This chapter deals with theoretical aspects which form the basis of computational techniques used for calculating various properties of the manganites considered in the present thesis and understanding the formation of manganites by two popular methods: ball milling and sol-gel. The computational work performed is based on *state-of-the-art* Density Functional Theory (DFT). The present chapter starts with a brief history and idea of DFT followed by the original thought of Hohenberg and Kohn and their two theorems; the foundations of DFT. The subsequent section discusses the Kohn-Sham formulation, Local Density Approximation (LDA), Local Spin Density Approximation (LSDA) and Generalized Gradient Approximation (GGA) adopted for the exchange energy term. Finally, the computational details for Fe doped LSMO are discussed.

3.1 Electronic Structure calculations

As we know that the materials are made up of atoms and atoms are in turn made up of nuclei and electrons such that the net charge of an atom is zero. Therefore, the matter is considered as a collection of interacting electrons and ions [1, 2]. Moreover, the electrons are quantum particle that their critical behavior can only be studied using quantum mechanics. According to quantum mechanics, the electrons cannot be localized to a particular point in space, but they are best thought of as matter waves characterized by a wave function.

The probability of finding a single electron for any wavefunction ψ at the arbitrary point x in spaceis given by $\psi(x)\ \psi^*(x)$. We can determine the wavefunction by solving the time independent Schrödinger equation (Eq. 1). The motion of electrons in atoms is described using the electronicstructure theory. The exact theory for such systems is expressed by well-known many body Schrödinger equation.

$$\hat{H}\psi(R_I, r_i) = E\psi(R_I, r_i) \quad (1)$$

Where E, is the energy eigen value of the system, Ψ (R_I, r_i) is the many body wave function that describes the ground state of the system, R_I represent the ionic position, while the r_i describes the position of the electrons and H is the Hamiltonian.

According to Born-Oppenheimer approximation, electrons are muchlighter than the nuclei that they always find their optimal distribution for any given configuration around the nuclei. Solving the electronic problem for a range of nuclear configuration gives potential energy surface.

The Hamiltonian of non-relativistic electronicmany body Schrödinger equation keeping the nuclei fixed under Born-Oppenheimer approximation can be defined as follows:

$$\hat{H} = \frac{-\hbar^2}{2m}\sum_{i} \nabla_i^2 - \sum_{A} \frac{\hbar^2}{2M_A}\nabla_A^2 - \sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \qquad (2)$$

where, the suffixesi andj refers tothe electrons and nuclei respectively.

For heavier atoms, inner electrons are held tightly to the nucleus andtheir velocities increase with increase in theatomic number. As these velocities reach to the speed of light, relativistic effects become more prominent. In general, the relativistic effects are considered for the atoms with atomic number more than 25.

To solve the Schrödinger equation formaterials having large number of atoms using DFT approach, it is necessary tounderstand certain approximations employed for solving many body Schrödinger equation. There exist largenumber of model Hamiltonians such as Huckel, tight-binding, the Hubbard and Heisenberg, the BCS [3] etc. However, for finite systems, one can use the configuration interaction method [4].

3.2 The Born-Oppenheimer Approximation

In the early days of development of quantum mechanics, Born formulated an adiabatic approximation for solving the Schrödinger equation for a real system containing both electrons and ions. It was widely known that quantum mechanics could predict the properties of solids, considering only the electromagnetic interactions. However, the practical difficulty arises in dynamics of combined system of electrons and nuclei. In this case, the electrons move comparatively faster than the nuclei due to their smaller mass. Hence, one can assume that the electrons in anatom adjust instantaneously to the given configuration of the ions. This implies that electron remaining in an instantaneous ground state follow the ionic motion of the electronic Hamiltonian. The Born-Oppenheimer approximation for fixed set ofcoordinates R = {R_I} can be given as,

$$H_R^{B^0}\psi_R = (H_{RR} + H_{ne} + H_{nn})\psi_R = (\frac{-\hbar^2}{2m_c}\sum_i \frac{\partial^2}{\partial r_i^2} + V_{ne} + V_{ee} + V_{nn})\psi_R = E_R\psi_R \qquad (3)$$

Where, $\Psi(R_I, r_i)$, is the function of the electronic co-ordinates r_i and also depends parametrically on the ionic coordinates R_I. The kinetic energy of the ions is not considered in the Hamiltonian due to very heavy masses of nuclei. The term V_{II} is also neglected in the above equation, as it is not relevant to the problem of describing the electrons since V_{II} is constant for a fixed nuclear configuration.

The resulting separation of the states among electronic and ionic degrees of freedom is a very useful simplification of the problem and allows one to treat ions within classical framework. However, the electronic part is still a many body quantum problem as the electronic wavefunction of the system depends on the coordinates of all the electrons and cannot be decoupled in single electron contributions because of their mutual interactions. This makes the solution complex as it requires the solution of a coupled differential equation of $3N_e$ degrees of freedom where N_e is the number of electrons. For atoms and smaller molecules, the number of electrons is usually in the range of $N_e \sim$ 1-100. However, for a solid the number of electrons is greater than hundred. Hence, the problem is still too complicated for practical computations to solve suggesting further simplifications. However, the solution is achieved by applying the well-known Density Functional Theory (DFT) on the Hartree–Fock equation.

3.3 Density Functional Theory (DFT)

Walter Kohn was awarded the Nobel Prize in Chemistry in 1998 for developing of the Density Functional Theory (DFT). The DFT based first principles calculations is presently the most successful and promising approach for computing the ground state electronic structure and related properties of matter. The DFT in its original development provides the ground state properties of a systemin which the electron density plays a key role. The density functional theory has been generalized to deal with many different situations: spin-polarized systems, multicomponent systems such as nuclei and electron hole droplets, free energy at finite temperatures, superconductors with electronic pairing mechanisms, relativistic electrons, time-dependent phenomena and excited states, bosons, etc [5]. DFT has received great deal of help in the development from the famous Thomas-Fermi model and the Hartree-Fock-Slater method. The Thomas-Fermi model is a statistical model developed by Thomas [6] and Fermi [7] where the concept of density to DFT has been taken.

In the Thomas Fermi model, the kinetic energy of an atom is expressed by the functional of electron density, and two added classical electronic densities representing nuclear-electron and electron-electron interactions. The model worked well with slowly changing density.

Eventhough, their model did not include all exchange and correlations effects, it worked quite well as a predecessor of the DFT calculations.

Dirac [8] in 1928, enhanced the capacity of Thomas-Fermi model by incorporating the exchange interaction. Although the Thomas-Fermi model is an important foundational step, its applications are very limited. The Hartree-Fock-Slater method is another ab initio method which is based on the ideas of Hartree [9] and Fock [10], in which the many-electron wave function is approximated using Slater determinant. The variational principle can be used to derive a set of N coupled equations arising for the N spin orbitals which can be solved self consistently. An exact solution can only be obtained for a hydrogen-like one-electron atom.

Slater considered the exchange potential in Hartree-Fock model, but still the many electron wavefunctions and requires enormous computational effort. In DFT approach, all physical quantities of interest are calculated using ground state density of the many electron system. Therefore, the knowledge of the ground state density becomes crucial instead of the knowledge of many-body wave function of the system.

The core spirit of the DFT founded by Hohenberg and Kohn [11] is to substitute the complicated many-electron wavefunction containing 3N variables (N is the number of electrons, and each electron has three spatial variables), with the functional of electron density, which contains only three variables and hence making it easy to handle. Hohenberg and Kohn proposed two theorems. The first theorem points out that the ground state energy uniquely depends on the electron density, which means that it is a functional of electron density whereas the second theorem states that the proved ground state energy can be obtained by minimizing the total energy of the system with respect to the electron density.

To determine the electron density in the DFT based calculation; Kohn and Sham [11] in 1965 introduced a system of N non-interacting one electron wave functions (ψ_i). Therefore, there are N solutions of the Schrödinger equation in an effective potential V_{eff} (r) developed for any system. These effective one electron Schrödinger equations are called Kohn−Sham equations and can be written as:

$$\left[\frac{-h^2}{2m}\nabla^2 + V_{eff}(r)\right]\psi_i(r) = E_i\psi_i(r) \tag{4}$$

The first term in the external potential describes the interaction between the electrons and the nuclei. The second term represents the electrostatic interaction between the electrons themselves. The exchange–correlation potential is given by,

$$V_{XC}(r) = \frac{\delta E_{xc}}{\delta n(r)} \tag{5}$$

with E_{XC} as the exchange-correlation energy and the n(r) as electron density and is given by,

$$n(r) = \sum_{f-1}^{N} \left|\psi_f(r)\right|^2 \tag{6}$$

The Kohn-Sham equations are solved self-consistently and in each cycle of calculation, the exchange-correlation potential is calculated with an appropriate approximation for the exchange-correlation energy. Kohn-Sham equationbecomes exact if the exchange-correlation is exact. Therefore, the determination and approximation of the exchange-correlation potential is crucial problem in the solution of the Kohn-Sham equations. In brief, DFT maps the many body problems to an effective single particle Schrödinger equation by introducing an exchange-correlation functional.

3.3.1 Hohenberg-Kohn Theorems

Density functional theory was proven to be the exact theory of many-body systems by Hohenberg and Kohn in 1964. The theory is constructed based on two theorems [12].

Theorem I: The ground state particle density n(r) of a system of interacting particles in an external potential $V_{ext}(r)$ uniquely determines the external potential $V_{ext}(r)$. Thus, the ground state particle density determines the full Hamiltonian, except for a constant shift of the energy. In principle, all the states including ground and excited states of the many-body wavefunctions can be calculated. This means that the ground state particle density uniquely determines all properties of the system completely.

Proof: For simplicity, here the case for which the ground state of the system is non-degenerate is considered. It can be proven that the theorem is also valid for systems with degenerate ground states [10]. The proof is based on total-energy minimization principle. Suppose, there are two different external potentials $V_{ext}(r)$ and $V'_{ext}(r)$ which differ by more than a constant and lead to the same ground state density $n_0(r)$. The two external potentials would give two different Hamiltonians, $\hat{H}$ and $\hat{H}'$, which have the same ground state density $n_0(r)$ but have different ground state wavefunctions, Ψ and Ψ' given by

$$\hat{H}\psi = E_0\psi \tag{6}$$

$$\hat{H}'\psi' = E \tag{7}$$

Since Ψ' is not the ground state of $\hat{H}$,

$$E_0 = \langle\psi'|\hat{H}|\psi'\rangle < \langle\psi'|\hat{H}|\psi'\rangle \tag{8}$$

Assuming that the ground state is not degenerate, the inequality strictly holds. Because we have identical ground state densities for the two Hamiltonians, we can rewrite Eq. (8) as

$$\langle\psi^{(2)}|H^{(1)}|\psi^{(2)}\rangle = \langle\psi^{(2)}|H^{(2)}|\psi^{(2)}\rangle + \int dr\left[V_{ext}^{(1)}(r) - V_{ext}^{(2)}(r)\right]n_0(r) \tag{9}$$

Exchanging labels in Eq. (9), we obtain

$$\langle\psi^{(1)}|H^{(2)}|\psi^{(1)}\rangle = \langle\psi^{(1)}|H^{(1)}|\psi^{(1)}\rangle + \int dr \left[V_{ext}^{(2)}(r) - V_{ext}^{(1)}(r)\right] n_0(r) \tag{10}$$

Adding Eq. (9) and (10), we get

$$E_0' + E_0 < E_0 + E_0' \tag{11}$$

Which leads to inconsistency and therefore provides by reduction and absurdum the proof that $V(\vec{r})$ is truly a unique functional of $n(\vec{r})$.

Theorem II: The ground state energy can be derived from the electron density by the use of variational calculus. The electron density, which provides a minimum of the ground state energy, is therefore the exact ground state density.

Since the external potential is uniquely determined by the density and since the potential in turn uniquely determines the ground state wavefunction, all the other observables of the system such as kinetic energy can be uniquely determined. Then onemay write the energy as a functional of density. Total energy expression from wavefunction representation to density representation can be written as

$$F[n(r)] \equiv T[n(r)] + E_{int}[n(r)] \tag{12}$$

where $T[n(r)]$ is the kinetic energy and $E_{int}[n(r)]$ is the interaction energy of the particles. According to variational principle, for any wavefunction ψ', the energy function $E[\psi']$:

$$E[\psi'] \equiv \langle\psi'|\hat{T} + V_{int} + \hat{V}_{ext}|\psi'\rangle \tag{13}$$

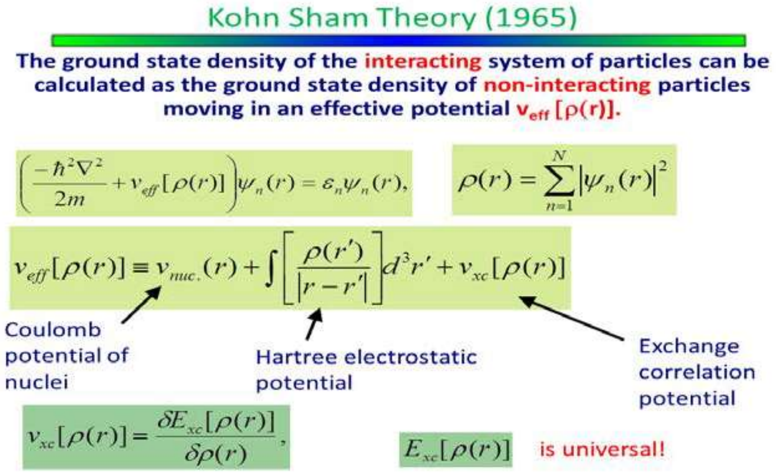
has its global minimum value only when ψ' is the ground state wavefunction ψ_0, with the constraint that the total number of the particles is conserved. According to HK theorem I, if ψ' correspond to a ground state with particle density $n'(r)$ and external potential $V_{ext}'(r)$, then $E[\psi']$ is a functional of $n'(r)$.

According to variational principle:

$$\begin{aligned} E[\psi'] &\equiv \langle \psi' | \hat{T} + V_{int} + \hat{V}_{ext} | \psi' \rangle \\ &= E[n'(r)] \\ &= \int n'(r) V'_{ext}(r) dr + F[n'(r)] \qquad (14) \\ &> E[\psi_0] \\ &= \int n_0(r) V_{ext}(r) dr + F[n_0(r)] \\ &= E[n_0(r)] \end{aligned}$$

Thus the energy functional $E[n(r)] \equiv \int n(r) V_{ext}(r) dr + F[n(R)]$ evaluated for the correct ground state density $n_0(r)$ is indeed lower than the value of this functional for any other density $n(r)$. Therefore by minimizing the total energy functional of the system with respect to variations in the density $n(r)$, one could find the exact ground state density and energy [13].

3.3.2 Kohn-Sham Equations



Kohn Sham Theory (1965)

The ground state density of the interacting system of particles can be calculated as the ground state density of non-interacting particles moving in an effective potential $v_{eff}[\rho(r)]$.

$$\left(\frac{-\hbar^2 \nabla^2}{2m} + v_{eff}[\rho(r)] \right) \psi_n(r) = \varepsilon_n \psi_n(r), \qquad \rho(r) = \sum_{n=1}^{N} |\psi_n(r)|^2$$

$$v_{eff}[\rho(r)] \equiv v_{nuc.}(r) + \int \left[\frac{\rho(r')}{|r-r'|} \right] d^3r' + v_{xc}[\rho(r)]$$

$$v_{xc}[\rho(r)] = \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)},$$

$E_{xc}[\rho(r)]$ is universal!

Fig. 3.1: Basic equations of the Kohn-Sham theory [5].

Kohn-Sham approach can be regarded as an attempt to include the benefits of the Hartree-Fock formalism in density functional theory while preserving all the electron correlations. Utilizing the Hohenberg-Kohn theorems [13], we minimize the total energy with respect to the orbitals in order to obtain the orbitals corresponding to the ground state energy. The minimization is performed with respect to $\varphi_i^*(r)$ instead of $\varphi_i(r)$ using chain rule for functional derivatives. This works for all the terms except for kinetic energy. Kinetic energy may be differentiated directly with respect to the orbitals. Thus, we have,

$$\frac{\delta E_e}{\delta\varphi_i^*(r)} = \frac{\delta T_s}{\delta\varphi_i^*(r)} + \left[\frac{\delta E_{ext}}{\delta n(r)} + \frac{\delta E_{Hartee}}{\delta n(r)} + \frac{\delta E_{xc}}{\delta n(r)}\right]\frac{\delta n(r)}{\delta\varphi_i^*(r)} = \varepsilon_i\varphi_i(r) \tag{15}$$

$$-\frac{1}{2}\nabla^2\varphi_i(r) + \left[V_{ext}(r) + \int dr' \frac{n(r)'}{|r-r'|} + \epsilon_{xc}[n] + n(r)\frac{\delta\epsilon_{xc}[n]}{\delta n(r)}\right]\varphi_i(r) = \varepsilon_i\varphi_i(r) \tag{16}$$

Eq. (16) is in fact a system of equations, which when solved simultaneously represent the many-particle system in terms of single-particle orbitals. Each of these equations resemble a single particle Schrödinger equation

$$[T + V_{eff}]\varphi_i(r) = \epsilon_i\varphi_i(r) \tag{17}$$

with the important difference that V_{eff} which we have defined to be the sum of the terms V_H, V_{xc} and V_{ext}, depends on the density and indirectly on the orbitals. As a result, we have the unusual situation that any changes in the orbitals also effect the potential on which they in turn depend [13].

3.4 Local Density Approximation (LDA)

The main problem with KS-DFT is the proper selection of exchange and correlation interaction. The solutions of exchange and correlation energy, though far from actual simplest approximations are the Local-Density Approximation (LDA) and Generalized Gradient Approximation (GGA). LDA uses the uniform electron gas model to get the exchange energy (the exact value can be achieved from the Thomas-Fermi model), and to get the correlation energy from fits to the uniform electron gas [5] whereas GGA is based upon the inclusion of density gradient. In many multi-body problems, GGA gives reasonable satisfactory results with experimental data as compared to LDA for most material properties. Despite LDA and GGA give satisfactory results; it's still difficult to treat the strongly correlated systems, band gap in semiconductors, and strong dispersion systems in DFT [13]. The simplest approximation LDA assumesthat the density can be treated locally as uniform electron gas; the exchange correlation energy at each point in the system is the same as that of the uniform electron gas of the same density originally introduced by Kohn and Sham [12] and holds quite good for a slowly varying density. Using this approximation, the exchange-correlation energy for a densityis given by

$$\mathrm{E}_{\mathrm{xc}}^{\mathrm{LDA}} = \int \rho(\mathrm{r})\epsilon_{\mathrm{xc}}(\rho)\mathrm{dr} \tag{18}$$

Where $\epsilon_{\mathrm{xc}}(\rho)$ is the exchange-correlation energy per particle of a uniform electron gas of density ρ [14].

For practical use of the LDA in calculations, it is necessary to determine the exchange-correlation energy for a uniform electron gas for a given density. It is common to split $\epsilon_{\mathrm{xc}}(\rho)$ into exchange and correlation potentials as given by [15]

$$\epsilon_{\mathrm{xc}}(\rho) = \epsilon_{\mathrm{x}}(\rho) + \epsilon_{\mathrm{c}}(\rho) \tag{19}$$

$$\mathrm{v}_{\mathrm{xc}}^{\mathrm{LDA}} = [\delta(\mathrm{r})] = \frac{\delta \mathrm{E}_{\mathrm{xc}}^{\mathrm{LDA}}}{\delta\rho(\mathrm{r})} = \epsilon_{\mathrm{xc}}(\rho) + \rho(\mathrm{r})\frac{\partial\epsilon_{\mathrm{xc}}(\rho)}{\partial\delta} \tag{20}$$

$$\epsilon_{\mathrm{x}}[\rho(\mathrm{r})] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\rho(\mathrm{r}) \tag{21}$$

3.5 Local Spin Density Approximation (LSDA)

The extension of density functional theory to spin-polarized systems is straight forward for exchange where the exact spin-scaling is known, but for the consideration of correlation, further approximations must be employed. A spin-polarized system in DFT employs two spin-densities, ρ_α and ρ_β with $\rho = \rho_\alpha + \rho_\beta$, and the form of the local-spin-density approximation (LSDA) is [16]

$$E_{xc}^{LDA}[\rho_\alpha, \rho_\beta] = \int dr\, \rho(r)\epsilon_{xc}(\rho_\alpha, \rho_\beta) \qquad (22)$$

For the exchange energy, the exact result (not just for local density approximations) is known in terms of the spin-unpolarized functional [17],

$$E_x[\rho_\alpha, \rho_\beta] = \frac{1}{2}(E_x[2\rho_\alpha] + E_x[2\rho_\beta]) \qquad (23)$$

The spin-dependence of the correlation energy density is achieved by introducing the relative spin-polarization [16],

$$\zeta(r) = \frac{\rho_\alpha(r)-\rho_\beta(r)}{\rho_\alpha(r)+\rho_\beta(r)} \qquad (24)$$

where $\zeta = 0$ and $\zeta = \pm 1$ correspond to the paramagnetic and ferromagnetic spin-unpolarized situations. The spin correlation energy density for a given values of the total density and relative polarization,$\varepsilon_c(\rho, \zeta)$ is constructed so as to interpolate the extreme values. Several forms have been developed in conjunction with LDA correlation functional [18, 19].

3.6 Generalized Gradient Approximation (GGA)

As mentioned above, the LDA neglects the inhomogeneities of the real charge density which could be very different from the homogeneous electron gas (HEG). The XC energy of inhomogeneous charge density can be significantly different from the HEG result. This leads to the development of various Generalized Gradient Approximations (GGAs) which include density gradient corrections and higher spatial derivatives of the electron density and give better results than LDA in many cases. Three most widely used GGAs are the forms proposed by Becke [20] (B88), Perdew et al. [21], and Perdew, Burke and Enzerh [22, 23]. The definition of the XC energy functional of GGA is the generalized form in Eq. 22 of LSDA to include corrections from density gradient $\nabla\rho(r)$ as

$$E_{XC}[\rho] = \int \rho(r)\varepsilon_{xc}[\rho(r)]dr + \int F_{XC}[\rho(r), \nabla\rho(r)]dr \qquad (25)$$

where the function F_{XC} is asked to satisfy a number of formal conditions for the exchange-correlation hole, such as sum rules, long-range decay and so on. This cannot be done by considering directly the bare gradient expansion. What is needed from the functional is a form that mimics a re-summation to infinite order, and this is the mainidea of the GGA, for which there is not a unique recipe. Naturally, not all the formal properties can be enforced at the same time, and this differentiates one functional from another. The Perdew-Wang 1991 (PW91) functional is an analytic fit to this numerical GGA, designed to satisfy several further exactconditions [5]. Plane waves and pseudopontential are the hallmarks of the method, andthey form a very natural alliance, since they are fundamental that their strengths and weaknesses deserve special attention.

3.7 The Pseudopotential Approximation

The fundamental theory of the pseudopontential began as an extension of the orthogonalized plane-wave (OPW) method. Aside from the possibility it offers of refining OPW calculations, it also provides apartial explanation for the success of nearly free electron calculations in fitting actual band structures. Its purpose is to describe the implementation of electronic pseudopotentials in modern electronic calculations [24-26]. Pseudopotentials are not unique and give the freedom to choose forms that simplify the calculations and the interpretation of the resulting electronic structure. The advent of ab-initio norm conserving and ultrasoft pseudopotentials has led to accurate calculations that are the basis for much of the current research and development of newmethods in electronic structure [27]. Pseudopotential approximation replaces the actual nuclear potential in the electron-nuclear interactions with a much weaker counterpart corresponding to ions. The core electrons have screening effect which results in a weaker potential. The core region is defined by a cutoff-radius r_c chosen so that the nodes of true valence wavefunction are contained within it. Outside the core region the pseudo-wavefunction matches exactly the true valence wave function, while inside the core region the former is much smoother than the latter (see Fig. 3.2). There are mainly twokinds of pseudopotentials; (i) Norm-Conserving and (ii) Ultrasoft.

The different approach known as ultrasoft pseudopotentials reaches the goal of accurate calculations by a transformation that re-expresses the problem in terms of asmooth function and an auxiliary function around each ionic core that represents the rapidly varying part of the density.

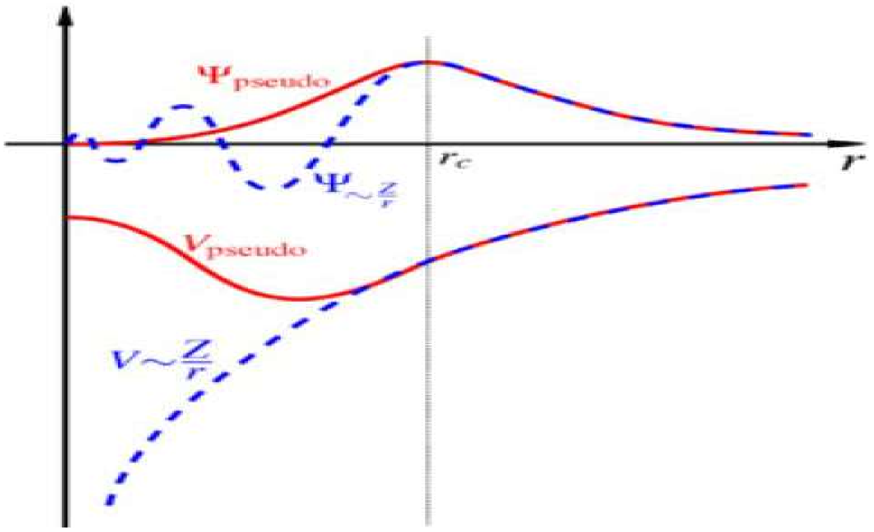


Fig. 3.2: Schematic representationof the pseudopotential method [5].

3.8 First principle calculation of Fe doped LSMO manganite system

Ferromagnetic perovskite manganites attract much attention because of its interesting properties such colossal magnetoresistance as found in some phases [28]. A first-principles calculation makes better understanding and characterization of such devices. The structural and electronic properties of rhombohedral Fe doped LSMO are investigated from first-principles calculations based on density-functional theory. A number of previous studies have used DFT calculationsto obtain parameters of typical Hamiltonians for manganite systems [29-32]. Beyond-DFT approaches are particularly necessary to correctly predict structural distortions, magnetic energies and bandgap in $LaMnO_3$, since they are wrongly described by DFT [33-35]. DFT is unable to describe the JT instabilities, and stabilize a metallic ferromagnetic solution in contrast to experimentally observed JT-distorted AFM insulating state [32].

In parallel, many studies within density-functional theory (DFT) have been performed. Since the pioneering works of Pickett and Singh [36, 37] gave a clear description of the electronic and magnetic structure of LSMO, many papers were devoted to the Fermi surface study of this important material [38].

In this scenario, apart from providing a detailed structural and electronic understanding of the Fe doped LSMO insulator-metal-transition (IMT) and of the associated competition between distorted and undistorted phases, our calcualtions predicts that the onset of metallicity is associated with FM spin transition and the FM-metal state. We give a detail description of the calculated electronic and structural properties of iron doped $LaSrMnO_3$.

3.9 VASP code for DFT calculations of Fe doped LSMO

Ab initio calculations have been performed within LDA to the exchange-correlation potential within the framework of density-functional theory using the quantum mechanical molecular dynamics simulation code; the Vienna ab-initio Simulation Package [39, 40] and is one of the most accurate schemes of solid-state electronic-structure calculations [41]. The ab-initio calculations in the present study for $La_{0.67}Sr_{0.33}Mn_{1-x}Fe_xO_3$ (x=0.15, 0.25 and 0.35) have been performed within the local density approximation (LDA) and local spin density approximation (LSDA) to the exchange correlation potential. We have used unit cell of LSMFO within ferromagnetic (FM) orders to simulate the rhombohedral R-3c structure. The Brillouin zone sampling was performed according to Monkhorst-Pack [42] method using 10 × 10 × 10 grid and 12 × 12 × 12 **k**-points, whereas the density of states was calculated using the tetrahedron method [42] to generate the **k**-points within the irreducible wedge of the Brillouin zone. For structural optimization procedure, each lattice parameter ($\vec{a}$, $\vec{b}$ and $\vec{c}$) as well as the corresponding angles between them) and all internal structure degree of freedom (all atomic positions) have been fully relaxed with the starting crystal parameters of the $LaSrMnFeO_3$ which was taken from our present XRD data [42].

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