c(E_4 - E_1)} \quad (83)$$

and for density

$$q_i = 6 \int_{-\infty}^{\mu} d\omega \int_0^1 dc \int_0^{1-c} db \int_0^{1-b-c} da \frac{(1 - a - b - c)\delta_{i,1} + a\delta_{i,2} + b\delta_{i,3} + c\delta_{i,4}}{\omega - E_1 + a(E_2 - E_1) + b(E_3 - E_1) + c(E_4 - E_1)} \quad (84)$$

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

$$r_i = \sum_{j \neq i} \frac{\omega - E_j}{\prod_{k \neq i, j} (E_k - E_j)} \text{lv} \left(\frac{\omega - E_j}{E_j - E_i} \right) \quad (85)$$

where

$$\text{lv}(x) = x \left[1 - x \log \left(1 + \frac{1}{x} \right) \right] \quad (86)$$

$$q_1 = \begin{cases} \frac{1}{4} & \omega > E_1 \\ \frac{\Theta(E_2 < \omega < E_1) \omega_2^4}{4E_{12}^2 E_{32} E_{42}} + \frac{\Theta(E_3 < \omega < E_1) \omega_3^4}{4E_{13}^2 E_{23} E_{43}} + \frac{\Theta(E_4 < \omega < E_1) \omega_4^4}{4E_{14}^2 E_{24} E_{34}} & \omega < E_1 \end{cases} \quad (87)$$

$$q_2 = \begin{cases} \frac{1}{4} & \omega > E_2 \\ \frac{\Theta(E_3 < \omega < E_2) \omega_3^4}{4E_{23}^2 E_{43} E_{13}} + \frac{\Theta(E_4 < \omega < E_2) \omega_4^4}{4E_{24}^2 E_{34} E_{14}} + \frac{\Theta(E_1 < \omega < E_2) \omega_1^4}{4E_{21}^2 E_{31} E_{41}} & \omega < E_2 \end{cases} \quad (88)$$

$$q_3 = \begin{cases} \frac{1}{4} & \omega > E_3 \\ \frac{\Theta(E_4 < \omega < E_3) \omega_4^4}{4E_{34}^2 E_{14} E_{24}} + \frac{\Theta(E_1 < \omega < E_3) \omega_1^4}{4E_{31}^2 E_{41} E_{21}} + \frac{\Theta(E_2 < \omega < E_3) \omega_2^4}{4E_{32}^2 E_{42} E_{12}} & \omega < E_3 \end{cases} \quad (89)$$

$$q_4 = \begin{cases} \frac{1}{4} & \omega > E_4 \\ \frac{\Theta(E_1 < \omega < E_4) \omega_1^4}{4E_{41}^2 E_{21} E_{31}} + \frac{\Theta(E_2 < \omega < E_4) \omega_2^4}{4E_{42}^2 E_{12} E_{32}} + \frac{\Theta(E_3 < \omega < E_4) \omega_3^4}{4E_{43}^2 E_{13} E_{23}} & \omega < E_4 \end{cases} \quad (90)$$

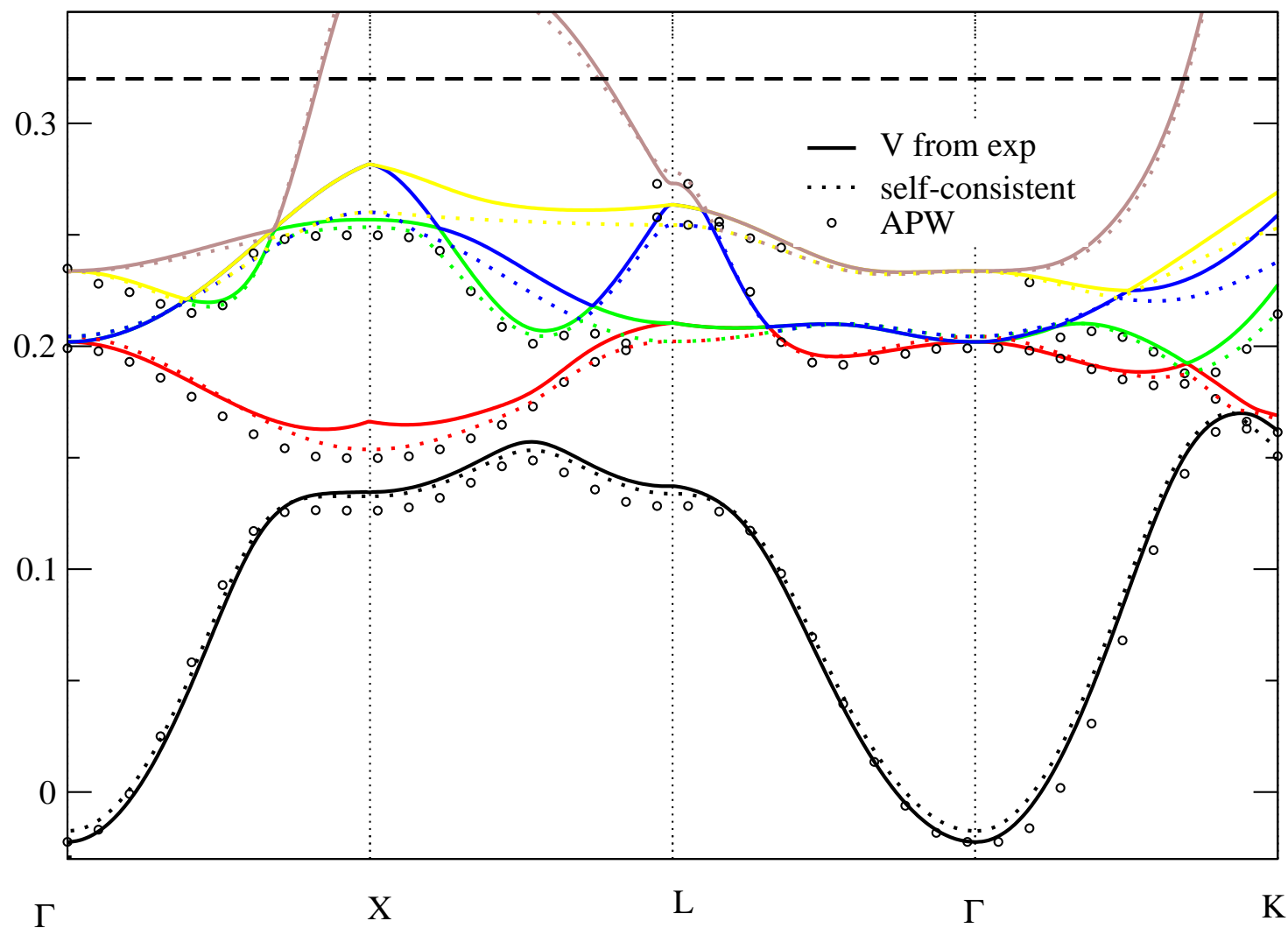
Here we used $\omega_i = \omega - E_i$, $E_{ij} = E_i - E_j$.

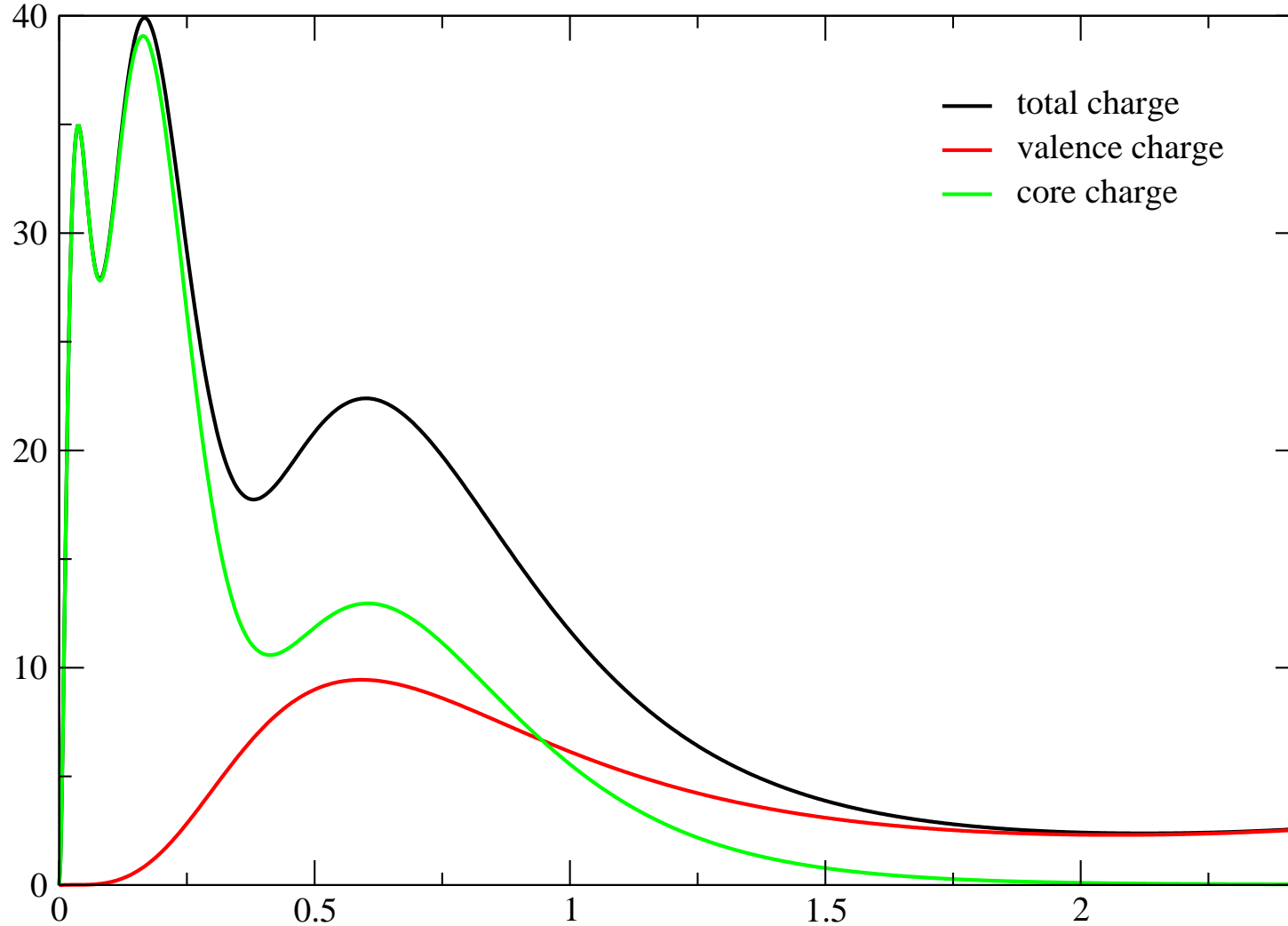
1 Putting it all together

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.