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THEORETICAL FORMALISM
AND METHODOLOGY
Chapter - 2

Theoretical formalism and methodology

In this chapter, we will discuss the theory, methods and approximations used in the calculations of DOS, band structures and magnetic moments.

2.1 Density Functional Theory:

Density functional theory (DFT) is a quantum mechanical theory for calculating the electronic structure of a many body systems. DFT is one the most widely used technique obtainable on computational condensed matter physics (Hohenberg and Kohn, 1964; Kohn and Sham, 1965), due to its applicability to large numbers of electron with complete precision. The principle of DFT is to explore an interacting many body system of fermions by using its density instead of many-body wave function. Although DFT has its theoretical roots in the Thomas-Fermi model, it was put on a solid hypothetical foundation by two Hohenberg-Kohn theorems (H-K) (Hohenberg and Kohn, 1964).

The ground state properties of a many-electron system are exclusively determined by an electron density that depends only on 3 spatial coordinates. The first H-K theorem thus reduces the many body problems of N electrons with 3N spatial coordinates by employing functional of the electron density. The second H-K theorem defines energy functional of the system and gives evidences to prove that the proper ground state density minimizes this energy functional. Thus, intractable many-body problem of interacting electrons in a static external potential, within the framework of Kohn-Sham DFT (KS-DFT) is reduced to a tractable problem of non-interacting electrons moving in an effective potential. The effective potential contains the external potential and the effects of Coulomb interactions between the electrons, the exchange and correlation interactions. Modeling the latter two interactions becomes the challenge within KS-DFT.
2.2 Theoretical details:

The nuclei of the many body system in an electronic structure calculations are seen as fixed (the Born Oppenheimer approximation), generating a static external state is represented by a wave function $\Psi(\vec{r}_1,\ldots,\vec{r}_N)$ satisfying the many-electron Schrödinger equation:

$$\hat{H} \Psi = \left[ \hat{T} + \hat{V} + \hat{U} \right] \Psi = \left[ \sum_i -\frac{\hbar^2}{2m} \nabla_i^2 + \sum_i V(\vec{r}_i) + \sum_i U(\vec{r}_i,\vec{r}_j) \right] \Psi = E \Psi \quad (2.1)$$

$$n(\vec{r}) = N \int d^3 r_1 \int d^3 r_2 \ldots \int d^3 r_N \Psi^*(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) \Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$$

where $\hat{H}$ is the electronic Hamiltonian, $N$ is the number of electrons, $\hat{T}$ is the N-electron kinetic energy, $\hat{V}$ is the N-electron potential energy from the external field, $\hat{U}$ is the electron-electron interaction energy for the N-electron system. The operators $\hat{T}$ and $\hat{U}$ are common for similar systems, so are called Universal operators. $\hat{V}$ is system dependent, so is non-universal. Now the difference between a single particle problem and the much more complex many particle problem is the interaction term $\hat{U}$. DFT provides a way to systematically map the many-body problem with $\hat{U}$ onto a single particle problem without $\hat{U}$. In DFT the particle density $n(\vec{r})$ for a normalized $\Psi$ is given by:

$$n(\vec{r}) = N \int d^3 r_1 \int d^3 r_2 \ldots \int d^3 r_N \Psi^*(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) \Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) \quad (2.2)$$

In reverse way, this relation states that for a given ground-state density $n_0(\vec{r})$ it is possible to construct the corresponding ground-state wave-function $\Psi_0(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$. In other words $\Psi_0(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$ is a functional of $n_0(\vec{r})$ and hence the ground state expectation values of an observable $\hat{O}$ is also a functional of $n_0(\vec{r})$.

$$O[n_0] = \left\langle \Psi[n_0] \left| \hat{T} + \hat{V} + \hat{U} \right| \Psi[n_0] \right\rangle \quad (2.3)$$
In particular, the ground state energy is a functional of \( n_0(\vec{r}) \)

\[
E_0 = E_0[n_0] = \left< \Psi[n_0] \right| \hat{T} + \hat{\mathcal{V}} + \hat{\mathcal{U}} \left| \Psi[n_0] \right>
\]

(2.4)

\[
= \left< \Psi[n_0] \right| \hat{T} \left| \Psi[n_0] \right> + \left< \Psi[n_0] \right| \hat{\mathcal{V}} \left| \Psi[n_0] \right> + \left< \Psi[n_0] \right| \hat{\mathcal{U}} \left| \Psi[n_0] \right>
\]

(2.5)

\[
= \mathcal{T}[n_0] + \mathcal{V}[n_0] + \mathcal{U}[n_0]
\]

(2.6)

where the contribution of the external \( \left< \Psi[n_0] \right| \hat{\mathcal{V}} \left| \Psi[n_0] \right> \) potential can be written in terms of the ground-state density \( n_0 \)

\[
\mathcal{V}[n_0] = \int \mathcal{V}(\vec{r}) n_0(\vec{r}) d^3 r
\]

(2.7)

More commonly, the contribution of the external potential \( \left< \Psi \right| \hat{\mathcal{V}} \left| \Psi \right> \) can be written clearly in terms of the density \( n \) as

\[
\mathcal{V}[n] = \int \mathcal{V}(\vec{r}) n(\vec{r}) d^3 r
\]

(2.8)

A system is defined by a definite non-universal functional \( \mathcal{V} \), as \( \mathcal{T}[n] \) and \( \mathcal{U}[n] \) are universal.

For a given system with \( \mathcal{V} \) as its external potential

\[
E[n] = \mathcal{T}[n] + \mathcal{U}[n] + \int \mathcal{V}(\vec{r}) n(\vec{r}) d^3 r
\]

(2.9)

In regard to \( n(\vec{r}) \), taking for granted one has got dependable terms for \( \mathcal{T}[n] \) and \( \mathcal{U}[n] \).

A successful reduction of the energy functional will produce the ground state density \( n_0(\vec{r}) \) and thus all other ground state observables.

The second KS-theorem makes it possible to use the variational principle of Rayleigh-Ritz in order to find the ground-state density. Out of the infinite number of
possible densities, the one which minimizes $E[n]$ is the ground-state density corresponding to the external potential $V(\vec{r})$. Of course, this can be done only if (an approximation to) \( \langle \Psi[n]\| T + \hat{V} \| \Psi[n] \rangle \) is known. But having found $n(\vec{r})$, all knowledge about the system is within reach.

It is useful to stress the meaning of the energy functional $E[n]$ once more. When it is evaluated for the density $n(\vec{r})$ corresponding to the particular $V(\vec{r})$ for this solid, it gives the ground state energy. When it is evaluated for any other density however, the resulting number has no physical meaning (Cottenier, 2002).

Taking the energy functional without electron-electron interaction energy term

$$E_s[n] = \langle \Psi_S[n] \| \hat{T}_S + V_S \| \Psi_S[n] \rangle$$  \hspace{1cm} (2.10)

where $\hat{T}_S$ indicates the non-interacting kinetic energy and $\hat{V}_S$ is an external effectual potential in which the particles are moving. Clearly, if $\hat{V}_S$ is $n_S(\vec{r}) = n(\vec{r})$ selected be

$$\hat{V}_S = \hat{V} + \hat{U} + (\hat{T} - \hat{T}_S)$$  \hspace{1cm} (2.11)

Consequently, we can solve the Kohn-Sham equations of this assisting non-interacting system,

$$-\frac{\hbar^2}{2m} \nabla^2 + V_S(\vec{r}) \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r})$$  \hspace{1cm} (2.12)

which produces the $\phi_i$ orbital that reproduces the density $n(\vec{r})$ of the authentic many-body system

$$n(\vec{r}) = n_S(\vec{r}) = \sum_{i=1}^{N} |\phi_i(\vec{r})|^2$$  \hspace{1cm} (2.13)

The effective single-particle potential can be written in more detail as
\[ V_S(\vec{r}) = V(\vec{r}) + \int \frac{e^2 n_S(\vec{r})}{|\vec{r} - \vec{r}'|} d^3 r' + V_{xc}[n_S(\vec{r})] \]  \hspace{1cm} (2.14)

The second term in the above Eq. (2.14) stands for the so-called Hartree expression with the electron-electron Coulomb repulsion, while the last expression \( V_{xc} \) is called the exchange correlation potential. Now, the Hartree expression and \( V_{xc} \) depend on \( n(\vec{r}) \) which depends on the \( \phi_i \) which in turn relies on \( \hat{V}_S \). Now the problem is that the Kohn-Sham equation has to be solved in a self-consistent way. One typically begins with a first guess \( n(\vec{r}) \) then works out the corresponding \( \hat{V}_S \) and solves the Kohn-Sham equations for the \( \phi_i \) (Kohn and Sham, 1965). The techniques in DFT are complex and different and can be understood by considering the following two approaches.

Firstly the techniques that apply a local density rough calculation (LDA). The LDA is decided exclusively and based on the qualities of the electron density. The significant supposition of this approximation is that for a molecule with many electrons in a gaseous state, the density is consistent throughout the molecule. This is not the case for molecules where the electron density is decidedly not consistent. This approximation does however work well with electronic band structure of solids and hence illustrates the scope of energies in which electrons are allowed or not allowed. Outside of these applications, however, LDA’s are not very acceptable.

Secondly, the technique that unites the electron density calculations with a gradient correction factor. A gradient in mathematics is a function that measures the rate of change of some property. In this case, the gradient seems to explain the non-uniformity of the electron density, and as such is known as gradient-corrected.
2.3 Kohn-Sham Equation:

Since the total energy of the system is

\[ E(n) = T(n) + \int V_{ext}(r)n(r)dr + V_n[n] + E_{XC}[n] \]  \hspace{1cm} (2.15)

where \( T \) is the kinetic energy of the system, \( V_{ext} \) is an external potential acting on the system, and

\[ V_n = \frac{e^2}{2} \int \frac{n(r)n(r')}{|r - r'|}dr dr' \]  \hspace{1cm} (2.16)

is the Hartree energy and \( E_{XC} \) is the exchange-correlation energy.

The straightforward application of this formula has two barriers: First, the exchange-correlation energy \( E_{XC} \) is not known precisely, and second, the kinetic term must be created in terms of the charge density. As was first suggested by Kohn and Sham (1965), the charge density \( n(r) \) can be written as the sum of the squares of a set of orthonormal wave functions \( \phi_i(r) \):

\[ n(r) = \sum_{i}^{N} |\phi_i(r)|^2 \]  \hspace{1cm} (2.17)

Equation (2.17) represents the solution to the Schrodinger equation for \( N \) non-interacting electrons moving in an effectual potential \( V_{eff}(r) \) given by

\[ -\frac{\hbar^2}{2m} \nabla^2 \phi_i(r) + V_{eff}(r)\phi_i(r) = \varepsilon_i \phi_i(r) \]  \hspace{1cm} (2.18)

where the effectual potential is defined to be

\[ V_{eff}(r) = V_{ext}(r) + e^2 \int \frac{n(r')}{|r - r'|}dr' + \frac{\delta E_{XC}[n]}{\delta n} \]  \hspace{1cm} (2.19)
This system is then solved iteratively until self-consistency is approached. Note that the eigen values $\varepsilon_i$ have no physical meaning but the total sum matches the energy of the entire system $E$ through the equation:

$$E = \sum_{i}^{N} \varepsilon_i - V_{\mu} \left[ n \right] + E_{xc} \left[ n \right] - \int \frac{\delta E_{xc} \left[ n \right]}{\delta n(r)} n(r) dr$$  \hspace{1cm} (2.20)

There are several ways in which Kohn-Sham theory can be applied depending on what is being examined. In solid state calculations, the local density approximations are still commonly used along with plane wave basis sets, as an electron gas approach is more suitable for electrons delocalized through an infinite solid. In molecular calculations, however, more complicated functional are needed, and a huge variety of exchange-correlation functional have been developed for chemical applications. Some of these are incompatible with the uniform electron gas approximation; however, they must reduce to LDA in the electron gas limit. The main difficulty with DFT is that the precise functional for exchange and correlation are not identified except for the free electron gas. However, rough calculations exist which allow the calculation of certain physical parameters rather precisely. In physics the most widely used approximation is the local-density approximation (LDA).

2.4 Local Density Approximation:

One of the efficient rough calculation techniques for working out the exchange-correlation term in the density functional theory (DFT) is the local density approximation (LDA). LDA has widely been applied to portray a variety of close-ranged exchange-correlation interactions for instance, covalent bonding systems. However, LDA has serious limitation that this approximation cannot provide estimation to the long-ranged exchange-correlation interaction as typified by the Van der Waals (VdW) interaction. The VdW interaction is one of the long-ranged electronic interactions which mainly add
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to the first stage of the material reactions such as the chemical reaction, crystal growth and physical absorption. To assess the VdW interaction, many efforts have been devoted to develop useful calculating recipes for the non-local exchange-correlation term. Kohn and Sham applied LDA approximation to DFT of Kohn and Sham (1965). The Hohenberg-Kohn theorem states that the energy of the ground state of a system of electrons is a functional of the electronic density especially, the exchange and correlation (XC) energy is also a functional of the density (this energy can be seen as the quantum part of the electron-electron interaction). This XC functional is not identified accurately and must be approximated. LDA is the simplest approximation for this functional, it is local in the sense that the electron exchange and correlation energy at any point in space is a function of the electron density at that point only.

The XC functional is the total of a correlation functional and an exchange functional:
\[
E_{xc} = E_x + E_c
\]  
\hspace{2cm} (2.21)

LDA uses the exchange for the uniform electron gas of a density equal to the density at the point where the exchange is to be assessed

\[
E_{xc} = \int d^3r \ n(\vec{r}) \left( \frac{-3e^2}{4\pi} \right) \left( 3\pi^2 n(\vec{r})^{2/3} \right)
\]  
\hspace{2cm} (2.22)

It is found that all quantities are represented as functional of the electronic charge density. The significant point that makes this system easier to solve is that the efficient possibility is local. Therefore there is no more complication added in solving Schrodinger equation. Of course, this is only true if the exchange-correlation energy can be portrayed as a function of the local charge density. A technique of doing this is known as the local density approximation (LDA). As mentioned above in LDA, the exchange-
The correlation energy of an electronic system is built by taking for granted that the exchange-correlation energy for each electron at a point \( \vec{r} \) in the electron gas is equal to the exchange-correlation energy for each electron in an identical electron gas that has the same electron density at the point \( \vec{r} \). It follows therefore

\[
E_{xc} \left[ n(\vec{r}) \right] = \int \varepsilon_{xc}(n(\vec{r}))n(\vec{r})d\vec{r}
\]

(2.23)

with

\[
\varepsilon_{xc}(n(\vec{r})) = \varepsilon_{xc}^{\text{hom}}(n(\vec{r}))
\]

(2.24)

where \( \varepsilon_{xc}^{\text{hom}}(n(\vec{r})) \) is exchange-correlation energy in identical electron gas. Equation (2.24) is the supposition that the exchange-correlation energy is purely local. Several parameterizations for \( \varepsilon_{xc}^{\text{hom}}(n(\vec{r})) \) exist, such as parameterization of Perdew and Zunger (1981).

2.5 Generalized Gradient Approximation:

The generalized gradient approximation (GGA) has attracted much attention for its abstract simplicity and moderate computational workloads. At present, two GGA functional, one suggested by Becke and Perdew (BP) and one suggested more recently by Perdew and Wang (PW), are the most popular ones in the literature (Perdew et al., 1996). Many calculations assessing the accuracy of the GGA have been reported and commonly demonstrate that the GGA substantially corrects the LDA error in the cohesive energies of molecules and solids. Generalized gradient approximations (GGA’s) to the exchange-correlation (XC) energy in density-functional theory are at present receiving increasing attention as a straightforward substitute to improve over the local-density approximation (LDA) in \textit{ab initio} total-energy calculations (Kresse and Furthmuller, 1996). The lattice parameters always rise in comparison with the LDA, a
closer agreement with experimental data is reported for alkali metals, 3d metals, and some 4d metals.

2.6  Local Spin density approximation:

For magnetic materials, the LDA is extended to include spin-polarization, resulting in the local spin density approximation or LSDA. The $E_{\alpha}[n^\sigma(r)]$ energy is a functional of both the spin-up and down spin densities. With such distinction, the Kohn-Sham equation can be written as:

$$\left[ -\frac{1}{2} \nabla^2 + V_{KS}^\sigma \right] \phi_i^\sigma(r) = e_i^\sigma \phi_i^\sigma(r) \quad (2.25)$$

where $V_{KS}^\sigma$ and $n^\sigma(r)$ are the spin extension of the previous quantities.

$$V_{KS}^\sigma(r) = v(r) + e^2 \int \frac{\rho(r')}{r-r'} dr' + \frac{\delta E_{\alpha}[n^\uparrow,n^\downarrow]}{\delta \rho^\sigma(r)}$$

$$v_{xc}^\sigma(r) = \frac{\delta E_{\alpha}[n^\uparrow,n^\downarrow]}{\delta \rho^\sigma(r)}, \sigma(r) = \sum |\phi_i^\sigma|^2, \rho(r) = \sum \sigma \rho^\sigma(r) \quad (2.26)$$

The imbalance between $n^\uparrow$ and $n^\downarrow$ producing the magnetization $M = n^\uparrow - n^\downarrow$, is given by the exchange-correlation potential $U_{\alpha,xc}(r)$ which accounts for the different populations $n^\uparrow$ and $n^\downarrow$ by the derivative. In the local spin density approximation (LSDA), the exchange and correlation contributions are separated as:

$$E_{x}^{\text{LSDA}}[\rho(r)] = \sum_{\sigma} \int \epsilon_{xc}^{\text{hom}}(\rho^\sigma(r)) \rho^\sigma(r) dr$$

$$E_{c}^{\text{LSDA}}[\rho(r),\xi(r)] = \int \left[ \epsilon_{c}^{U}(\rho(r)) + f(\xi(r))(\epsilon_{c}^{P}(\rho(r)) - \epsilon_{c}^{U}(\rho(r))) \right] \rho(r) dr$$

where $\xi(r) = [n^\uparrow(\rho(r)) - n^\downarrow(\rho(r))]/[n^\uparrow(\rho(r)) - n^\downarrow(\rho(r))]$ is the normalized magnetization, $f(\xi(r))$ is a smoothing function, and $\epsilon_{c}^{P}$ and $\epsilon_{c}^{U}$ are proper functional
representing the correlation energies for the spin-polarized and unpolarized systems, respectively.

2.7 The full-potential linearized augmented-plane wave (FP-LAPW) method:

The full-potential linearized augmented-plane wave (FP-LAPW) technique is well known to allow most precise calculation of the electronic structure and magnetic qualities of crystals and surfaces. The application of atomic forces has greatly maximized its applicability, but it is still commonly supposed that FP-LAPW computations need considerable higher computational effort in comparison with the pseudopotential plane wave (PPW) based techniques. FP-LAPW has recently showed important progress. For example, researchers habitually work out magnetism and nuclear quantities (for example, isomer shifts, hyperfine fields, electric field gradients, and core level shifts). Also, forces and molecular dynamics have been applied, and recent optimizations have decreased the CPU time of FP-LAPW calculations significantly. Nevertheless, because the computational expense and memory requirements are still fairly high, FP-LAPW implementations are suitable only to fairly complicated systems. One successful implementation of the FP-LAPW technique is the program package WIEN2K, a code enhanced by Blaha, Schwarz and coworkers (Blaha et al., 2008). It has been successfully implemented to a various scope of difficulties such as electric field gradients and systems such as high-temperature superconductors, minerals, surfaces of transition metals, or anti-ferromagnetic oxides and even molecules (Ernst et al., 2005). So far the main disadvantage of the FP-LAPW-technique in comparison with the pseudopotential plane-wave (PPW) method has been its higher computational expense. This may be largely because of an inconsistency in optimization efforts spent on both techniques, and so we have investigated the FP-LAPW technique from a computational arithmetical viewpoint.
Lately, the development of the Augmented Plane Wave (APW) techniques from Slater’s APW, to LAPW and the new APW+lo was portrayed by Schwarz et al. (2003). One of the most precise techniques for performing electronic structure calculations for crystals is the FP-LAPW technique. It is based on DFT for the handling of exchange and correlation and uses (for example, the LSDA). Effects, for valence states relativistic, can be incorporated either in a scalar relativistic handling or with the second dissimilarity technique including spin-orbit coupling. Core states are treated fully relativistically.

The FP-LAPW technique, which is like most energy-band techniques is a process for solving the Kohn-Sham equations for the ground state density, total energy, and (Kohn-Sham) eigen values (energy bands) of a many-electron system by presenting a basis set which is particularly modified to the problem.

This alteration is achieved by partitioning the unit cell (Fig. 2.1) into (I) non-overlapping atomic circles (centered at the atomic sites) and (II) an interstitial region, that’s to say, a region between two spaces. In the two sorts of regions diverse basis sets are used:

(i) Inside atomic sphere \( \mathbf{t} \) of radius \( \mathbf{R}_t \) a linear combination of radial functions times spherical harmonics \( Y_{lm}(r) \) is used:

\[
\phi_{lm} = \sum_{lm} \left[ A_{lm} u_l(\vec{r}, E_l) + B_{lm} \tilde{u}_l(\vec{r}, E_l) \right] Y_{lm}(r)
\]

(2.28)

where \( u_l(r, E_l) \) is the (at the origin) normal way out of the radial Schrödinger equation for energy \( E_l \) and the spherical part of the potential inside sphere, \( \tilde{u}_l(r, E_l) \) is the energy derived of \( u_l \) taken at the similar energy. A linear mixture of these two functions comprise the linearization of the radial function; the coefficients \( A_{lm} \) and \( B_{lm} \) are functions of \( k_n \) decided by requiring that this root function \( \tilde{u}_l \) goes with the equivalent
Figure 2.1: Partitioning of the unit cell into atomic spheres (I) and an interstitial region (II)
basis function of the interstitial region; \( u_i \) and are achieved by numerical integration of the radial Schrödinger equation on a radial mesh inside the sphere.

\( (ii) \) In the interstitial zone a plane wave extension is applied

\[
\phi_{ln} = \frac{1}{\sqrt{W}} e^{ik\cdot r}
\]

where \( k_n = k + k_m, k_m \), are the mutual lattice vectors and \( k \) is the wave vector inside the first Brillouin zone. Each plane wave is increased by an atomic-like function in every atomic sphere.

The solutions to the Kohn-Sham equations are extended in this joint basis set of LAPW’s according to the linear dissimilarity technique

\[
\psi_k = \sum_n C_n \phi_{kn}
\]

and the coefficients \( C_n \), are decided by the Rayleigh-Ritz variation rule. The union of this basis set is controlled by a disconnected parameter \( R_{mi} K_{max} = 6 - 9 \), where \( R_{mi} \) is the smallest atomic sphere radius in the unit cell and \( K_{max} \) is the magnitude of the largest \( K \) vector.

Additional (\( K_n \) independent) basis functions can be added to improve upon the linearization and to make possible a reliable treatment of semi core and valence states in one energy window. They are called “local orbitals” and consist of a linear combination of 2 radial functions at 2 dissimilar energies and one energy derivative:

\[
\phi_{lm}^{LO} = \left[ A_{lm} u_l(\vec{r}, E_{1,l}) + B_{lm} \dot{u}_l(\vec{r}, E_{1,l}) + C_{lm} u_l(\vec{r}, E_{2,l}) \right] Y_{1,l}(\hat{r})
\]

The coefficients \( A_{lm}, B_{lm}, \) and \( C_{lm} \), are decided by the necessities that \( \phi_{lm}^{LO} \) should be regularized and has zero value and slope at the sphere border.
The FP-LAPW technique, in its general form, extends the potential in the following form

\[
V(\vec{r}) = \begin{cases} 
\sum_{lm} V_{lm}(\vec{r})Y_{lm}(\vec{r}) & \text{inside sphere} \\
\sum_{k} V_{k}e^{ikr} & \text{outside sphere}
\end{cases}
\]

(2.32)

2.8 The WIEN2k Code:

The calculations in this work are performed using the WIEN2k computer package (Blaha et al., 2008). This program contains several sub-programs, which are described briefly below. There are two major parts in the program, the initialization and the self-consistent field (SCF) cycle. The flow chart of the code is given in Fig. 2.2.

- **Initialization** (Setting up the unit cell and generating the initial density):
  
  In this sub-program, atomic densities are generated and superimposed to obtain a initial crystal density for the SCF calculation. Additionally, the atomic potentials and, optionally, atomic valence densities are created. Information about \(l,m\) values of the lattice harmonics representation and number of Fourier coefficients of the interstitial charge density are inserted as input file in this part.

- **LAPW0** (Construction of the effective potential):

  The Poisson equation is solved and the total potential is computed as the sum of the Coulomb and the exchange-correlation potential in the LAPW0 program. The electron (spin) density is used as input and the spherical \((l=0)\) and the non-spherical parts of the potential are generated. The exchange-correlation potential is computed numerically on a
Figure 2.2: Flow chart of WIEN2k code
grid. Additionally, the Hellmann-Feynman force contribution to the force is also determined

- **LAPW1** (Solving the Kohn-Sham equations of valence electrons):

  The Hamiltonian and the overlap matrix are set up in LAPW1. Their diagonalization provides the eigenvalues and eigenvectors. Both the LAPW and the APW+lo methods are supported. For maximum efficiency a mix of both is recommended, i.e. the APW+lo basis functions are used for physically meaningful \( l \) values, while LAPW basis functions are employed to describe higher \( l \)-values functions.

- **LAPW2** (Construction of the new electron density):

  The Fermi-energy is computed. The electronic charge densities are expanded according to the representation of Eq. 2.28 for each occupied state and each \( k \)-vector. Afterwards the corresponding (partial) charges inside the atomic spheres are obtained by integration.

- **LCORE** (The treatment of the core electrons):

  The potential and the charge density of the core electrons are computed.

- **LMIXER** (Generating the input density for the next iteration):

  The electron densities of core, semi-core, and valence states are combined to yield the total new density. Taking only the new densities would, however, lead to instabilities in the iterative SCF process. To have a stable SCF cycle new and old densities need to be mixed, to obtain a new density.

\[
n_{\text{new}}^{n+1} = (1 - \alpha)n_{\text{new}}^n + \alpha n_{\text{old}}^n
\]

(2.32)

here \( \alpha \) is a mixing parameter. In the WIEN2k code this is done (mainly) using the Broyden scheme. The total energy and the atomic forces are computed in mixer, as well.
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It is well known that for localized electrons LDA and GGA methods are not accurate enough for a proper description of some of the strongly correlated systems. Thus other methods like LDA+U and Orbital polarization are also implemented in this program. In Wien2k (Blaha, 2008) the effective Coulomb-exchange interaction ($U_{\text{eff}} = U - J$) is used for the LDA+U calculations (Anisimov, 1997). This particular scheme is used in Wien2k to include double-counting corrections, however, it neglects multipole terms. It should be mentioned that the $+U$ was used on top of GGA rather than LSDA parametrization of the exchange-correlation functional. No significant differences were observed using one or the other of the parameterizations.