Density Functional Theory with a Linearized Augmented Plane Wave Basis

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I. INTRODUCTION

The forumulation of quantum mechanics in the early half of the twentith century gave the foundation for understanding the interactions between electrons and nuceli. However when an interacting system composed of many particles is considered the use of quantum mechanics is cumbersome. Very quickly the calculations are intractable by hand and even with the invention of computers these systems cannot be solved exactly. Progress in this field has been made in finding methods where sufficently accurate results can be found in a useful ammount of time. The improvement of computers over the last twenty years to the point where personal computers can handle calculations which were relegated to super computers is an important milestone. However for most problems the advance in computation is not enough, more simplifications are needed.

The development of Density Functional Theory (DFT) simplifies calculations enormously from those of quantum mechanics significantly lowering computational costs. The development of DFT can be traced back to the work of Hohenberg and Kohn[3]. They found that the ground state of a many body system is uniquely determined by a unique mapping from the electron density. This greatly simplifies calculations since a problem with N electrons, a system with 3N degrees of freedom, reduces to a system of 3 degres of freedom.

While the work of Kohn, Hohenberg and others showed that a complex problem can become much simpiler by defining a functional of electronic density, they did not give any hint on the exact form of the functional. While most of the functional is well defined, the exhange-correlation part is not. Thus approximations the exchange-correlation part of the functional have to be made which go under a variety of names (LDA,GGA,etc). The simpilitest approximation, Local Density Approximation (LDA), has significantly improved in its implimentation over the last thirty years. With the initial formulation developed by Kohn and Sham[6] these authors showed that the many body system of interacting electrons and nuceli can be reduced to many single particle equations. In practice the problem is still not solved.

The simplest basis that can be used is planewaves. However in a bulk material the number of planewaves needed approaching infinity. This is obviously computationally intractable. Also near the nuceli the electron wavefunctions have many wiggles requring many planewaves in the wavefunction expansion. Luckly there are more usefull approximations which can be made to solve this problem. The two which will be discussed here are the APW and the LAPW approximation. These approximations find ways to reduce the number of planewaves used. However DFT is not the perfect method for every calculation. The functional as well as basis approximations used do vary in accuracy from one problem to another, there is not one approximation which works in all situations. In general, DFT has problems in strongly correlated systems,in band gap calculations of semiconductors and as we will see near quantum critical points[8].

II. FOUNDATIONS OF DFT

A. Work of Kohn and Hohenberg

In their ground breaking paper Kohn and Hohenberg introduced the world to DFT. This section follows their work[3]. To begin, consider a uniform electron gas under an external potential $v(r)$ and mutual Coulomb repulsion. The Hamiltonian can be written as:

$$H = T + V + U \tag{1}$$

where

$$T = \frac{1}{2}\int \nabla\psi^*(r)\nabla\psi(r)dr \tag{2}$$

$$V = \int v(r)\psi^*(r)\psi(r)dr \tag{3}$$

$$U = \frac{1}{2}\int \frac{1}{|r-r'|}\psi^*(r)\psi^*(r')\psi(r')\psi(r)drdr' \tag{4}$$

where T is the kinetic energy, V is the potential energy due to the external potential and U is the potential energy from mutual Coulomb repulsion. To make things easier assume that the ground state is nondegenerate. Let the electronic density, which is a function of $v(r)$ in the ground state Ψ be defined as:

$$n(r) = \langle\Psi|\psi^*(r)\psi(r)|\Psi\rangle \tag{5}$$

Conversely it turns out that $v(r)$ is a unique functional of $n(r)$. The proof goes as follows: Assume that another potential exists, $v'(r)$, with another ground state Ψ' which gives rise to to the same electronic density given by $v(r)$ with ground state Ψ. Ψ' cannot be the same as Ψ since they are eigenvectors of different Hamiltonians. Let the energies (hamiltonian) associated with Ψ' be E' (H') and the energies (hamiltonian) associated with Ψ be E (H). Since the ground state is the lowest energy:

$$E' = \langle\Psi'|H'|\Psi'\rangle < \langle\Psi|H'|\Psi\rangle = \langle\Psi|H + V' - V|\Psi\rangle \tag{6}$$

thus

$$E' < E + \int [v'(r) - v(r)]n(r)dr \tag{7}$$

If we interchage the prime and unprimed quantities

$$E < E' + \int [v(r) - v'(r)]n(r)dr \tag{8}$$

Adding the last two equations we arrive at the absurd result:

$$E + E' < E + E' \tag{9}$$

Thus $v(r)$ is a unique functional (within a constant) of $n(r)$. Since H is fixed by a choice of $v(r)$ the many particle ground state is a unique functional of $n(r)$. QED.

The above proof introduces the idea that a vector field (the wave functions) can be mapped to a scalar field (the energies) via the electron density $n(r)$. This concept is very important in DFT. Moreover, the proof can be generalized to degenerate ground states. Next it is constructive to define a universal functional $F[n]$ and from this we can arrive at the energy functional $E[n]$ and show that $E[n]$ is at it's minimum for the correct $n(r)$.

Let the functional $F[n]$ be defined as a functional that is concered with only the kinetic and electron interaction energies:

$$F[n(r)] = \langle\Psi|T + U|\Psi\rangle \tag{10}$$

It should be noted that $F[n]$ is a universal functional valid for any external potential and an arbitrary number of particles. From this and a given external potential $v(r)$ the energy functional is defined as

$$E_v[n] = \int v(r)n(r)dr + F[n] \tag{11}$$

For the correct electronic density $E_v[n]$ is just the ground state energy. To see that $E_v[n]$ is at its minimum for the correct electronic density the restriction on $n(r)$ applies

$$N[n] = \int n(r)dr = N \tag{12}$$

where N is the number of particles in the system. The energy functional of Ψ' is

$$\mathcal{E}[\Psi'] = \langle\Psi'|V|\Psi'\rangle + \langle\Psi'|T + U|\Psi'\rangle \tag{13}$$

where Ψ' are variations in the true ground state Ψ. $\mathcal{E}$ has a minimum for the ground state Ψ assuming that the number of particles is kept constant. Again let Ψ' be the ground state of another external potential $v'(r)$. This would imply

$$\mathcal{E}[\Psi'] = \int v(r)n'(r)dr + F[n'] > \mathcal{E}[\Psi] = \int v(r)n(r)dr + F[n] \tag{14}$$

Thus we have established that $E_v[n]$ is at a minimum for the true electronic density. Note that all of the above work is exact. But what is this universal functional $F[n]$? Each flavor of DFT approximates this functional in a different way. In the next section we will look at some of them. Since the above work has been concerned with homogenious systems, another question would be how does this apply to inhomogenious systems? The work of Kohn and Sham attempt to answer this and in the process give birth to LDA[6].

B. The Local Density Approximation

In search of the universal functional $F[n]$ arrive at the use of approximations. This work follows the work of Kohn and Sham closely[6]. The long range of Coulomb interactions makes it convient to move it out of the universal functional $F[n]$ in the following way

$$F[n] = \frac{1}{2}\int \frac{n(r)n(r')}{|r-r'|}drdr' + G[n] \tag{15}$$

where G[n] is a universal functional of the density. This implies that $E_v[n]$ becomes

$$E_v[n] = \int v(r)n(r)dr + \frac{1}{2}\int \frac{n(r)n(r')}{|r-r'|}drdr' + G[n] \tag{16}$$

We have narrowed down the form of $F[n]$ but have paid the price of introducing another universal functional $G[n]$. Thus $G[n]$ must be

$$G[n] = T_s[n] + E_{xc}[n] \tag{17}$$

where $T_s[n]$ is the kinetic energy of noninteracting electrons with density $n(r)$ and E_{xc} is the exchange and correlation energy of an interacting system of electrons also with density $n(r)$. It should be noted that for an arbitrary $n(r)$ there does not exist an exact expression for $E_{xc}[n]$. But if we assume (our first approximation) that the electronic density is varying slowly spacially it can be shown that

$$E_{xc}[n] = \int n(r)\epsilon_{xc}(n(r))dr \tag{18}$$

where $\epsilon_{xc}(n)$ is the exchange and correlation energy per electron of a uniform electron gas of density n. $\epsilon_{xc}(n)$ is found from other theories or experiment. If the form of (18) reflects the physical system in question then our approximation is valid.

We can define the electronic density with the approximation that it varies slowly as, for a small change in $n(r)$:

$$\int \delta n(r)dr = 0 \tag{19}$$

Using this with (18):

$$\int \delta n(r)[\phi(r) + \frac{\delta T_s[n]}{\delta n(r)} + V_{xc}]dr = 0 \tag{20}$$

where

$$\phi(r) = v(r) + \int \frac{n(r')}{|r-r'|}dr' \tag{21}$$

and

$$V_{xc} = \frac{d(n\epsilon_{xc}(n))}{dn} \tag{22}$$

V_{xc} is the exchange and correlation potential of a uniform gas density n. For a given ϕ and V_{xc} one can obtain $n(r)$ via the single particle Schrodinger equation.

$$[-\frac{1}{2}\bigtriangledown^2 + (\phi(r) + V_{xc}(n(r)))]\psi_i(r) = \epsilon_i\psi_i(r) \tag{23}$$

where $n(r)$ is

$$n(r) = \sum_{i=1}^{N} |\psi_i(r)|^2 \tag{24}$$

This is the LDA approximation. We have shown that the many particle problem can be reduced to many single particle problems. It must be stressed that the local density approximation assumes that the exhange-correlation

energy functional is purely local. Equations (21)-(24) must be solved self-consistantly (see Figure 1). First one begins with a trial electronic density, $n(r)$, constructs $\phi(r)$ and V_{xc} and then finds a new $n(r)$ from the single particle Shrodinger equation. The resulting energy from this process is

$$E = \sum_{i=1}^{N} \epsilon_i + \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} dr dr' + \int n(r) v(r) dr + E_{xc} \tag{25}$$

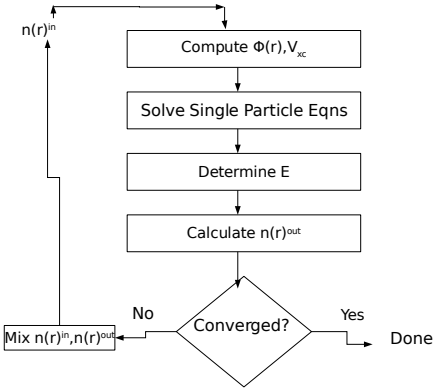

FIG. 1: Flow chart for self consistent density functional calculations[1]

The results above are exact in two limiting cases: (1) *slowly varying densities* and (2) *high densities*[2]. Limiting case (1) is met when $\frac{r_s}{r_0} \ll 1$ where r_s is the Wigner-Seitz radius and r_0 is the typical length where there is an appreciable change in density. Limiting case (2) is met when $\frac{r_s}{a_0} \ll 1$ where a_0 is the Bohr radius. In this limit the entire exhange and correlation energy is smaller than the kinetic energy by a factor of $\frac{r_s}{a_0}$. Thus the inaccuracy of the exhange-correlation energy is negligable. What is interesting about this is that this procedure links these two seemingly distant regimes.

When one leaves these two limiting cases LDA is still successful in calculating electronic properties in many instances. In contrast, a number of attempts of improving the local density approximation have failed in any noticable improvements over LDA. Theories on why this is the case can be found[2].

Now that we have defined the Hamiltonian, as well as the eigenvalues, the reader might think that the problem is sufficently solved and it is time to go home to enjoy a stiff drink. Unfortunatly this is not the case! While the single particle equations are simple, there are a lot of them. In order to calculate any result in a usefull ammount of time a suitable basis must be constructed. The rest of this paper will be devoted to this topic.

III. PLANEWAVES

In the last section it was shown that a many body system can be reduced to many single body systems. In pratice this is not the end of the story, there still exists a large number of noninteracting electrons moving in a static potential of a large number of nuclei whose wave function must be calculated. Since each wave function extends over the entire solid the basis set required approaches infinity quickly. Moreover the electron wave functions near the nuceli have lots of wiggles which require a large expansion of planewaves to mimic. Finding a method to smooth out these wiggles is important in lowering computational cost. Planewaves will make up the majority of the basis sets discussed in the rest of this paper, but why? The answer is simple: planewaves are easy to work with. In theory you could use any set of othogonal functions as your basis but this is complicated and the researcher may spend more time getting his basis to work rather than doing physics.

A. Bloch's Theorem

Bloch's theorem comes to the rescue. If the lattice in question is periodic the crytstal momentum k is a good quantum number and gives the boundary condition for the single particle wave functions ψ_i.

$$\psi_i(r) = exp[ik \cdot r] f_i(r) \tag{26}$$

where

$$f_i(r) = \sum_G c_{i,G} exp[iG \cdot r] \tag{27}$$

resulting in

$$\psi_i(r) = \sum_G c_{i,k+G} exp[i(k+G) \cdot r] \tag{28}$$

where G is the reciprocal lattice vectors. These reciprocal lattice vectors are defined by $G \cdot l = 2\pi m$ for all l where l is a lattice vector of the crystal and m is an integer. Thus each electron wave function can be written as a sum of plane waves. In dealing with a large number of electrons there will be a large set of k points to use. In a bulk material the number of electrons reaches infinity thus so does the number of planewaves needed. Bloch's theorem changes the problem from calculating an infinite number of electron wave functions to calculating a finite number of electron wave functions at an infinite number of k points[2]. Error is introduced in sampling a finite number waves in the electron wave function expansion. In this sampling it is important to know which points to keep and which to throw out. Typically the coefficents $c_{i,k+G}$ with a small kinetic energy $(\hbar^2/2m)|k+G|^2$ are more important than those with large kinetic energy. Thus our basis can be truncated at some cut off kinetic energy. This truncation will also lead to an error. To see how this effects the problem calculations are done at some cut off energy, then repeated for a higher cut off energy until the calculated total energy has converged.

Also an important property of this basis to note is that the planewaves are diagonal in momentum. Thus they are eigenfunctions of the kinetic energy operator $(p^2/2m)$. While this make make the computations less intensive for a large system the number of basis functions will be intractably large for systems that contain both valence and core electrons. One way of dealing with this problem is the introduction of an augmented plane wave basis which, as we will soon see, reduces the number of plane waves needed in the basis.

IV. PLANEWAVE METHOD

Methods have been developed to reduce the complexity of the problem. The two that will be discussed in this section are the Augmented Plane Wave (APW) Method and the Linearized Augmented Plane Wave (LAPW) Method. As their names suggest, they too use a planewave basis set but only in some regions. APW approximates the electron wave functions near the nuclei as the solutions to the radial Schrodinger equation. The reason is that electron wave functions near the nuclei are strongly varying, thus they require a large number of planewaves for a good approximation (see Figure 2). The regions are generally constructed as spheres. So inside these spheres the eigenstates of the radial Schrodinger equation are used and outside plane waves are used. The motivation behind using such functions are as follows. Since the electrons close to the nucleus are tightly bound their wave functions will look like the the radial wave functions of a single atom. Meanwhile planewaves are the solution to Schrodinger's equations in a constant potential. In a metal the text book approximation of electrons in a square well turns out to be successful as crude as it may be. The APW method was the first proposed but as we will see it has its problems. In response the LAPW method was developed which proves to be a much more accurate.

A. Augmented Plane Wave Method

The augmented planewave method (APW) was origonally proposed by Slater. The method goes as follows: Near an atomic nucelus the potential and wavefunctions are similar to those in an atom (they are strong varying but nearly spherical) but in the space between atoms both the potential and wavefunctions are smoother. Thus space is divided into two regions with different basis sets, one using the radial Schrodinger equation close to the atom and the other region using plane waves between atoms. The wave functions can be defined as follows[1]:

$$r \in I; \psi(r) = \Omega^{-1/2} \sum_G c_G e^{i(k+G \cdot r)} \tag{29}$$

$$r \in S; \psi(r) = \sum_{l,m} A_{lm} u_l(r) Y_{lm}(\hat{r}) \tag{30}$$

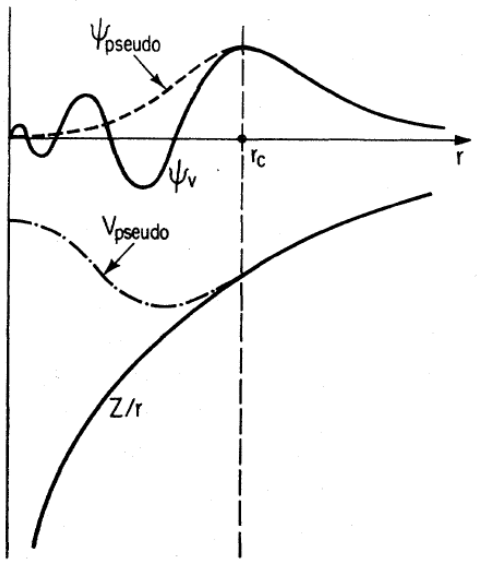

FIG. 2: Figure depicting the electron wavefunction and a pseudopotential wave function (pseudopotentals are not discussed here). Notice that the electron wave function close to the orgin is strongly varying.[2]

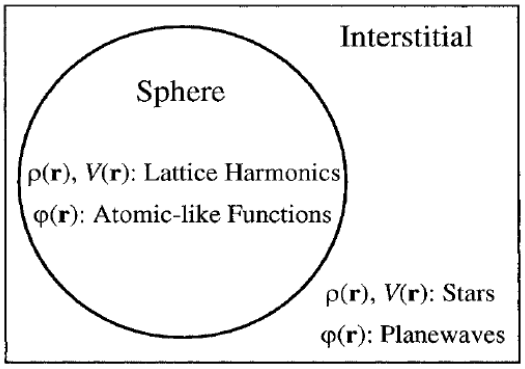

FIG. 3: The dual representation of the APW and LAPW methods. Stars and lattice harmonics are symmetrized planewaves and spherical harmonics used to represent the density and potential.[1]

where I denotes the interspacial region, S denotes the spherical region, Ω is the cell volume, and u_l is the regular solution of the radial Schrodinger equation:

$$[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l]ru_l(r) = 0 \tag{31}$$

The radial functions defined above are orthogonal to any eigenstate of the same Hamiltonian that vanishes on the sphere boundary. To see this note that:

$$(E_2 - E_1)ru_1(r)u_2(r) = u_2\frac{d^2u_1(r)}{dr^2} - u_1\frac{d^2u_1(r)}{dr^2} \tag{32}$$

where $u_1(r)$ and $u_2(r)$ are radial solutions at different energies E_1 and E_2. The overlap is constructed using this relation and integrating by parts. If $u_1(r)$ or $u_2(r)$ vanish then the surface terms vanish as well while the other terms cancel.

It should be noted that equations (29) and (30) are not necessarily continious at the sphere boundary. To ensure continuity the coefficents A_{lm} are defined in terms of c_G via the spherical harmonic expansion of the plane waves as

shown below.

$$A_{lm} = \frac{4\pi i^l}{\Omega^{1/2} u_l(R)} \sum_G c_G j_l(|k+G|R) Y^*_{lm}(k+G) \tag{33}$$

The origin is at the center of the sphere of radius R. The variational coefficents are A_{lm}, which are completely determined by the plane wave coefficnets c_G, and the energy parameters E_l. The augmented plane waves are therefore individual planewaves which are matched to radial functions in the spheres.

Unfortunatly the APW has its problems. If E_l is taken as a fixed parameter, instead of a variational coefficent, the APW method would just be the use of the APW's as a basis. Then the standard secular equation would be solved.

$$(H - \epsilon_i S) c_i = 0 \tag{34}$$

where H can be rewritten from equation (23) to the modern form:

$$H = -\frac{\hbar^2}{2m} \bigtriangledown^2 + e^2 \int \frac{n(r')}{|r-r'|} dr' + \frac{\delta \epsilon_{xc}}{\delta n(r)} + V_{ion}] \tag{35}$$

However this is not a workable scheme. The APWs are solutions of the Schrodinger euqation inside the spheres at a certain energy E_l. They do not have any variational freedom for the wave function to change as the band energy changes. Also E_l must be set to the band energy. This means that the energy bands cannot be obtained through one diagonalization. Instead the secular determinant must be solved as a function of energy. In other words, a set of E_l's must be generated and the secular equation diagonalized for each one! This is a costly computational task especially for general k points where the dimension of the secular equation cannot be folded down using symmetry and systems that have many bands. Also APW codes become less reliable as site symmetry and coordination decrease. Another problem with APW is called the asymptote problem. Note that $u_l(R)$ appears in the denominator of equation (33) if this term vanishes, as it can decouple the plavewaves and radial functions. Near the asymptote the relations between A_{lm} and c_G are strongly varying, thus the secular determinant is as well.

There have been many responses to these problems. The one we will look into in detail is the Linearized Augmented Planewave method.

B. LAPW Method

In the LAPW method the difficulties of the APW method are addressed by making the functions inside the spheres linear combinations of the radial functions with their derivatives with respect to the parameters E_l.

$$r \in I; \psi(r) = \Omega^{-1/2} \sum_G c_G e^{i(k+G.r)} \tag{36}$$

$$r \in S; \psi(r) = \sum_{l,m} A_{lm} u_l(r) + B_{lm} \dot{u}_l(r) Y_{lm}(\hat{r}) \tag{37}$$

where B_{lm} are the coefficients of the energy derivatives and the energy derivative $\dot{u}_l(r) Y_{lm}$ statisfies

$$[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l] r \dot{u}_l(r) = r u_l(r) \tag{38}$$

These functions are matched to the values and derivatives of the planewaves on the sphere boundaries. Plane waves augmented in this way are the LAPW basis functions. In a simliar way to the APW method, the LAPWs are plane waves in the interstitial region but in contrast in the spherical region they have more variational freedom. If E_l differs slightly from the band energy (ϵ_b) a linear combination will reproduce the APW radial function constructed at the band energy.

$$u_l(\epsilon_b, r) = u_l(E_l, r) + (\epsilon_b - E_l) \dot{u}_l(\epsilon_b, r) + O((\epsilon_b - E_l)^2) \tag{39}$$

where $O((\epsilon_b - E_l)^2)$ is the error that is quadratic in energy difference. Since the error is of such high order the LAPWs form a good basis set over a large energy region so that all valence bands may usually be treated with a single set of E_l. If $u_l(R)$ vanishes both its radial derivative and energy derivative ($\dot{u}_l(R)$) will be non-zero. Therefore there is

no asymptotic problem in the LAPW method so that there is no decoupling of the plane wave and radial sections of the basis. As an added bonus the LAPW method is more flexible inside of the spheres because of the added energy derivative term. However there is a cost, the basis functions must have continious derviatives. This requires more planewaves in solving the problem (a higher cutoff).

By carefully choosing the size of the LAPW spheres the computational costs can be downsized. On restriction on the sphere size is that they cannot be overlapping, meaning that the sume of two sphere radii of two atoms must not exceed the distance between atoms. Looking at nearest neighbor distances gives us a hint at what the pairwise sum of radii should be, but this does not fix individual radii. For example, consider the structure of NiAl which has a CsCl structure with lattice parameter 5.44 a_0[1]. The nearest neighbor distance is 4.711 a_0 so that the constraint on this structure is $r_{Ni} + r_{Al} \leq 4.711 a_0$. By looking at the periodic table it looks like the Al atom is larger than the Ni thus the Al spheres should be larger than the Ni spheres. However the spheres are for computational convenience and have nothing to do with atomic size. Plane wave cutoff usually scales as the inverse of sphere radius it would be a good starting point to set the nonoverlapping sphere radii to $r_{Ni}/r_{Al} \sim 1.4$. This would lead to a choice of $r_{Ni} = 2.70 a_0$ and $r_{Al} = 2.00 a_0$, going against our intial assumption. But this is the computationally efficient choice.

V. DFT APPLICATIONS

A. Application to bulk Cu

The the previous section we discussed the LAPW method and its improvments over the APW method. But how exactly is this method used? In this section we will discuss one of the first applications to of the LAPW method to bulk Cu which was one of the first published applications of this method[5]. In this study the new LAPW method is applied to Cu where the results can be compared with existing calcualtions. The method used here is simple enough to gain further insight into the LAPW method and how it is applied. It will be shown that the LAPW method gives reasonable results.

The Cu lattice is broken into spheres and interspacial regions, commonly called the muffin tin (MT) approximation. Inside the muffin sphere the radial solutions for the energy parameter E are:

$$H_l u_l - E u_l = 0 \tag{40}$$

where

$$H_l = -\frac{1}{r}\frac{d^2}{dr^2} r + \frac{l(l+1)}{r^2} + V(r) \tag{41}$$

Also the energy derivatives can be found by differentiating equation (40).

$$H_l \dot{u}_l - E \dot{u}_l = u_l \tag{42}$$

Requiring that the radial solutions are normalized may be written as

$$\int_0^R r^2 u_l^2 dr = 1 \tag{43}$$

where R is the radius of the sphere. Moreover the added bonus of orthogonality between u_l and $\dot{u}_l$ can be shown by differentiating the above equation with repect the E.

$$\int r^2 u_l \dot{u}_l dr = 0 \tag{44}$$

Outside the spheres the plane wave basis is defined as:

$$\psi(k+G) = \Omega^{-1/2} e^{i(k+G)\cdot r} \tag{45}$$

Inside the spheres the plane wave basis is defined as:

$$\psi(k+G) = \sum [A_{lm} u_l(E_l) + B_{lm} \dot{(u)}(E_l)] Y_l^m \tag{46}$$

Again Ω is the volume of the unit cell. Expanding the above equation in terms of spherical harmonics and bessil functions gives:

$$\psi(k+G, R) = 4\pi\Omega^{-1/2} \sum_{lm} i^l j_l(kR) Y_l^{m*} Y_l^m \tag{47}$$

E_0	−100	100	300	500	700	APW†
Γ_1	−103·0	−102·9	−102·9	−102·7	−102·2	−103·0
$\Gamma_{25'}$	304·6	300·8	300·4	301·1	308·2	300·3
Γ_{12}	368·2	361·1	359·8	360·2	365·5	359·4
X_1	166·0	165·3	165·4	168·1	183·2	165·2
X_3	202·6	201·2	201·2	203·6	218·3	201·2
X_2	412·1	403·5	401·7	401·8	404·6	401·7
X_5	427·3	418·2	416·3	416·3	418·5	416·3
$X_{4'}$	705·7	705·5	705·4	705·4	705·4	705·4
$W_{2'}$	221·0	219·4	219·4	221·2	233·5	219·3
W_3	274·8	271·8	271·5	272·7	282·1	271·2
W_1	364·3	358·5	357·6	357·8	361·9	357·8
W_1	428·9	419·0	416·7	416·7	419·4	416·4
W_3	1082·3	1065·4	1054·3	1048·1	1045·5	1039·5

FIG. 4: Eigenvalues for different values of the energy parameter E_l compared with known APW values.[5]

Using this, the requirement of continuity and derivative continuity at the sphere boundary gives

$$A_{lm}(k) = 4\pi R^2 \Omega^{-1/2} i^l Y_l^{m*} a_l \tag{48}$$

$$a_l = [j'_l(n)\dot{u}_l - j_l(n)\dot{u'}_l] \tag{49}$$

$$B_{lm}(k) = 4\pi R^2 \Omega^{-1/2} i^l Y_l^{m*} b_l \tag{50}$$

$$b_l = [j_l(n)u'_l - j'_l(n)u'_l] \tag{51}$$

Now we can solve the secular equation:

$$(H - \epsilon_i S)c_i = 0 \tag{52}$$

where

$$H_{nm} = \langle \psi_n | H | \psi_m \rangle \tag{53}$$

and the overlab matrix

$$S_{nm} = \langle \psi_n | \psi_m \rangle \tag{54}$$

Next a potential is chosen, in this case the Chodorow copper potential is used. The eigenvalues found by Koelling and Arbman for different values of E_l at different symmetry are shown, see Figure (4). There is very good agreement between the LAPW eigenvalues and the known values. This was a very important paper as it gave a tangible application to LAPW.

B. Application to $BaNi_2As_2$

In this section we will discuss a more modern application of the LAPW method. Here the $BaNi_2As_2$ superconductor is studied. LDA using the LAPW method is used. The spheres used vary in size with the Ba atoms having a radius of 2.2 a_0. The Ni and As atoms have spheres of radius 2.1 a_0. Below the band structure (Figure 5), the electronic DOS (Figure 6) and the Fermi Surface (Figure 7).

From these results it is obvious the impact the advancement in personal computers has in the field. Instead of calculating a set number of points the entire brillouin zone can be mapped. However, LDA does not always give a good representation of a solid as we will see in the next section.

C. Application to Ni_3Al and Ni_3Ga

In this section we will discuss a failure of LDA calculations using LAPW in describing Ni_3Al and Ni_3Ga[8]. Experiments have shown that strange phenomina occur near quantum critical points. In these compounds experiments

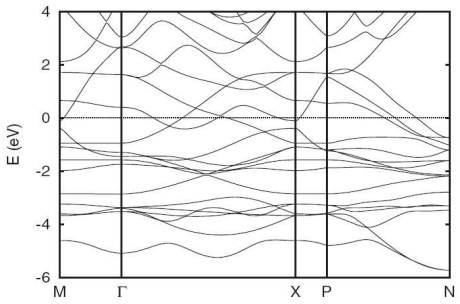

FIG. 5: Band Structure for $BaNi_2As_2$.[9]

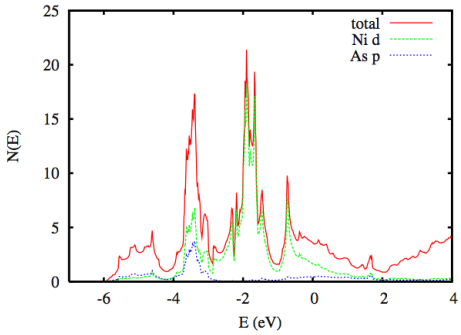

FIG. 6: Density of States for $BaNi_2As_2$.[9]

have shown that Ni_3Al is a weak itinerate ferromagnet with a $T_cof41.5K$ while Ni_3Ga is a strongly renormalized paramagnet. Moreover LDA predicts Ni_3Ga to be a ferromagnetic. However, LDA calculations on these compounds suggest that the tendency to magnetism is stronger in Ni_3Ga than Ni_3Al contrary to experimental results (see Figure 9). Both of these compounds are similar with respect to physical and electronic structure (see Figure 8) leading one to believe that seemingly subtle differences play a large role in these properties. The authors come to the conclusion that spin fluctuations are the key to understanding why LDA breaks down (see Figure 10). In their anaylisis they conclude that the LDA calculations give erroneous results since it is unresponsive to spin flucuations which leads to erronous results near quantum critical points.

VI. CONCLUSION

The work of Hohenberg, Sham and Kohn introduced density functional theory to the world and provided a means to use this theory in calculations. However this was not enough. While DFT simplified a many body problem to a single particle problem the latter still needed simplifications. In response many different methods have been developed. Two

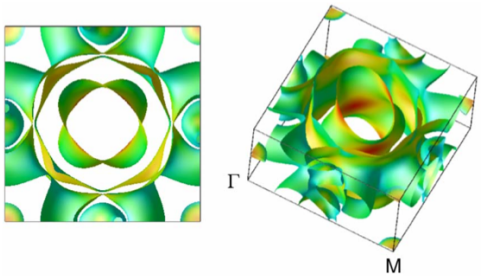

FIG. 7: Fermi Surface for $BaNi_2As_2$.[9]

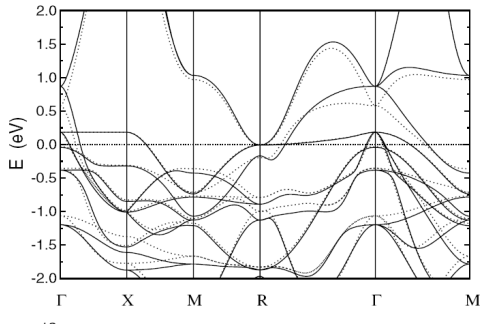

FIG. 8: Band Structure for Ni_3Al (solid lines) and Ni_3Ga (dashed lines).[8]

	$\|\Delta E\|$ (meV)	M (calc.)	M (expt.)	$N(E_F)$
Ni_3Al	10.3	0.71	0.23	3.2
Ni_3Ga	14.3	0.79	0.00	3.4

FIG. 9: Magnetic Energy and Fermi Density for Ni_3Al and Ni_3Ga compared with LDA calculations and experiment.[8]

of these methods discussed in this paper used plane waves as a basis. While any basis could be used Bloch's theorem makes plane waves plane waves the simple choice. The LAPW method attempts to limit the number of plane waves used by useing the radial Schrodinger equation in spheres which can be of arbitrary size. It should be noted that these spheres have nothing to do with the atoms in the lattice but are merely a computational convinence. Early work using the LAPW method to describe Cu was discussed with its results in good agreement with known data. However this early work was crude with only a set number of points in the brillouin zone calculated. A more recent paper on $BaNi_2As_2$ shows how far computation as come. The calculations can now calculate many more points more accuratley. However, LDA is not perfect, our last example shows this.

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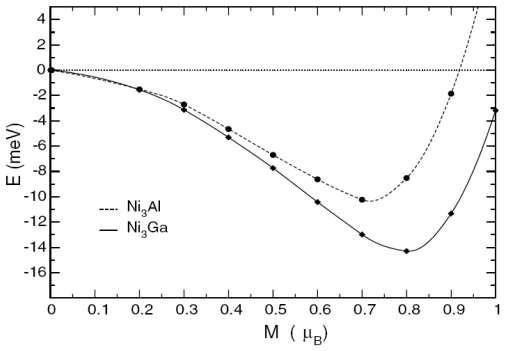

FIG. 10: Energy vs fixed spin moment for Ni_3Al and Ni_3Ga at experimental lattice parameters[8]