



## Introduction to band structure calculations using the LAPW method

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### ABSTRACT

This paper is a discussion on a brief introduction to the density functional theory (DFT). The formalism and the approximations made for easy computation has been mentioned along with the two theorems of Hohenberg and Kohn on which the density functional theory is based. In the end, the Kohn-Sham equation which turned density functional theory into a practical tool to obtain the ground state density has been explained along with the LAPW method.

**Key words:** Hatree Fock; density functional; linearized augmented plane wave; Kohn-Sham equation; density functional theory.

### INTRODUCTION

The study of the properties of a solid especially the electronic band structure is a complex quantum mechanical many body problem whose exact solution is well nigh impossible, as such many approximate methods have been developed. In general there are two types of methods for quantum mechanical approaches: Hartree Fock (HF) method and Density Functional Theory (DFT).<sup>1</sup> HF is based on wave function description in which exchange is treated but correlation is ignored. The density functional theory on the other hand is based on the electron density rather than on the wave function and treats both exchange and correlation but only approximately. In the density functional theory, the

calculation of ground state properties such as band structure, optical properties, lattice parameter, equilibrium volume, phonon frequencies, elastic constants etc, which are based on the calculation of the total energy, are described quite accurately. However, the treatment of excited states is not rigorously justified. This is due to the fact that the Hohenberg-Kohn<sup>1</sup> theorem is exact only for the ground state and that the Kohn-Sham (KS) eigenstates<sup>2</sup> must not be interpreted as single-electron states. Apart from this, approximations must be made also in the ground state calculations for describing exchange and correlation effects. In spite of this, the interpretation of the KS states in terms of excited states has been successful for a variety of materials. Moreover, it has been claimed that the KS wave functions hardly differ from the many-body wavefunctions.<sup>3-5</sup> Thus it can safely be stated that the density functional

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theory is one of the most successful methods for calculating lattice properties of a solid. We discuss here the basic formalism of band structure calculation by using the linearised augmented plane wave (LAPW) method.<sup>6-10</sup>

## FORMALISM

A solid is a collection of a heavy positively charged nuclei and lighter negatively charged electrons. If we have  $N$  nuclei, we are dealing with  $N+ZN$  electromagnetically interacting quantum particles. This is a quantum many body problem and the exact many particle hamiltonian for such a system is,

$$\hat{H} = -\frac{\hbar^2}{2} \sum_i \frac{\nabla_{\mathbf{R}_i}^2}{M_i} - \frac{\hbar^2}{2} \sum_i \frac{\nabla_{\mathbf{r}_i}^2}{m_e} - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\mathbf{R}_i - \mathbf{R}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} \quad (1)$$

where  $M_i$  is the mass of the nucleus at  $\mathbf{R}_i$ ,  $m_e$  is the mass of the electron at  $\mathbf{r}_i$ . The first term is the kinetic energy operator for the nuclei, the second term represents kinetic energy operator for the electrons. The last three terms describe the coulomb interaction between electrons and nuclei, between electrons and other electrons and between nuclei and other nuclei. It is impossible to solve Eq. (1) exactly, as such in order to obtain acceptable appropriate eigen states, approximations are made.

## BORN-OPPENHEIMER APPROXIMATION

In this approximation, the nuclei which are heavier and are therefore much slower than the electrons are taken stationary and are assumed to be in instantaneous equilibrium with the electrons. As a consequence, the nuclei do not move anymore and their kinetic energy is zero so that the first term in Eq. (1) vanishes and the last term reduces to a constant. Thus we are left with kinetic energy of the electron gas, the potential energy due to electron-electron interactions and the poten-

tial energy of the electrons in the (now external) potential of the nuclei. Thus the Hamiltonian can be written as,

$$\hat{H} = \hat{T} + \hat{V} + \hat{V}_{ext} \quad (2)$$

The quantum many body Hamiltonian obtained after Born-Oppenheimer approximation is much simpler than the original one but still far too difficult to solve. One of the well known methods used to reduce Eq. (2) to an approximate but tractable form is the density functional theory.

## DENSITY FUNCTIONAL THEORY

Density functional theory is a universal approach to the quantum mechanical many body problem, where the system of interacting electrons is mapped in a unique manner onto an effective non-interacting system with the same total density. It is based on the two theorems of Hohenberg and Kohn.<sup>1</sup>

**First theorem:** There is one to one correspondence between the ground state density  $\rho(\mathbf{r})$  of a many electron system and the external potential  $V_{ext}$ . This means that the ground state expectation value of any observable  $\hat{O}$  is a unique functional of the exact ground state electron density

$$\langle \psi | \hat{O} | \psi \rangle = O[\rho] \quad (3)$$

**Second theorem:** For  $\hat{O}$  being the hamiltonian  $\hat{H}$ , the ground state total energy functional  $H[\rho] = E_{V_{ext}}[\rho]$  is of the form

$$E_{V_{ext}}[\rho] = \langle \psi | \hat{T} + \hat{V} | \psi \rangle + \langle \psi | \hat{V}_{ext} | \psi \rangle \quad (4)$$

$$= F_{HK}[\rho] + \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} \quad (5)$$

where,  $F_{HK}[\rho] = \langle \psi | \hat{T} + \hat{V} | \psi \rangle$ , the Hohenberg-Kohn density functional is universal for any many electron system.  $E_{V_{ext}}[\rho]$  reaches its minimal value (equal to the ground state total energy) for the ground state density corresponding to  $V_{ext}$ . The consequence of the density functional theory is that the electron density  $\rho(\mathbf{r})$  uniquely defines the total energy  $E$

of a system and is a functional  $E[\rho]$  of particle potential, which consists of a classical mean-field part and an exchange-correlation part that in principle incorporates all correlation effects exactly.

### THE KOHN-SHAM EQUATIONS

The equations of Kohn and Sham<sup>2</sup> turned density functional theory into a practical tool to obtain the ground state density. The Kohn-Sham theorem can be formulated as:

The exact ground-state density  $\rho(\mathbf{r})$  of an N-electron system is

$$\rho(\mathbf{r}) = \sum_{i=1}^N \phi_i(\mathbf{r})^* \phi_i(\mathbf{r}) \quad (6)$$

Where the single-particle wave functions  $\phi_i(\mathbf{r})$  are the N lowest-energy solutions of the Kohn-Sham equation

$$\hat{H}_{KS} \phi_i = \varepsilon_i \phi_i \quad (7)$$

Where, the Kohn-Sham Hamiltonian is

$$\begin{aligned} \hat{H}_{KS} &= \hat{T}_o + \hat{V}_H + \hat{V}_{xc} + \hat{V}_{ext} \\ &= -\frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{e^2}{4\pi\epsilon_o} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + V_{xc}\{\rho(\mathbf{r})\} + V_{ext}(\mathbf{r}) \end{aligned} \quad (8)$$

where,  $V_{xc}$  is the exchange correlation potential and  $V_{ext}$  is the external potential from the nucleus. It must be noted that the single-particle wave function  $\phi_i(\mathbf{r})$  are not the wave functions of electrons but they describe mathematical quasi-particles without a direct physical meaning. Only the overall density of these quasi-particles is guaranteed to be equal to the true electron density. Also the single-particle energies  $\varepsilon_i$  are not single electron energies.

Both the Hartree operator  $V_H$  and the exchange-correlation operator  $V_{xc}$  depend on the density  $\rho(\mathbf{r})$ , which in turn depends on the  $\phi_i(\mathbf{r})$  which are being searched. This means we are dealing with a self-consistency problem. To overcome this, an iterative pro-

cedure<sup>11</sup> is needed (Fig. 1). Some starting density  $\rho_0$  is guessed, and a Hamiltonian  $H_{KS1}$  is constructed with it. The eigenvalue problem is solved and results in a set of  $\phi_1$  from which a density  $\rho_1$  can be obtained. Most probably  $\rho_0$  will differ from  $\rho_1$ . Now  $\rho_1$  is used to construct  $H_{KS2}$ , which will yield a  $\rho_2$ , etc. This procedure is continued till the series converges to a density  $\rho_f$  which will generate  $H_{KSf}$  which yields as solution again  $\rho_f$  so that this final density is in consistent with the Hamiltonian.

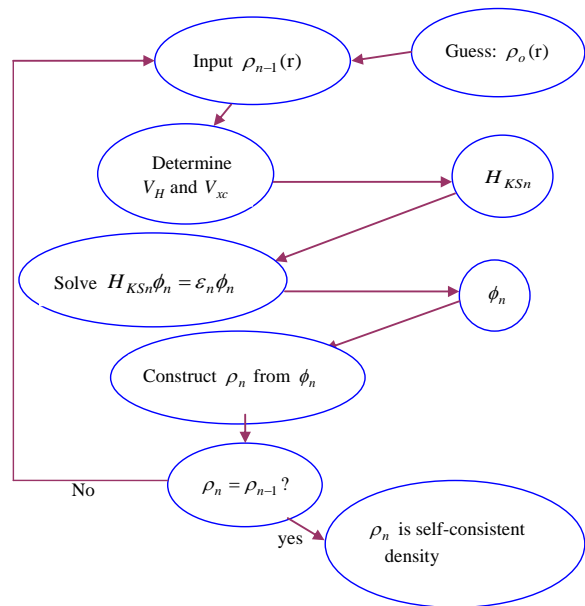


Figure 1. Flow chart for the n<sup>th</sup> iteration in the self consistent procedure to solve Kohn-Sham equations.

### THE LAPW METHOD

The linearised augmented plane wave (LAPW) method is based on the density functional theory for the treatment of exchange and correlation and uses, e.g. the local spin density approximation (LSDA). Like most energy-band methods, the LAPW method is a procedure for solving the Kohn-Sham equa-

tions for the ground state density, total energy and (Kohn-Sham) eigenvalues (energy bands) of a many electron system (crystal) by introducing a basis set which is especially adapted to the problem. This adaptation is achieved by dividing the unit cell into (I) non-overlapping atomic spheres (centered at the atomic sites) and (II) an interstitial region (Fig. 2).

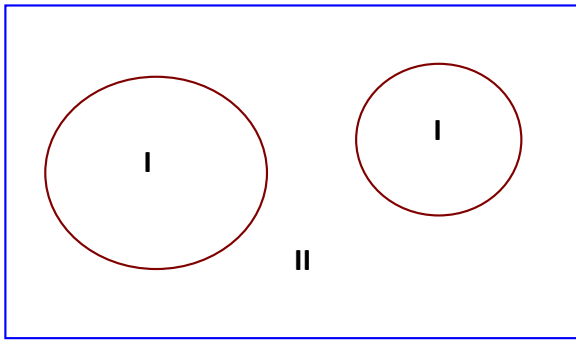


Figure 2. Partitioning of the unit cell into two: atomic spheres (I) and an interstitial region (II).

In the two types of regions different types of basis sets are used:

(a) Inside the atomic sphere I of radius  $R_i$ , a linear combination of radial functions times spherical harmonics  $Y_{lm}(r)$  is used as given below<sup>12</sup>

$$\phi_{\mathbf{k}_n} = \sum_{lm} [A_{lm, \mathbf{k}_n} u_l(\mathbf{r}, E_l) + B_{lm, \mathbf{k}_n} \dot{u}_l(\mathbf{r}, E_l)] Y_{lm}(\mathbf{r}) \quad (9)$$

where  $u_l(\mathbf{r}, E_l)$  is the (at the origin) regular solution of the radial Schrödinger equation for energy  $E_l$  (chosen normally at the centre of the corresponding band with  $l$ -like character) and spherical part of the potential inside the sphere I;  $\dot{u}_l(\mathbf{r}, E_l)$  is the energy derivative of  $u_l$  evaluated at the same energy  $E_l$ . A linear combination of these two functions constitutes the linearization of the radial function. The coefficients  $A_{lm}$  and  $B_{lm}$  are functions of  $\mathbf{k}_n$  determined by requiring that this basis function matches each plane wave (PW), the corresponding basis function of the interstitial region.  $u_l$  and  $\dot{u}_l$  are obtained by numerical

integration of the radial Schrödinger equation on a radial mesh inside the sphere.

(b) In the interstitial region II, a plane wave expansion is used

$$\phi_{\mathbf{k}_n} = \frac{1}{\sqrt{\omega}} e^{i\mathbf{k}_n \cdot \mathbf{r}} \quad (10)$$

where  $\mathbf{k}_n = \mathbf{k} + \mathbf{K}_n$ ;  $\mathbf{K}_n$  are the reciprocal lattice vectors and  $\mathbf{k}$  is the wave vector inside the first Brillouin zone. Each plane wave is augmented by an atomic-like function in every atomic sphere.

The solution to the Kohn-Sham equations are expanded in this combined basis set of LAPW's according to the linear variation method

$$\psi_{\mathbf{k}} = \sum_n C_n \phi_{\mathbf{k}_n} \quad (11)$$

and the coefficients  $C_n$  are determined by the Rayleigh-Ritz variation principle. The convergence of this basis set is controlled by a cut-off parameter  $R_{mt}K_{max} = 6 - 9$ , where  $R_{mt}$  is the smallest atomic sphere radius in the unit cell and  $K_{max}$  is the magnitude of the largest  $K$  vector in Eq. (11). On the basis of these approximations, FORTRAN programmes had been written and developed into a code called WIEN2k<sup>11</sup> code, which is a multiple tasked code. This code can be used to compute band structure as well as other properties like density of states, x-ray spectra, optical properties etc.

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