A 2D Multi-band Hubbard Model in Mean Field Approximation

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Contents

I. INTRODUCTION

Features of electronic structure sufficient for determination of important material properties, can often be obtained using a model Hamiltonian whose structure is simpler than that of the full crystal Hamiltonian. Band features include band gap, band width, similarities between adjacent bands, singularities of band derivatives and the density of band levels. The relationship between band features and material properties can be seen in very simple models. It is fundamental to note that the one dimensional kinetic energy band, $\frac{h^2k^2}{2m}$, for a free electron becomes periodic in k when a periodic potential, due to a chain of narrow deep potential wells, is added to its energy and that the band width becomes smaller as the distance between wells increases. If the electron is bound by the potential the width goes to zero and you are left a localized electron, i.e a particle in a box.

The usual assumptions for a practical theoretic determination of band structure are that, the material be a periodic crystal containing fixed ion cores and that the many-electron problem implied by the full Hamiltonian has been reduced to a one electron problem wherein each electron is assumed to see the same periodic potential due to the other electrons. If the valence electrons, those whose behavior characterize the material, are all bound they can be viewed as positioned at the fixed ion cores and the single electron assumption is valid. The most tightly bound electrons with no wave function overlap with near atoms are considered part of the atomic ion core. The lack of conduction electrons make these materials insulating and they are characterized by filled bands with large band gaps. For materials for which the approximations are less valid, semiconductors and metals, useful results are still obtained.

This "tight binding" of independent electrons assumption for a finite lattice of atoms allows a finite matrix form for the Hamiltonian whose eigenvectors determine electron densities. Quite generally ground state potentials, which appear as entries in the Hamiltonian, are again functions of electron density [1]. Thus a self-consistent iterative scheme can be applied to determine the single electron energies.

In this thesis the behavior, of a Hubbard Model is studied using an "LDA+U" approach introduced in conventional band theory by Anisimov, Zaanen and Andersen [2]. This is done in a two dimensional multi-band setting, and it is this multi-band feature that is new. The objectives of this research are (1) to obtain a working knowledge of the formalism, (2) to work out the necessary algorithms and produce a working code, and (3) to get some impression of the behavior of the solutions. To achieve the last of these the study uses a range of model parameters just sufficient to accomplish that task. I attempt next a summary of the well known approximations, made sufficient to introduce some notation, give due credit and hopefully orient the reader.

II. THE LOCAL DENSITY APPROXIMATION (LDA)

According to the developers of density functional theory (DFT), the exact form of all potentials seen by charge in any ground state system is completely determined by the distribution of that charge which is specified by the spin densities $n_\sigma(r)$. With the many body Hamiltonian of the system

$$H = H_{kin} + V(r) \tag{1}$$

as a function of the kinetic, ionic potential, and interaction terms Hohenberg and Kohn proved that the energy of the system

$$E[n] = < \psi(r)|H|\psi(r) > \tag{2}$$

is thus also a unique function of the electron density. Subject to constant electron number $\int n(r)dr$ we seek, within the density functional theory (DFT), the n(r) which minimizes the energy

$$E[n] = \frac{1}{2}\int e^2 \frac{n(r)n(r')}{|r-r'|} dr dr' + \int V_{ion}(r)n(r)dr + G[n] \tag{3}$$

where $V_{ion}(r)$ is the single electron potential due to the ions and any other external potential and $G[n]$ is a functional containing kinetic, exchange and correlation contributions. If we write $G[n] = T[n] + E_{xc}[n]$, separating out the kinetic part $T[n]$, the variational task is considerably simplified. With

$$E_{xc}[n] = \int n(r)\epsilon_{xc}(n(r))dr \tag{4}$$

we have

$$E[n] = \frac{1}{2}\int e^2 \frac{n(r)n(r')}{|r-r'|} dr dr' + \int V_{ion}(r)n(r)dr + T[n] + \int n(r)\epsilon_{xc}(n(r))dr \tag{5}$$

where $\epsilon_{xc}(n(r))$ is the exchange and correlation contribution energy density per electron for a uniform gas of interacting electrons. The value $E_{xc}(n)$ is the amount for a homogeneous electron gas of constant density n, and using this approximation is called the local density approximation (LDA). The variation requirements $\delta E/\delta n(r) = 0$ and $\int \delta n(r)dr = 0$ for a minimum, subject to $n(r) = \sum^{occ} |\psi_i(r)|^2$ gives

$$\int \delta n(r)[\int e^2 \frac{n(r')}{|r-r'|} dr' + V_{ion}(r) + \frac{\delta T[n]}{\delta n(r)} + \frac{d[n(r)\epsilon_{xc}(n(r))]}{d(n(r))}] = 0 \tag{6}$$

which when compared with the a noninteracting electron gas moving an effective potential

$$\int e^2 \frac{n(r')}{|r-r'|} dr' + V_{ion}(r) + \frac{\delta T[n]}{\delta n(r)} + \frac{d[n(r)\epsilon_{xc}(n(r))]}{d(n(r))} \tag{7}$$

shows that a solution to this equation is equivalent to the set of one-electron equations

$$(-\frac{h^2\nabla^2}{2m} + V(r) - E_i)\psi_i = 0 \tag{8}$$

This result was demonstrated by Kohn and Sham [3], with the effective potential V given by

$$V(r) = \int e^2 \frac{n(r')}{|r-r'|} dr' + V_{ion}(r) + \frac{d[n(r)\epsilon_{xc}(n(r))]}{d(n(r))} \tag{9}$$

Note that although eigenvectors are obtained for unoccupied states they are meaningless and ignored during the self consistent iteration (SCI) procedure. However, they do represent a degree of freedom and perhaps effect the result.

III. THE HUBBARD HAMILTONIAN WITH LDA+U

To find solutions computationally we describe the electron density as simply as possible. We must at least include the densities of the individual orbitals whose wave functions have significant overlap with nearby atoms. These point densities appear as occupation numbers in the model. Tightly bound electron can be treated as part of the ion core and the conduction electrons considered to be uniformly distributed throughout the material. A Hamiltonian which implements this point of view is a form of the Hubbard model due to Svane and Gunnarsson. [4]. To handle systems with correlated electrons more accurately the "$LDA + U$' term cited in the introduction is added.

With kinetic(T), electrostatic(U), on-site(V), LDA, and LDA+U terms, the total energy in the $LDA + U$ theory is taken to be

$$E = T + U + V + E_{xc}^{LDA} + E^{LDA+U}, \tag{10}$$

where, for site (atomic), orbital, and spin indices i, m, and σ respectively, the contributions are

$$T = \sum_{\sigma} \sum_{ii'mm'} t_{ii'mm'} < c_{im}^{\dagger} c_{i'm'} > \tag{11}$$

,

$$U = \frac{1}{2} \sum_{i} \sum_{mm'\sigma\sigma'} U_{mm'} n_{m\sigma} n_{m'\sigma'} \tag{12}$$

$$V = \sum_{i\sigma} \sum_{m} \epsilon_m n_m \tag{13}$$

$$E_{xc}^{LDA} = \sum_{i} \sum_{m} U_{mm} [n_{\uparrow} + n_{\downarrow}]^{\frac{4}{3}} [-a - b\frac{[1+\zeta]^{\frac{4}{3}} + [1-\zeta]^{\frac{4}{3}} - 2}{2^{\frac{4}{3}} - 2}] \tag{14}$$

$$E^{LDA+U} = \frac{1}{2} \sum_{i} [\sum_{mm'\sigma} U_{mm'} (n_{m\sigma} - n^{o})(n_{m'-\sigma} - n^{o}) + \sum_{\substack{mm'\sigma \\ m \neq m'}} (U_{mm'} - J_{mm'})(n_{m\sigma} - n^{o})(n_{m'\sigma} - n^{o})] \tag{15}$$

In the E_{xc}^{LDA} term, whose form is taken from Svane and Gunnarsson, the relative spin polarization is defined as

$$\zeta = \frac{n_{\uparrow} - n_{\downarrow}}{n_{\uparrow} + n_{\downarrow}} \tag{16}$$

In the E^{LDA+U} term $-\sigma$ refers to the spin opposite that of σ.

In all equations and in every appearance of the density variable n full indexing $n_{i,m,\sigma} = n_{\sigma_{m_i}}$ is implied. An index may be dropped where there is no coupling with another n in the term having a different value of that same index. The index may also be dropped when it has the same value in every term of a sum. For example the total electron density on an atom would appear as $\sum_{m\sigma} n_i$ Only the kinetic (hopping) term couples different lattice sites and in this term there is no hopping between the up and down spins so the total numbers of up and down spin are conserved separately.. Also $t_{iimm'\sigma} = 0$ so there is no kinetic hopping between orbitals on the same atom and hopping occurs only for near neighbors i and i'.

Recent results by Hess and Serene [5] with a bipartite single band Hubbard model indicate an E_{xc}^{LDA} factor with somewhat different character than above. They fit the exchange-correlation contribution to the thermodynamic potential Ω_{xc}, which is $[n_\uparrow + n_\downarrow]^{\frac{4}{3}}$ in Svane and Gunnarsson, with the power series.

$$\sum_j a_j [n_\uparrow + n_\downarrow]^j \tag{17}$$

Theirs was a serious many-body calculation done in the "fluctuation exchange approximation" for a single band Hubbard model of uniform density and zero external potential. The fit should be realistic for values of U that are not too large.

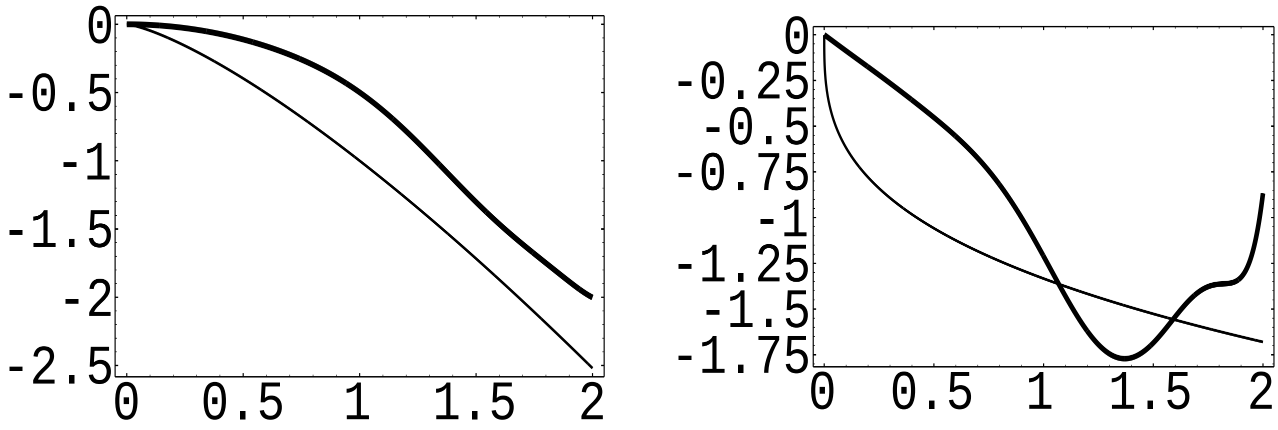

FIG. 1. Comparison of Ω_{xc} for usual LDA from Svane and Gunnarsson with the powers series fit of Hess and Serene (thick line). The right hand panel shows the derivatives of the curves in the right hand panel.

Results using this modifications will be compared to those with the usual E_{xc}^{LDA} term. In all that follows the Hamiltonian will be viewed in the tight binding picture. That is, all electron densities of interest are those occurring at point atomic sites. At each of these sites electron occupancy may occur on any of several orbitals and with either up or down spin. The wave function associated with a particular eigenstate is a finite set of numbers one for each spin of each orbital of each atom in the system. The square of that number is the probable occupation (occupancy) of the eigenstate with respect to that particular occupiable position in the system. The occupancy of an orbital is the sum of the occupancies of each occupied eigenstate. This sum is over each spin separately. Electron occupancy of a given spin on an orbital is a continuum; any value from zero to one is possible.

IV. THE LDA+U MATRIX ELEMENTS

An entry in the Hamiltonian matrix whose eigensystem is desired couples two possible locations of electron occupancy or one of these locations with itself if the element is diagonal. The value of an entry is the probability amplitude of being observed in the second location given the amplitude of being observed in the first location. A negative off diagonal entry indicates a positive probability of an electron hopping from an orbital on one atom to an orbital on a different atom. A negative diagonal entry indicates a binding potential i.e. tendency of an electron to stay on the present orbital thus the diagonal electrostatic (coulomb term) is positive. The forms of the potential entries are obtained from the Hamiltonian potential energies above by taking derivatives with respect to occupancy $n_{im\sigma}$. The off diagonal kinetic hopping entry can be viewed as a potential to move from one orbital to another so its function in the Hamiltonian matrix may be referred to at times as a potential. Thus, the total resulting potential acting on an electron eigenstate is

$$v = v^{kin} + v^{coul} + v^{ext} + v^{lda_{xc}} + v^{lda+u} \tag{18}$$

where the potentials felt by $n_{i,m,\sigma}$, some perhaps due to $n_{i'm'\sigma'}$ on other orbitals, are

$$v^{kin}_{im} = t_{m_i,m'_{i'}} \tag{19}$$

$$v^{coul}_{m} = U_{mm'} n_{m'} \tag{20}$$

$$v^{ext}_{m} = \epsilon_m \tag{21}$$

$$v^{lda_{xc}}_{\sigma} = \frac{\partial E^{LDA}_{xc}[n]}{\partial n_\sigma} \tag{22}$$

$$v^{lda+u}_{m\sigma} = \sum_{m'} U_{mm'}(n_{m'-\sigma} - n^o) + \sum_{m(\neq m')} (U_{mm'} - J_{mm'})(n_{m'\sigma} - n^o) \tag{23}$$

where

$$n^o = \frac{\sum_{m\sigma} n_{m\sigma}}{N_i} \tag{24}$$

is the average density per spin at a site i and the exchange constant $J_{mm'}$ is some fraction of $U_{mm'}$.

The absence of off diagonal terms between spins allows the computation of eigenstates for the spin up electrons to be performed independent of that for the down spin electrons. Thus it is generally possible to view hopping as taking place between orbitals since same spin hopping is implied.

V. IMPLEMENTATION

To actually obtain a self consistent solution a Hamiltonian matrix must be set up using the above potentials, its eigenvectors computed, densities obtained from the eigenvectors, and these new densities used to form new potentials for entry into a new matrix. This main computation loop and needed supporting routines are implemented in Fortran 90. Each major task performed by this code is now discussed beginning with handling of the input parameters.

Within the basic scheme and for each fixed number of orbitals there is a range of program activity that may be selected from by alteration of a single input file. As expected program input/output constituted the greatest organizational challenge. Additions to program capability require new inputs and outputs both of which interface to portions of code which to some reasonable level of assurance have been verified but which now do again require inspection. This hopefully due to catastrophic failure, as opposed to the presence an insrutible bug which unknowingly obscures a wonderful result. The following list of inputs is in outline form but there is enough interdependence that a major extension will be accompanied by a user interface. Major extension here means runtime program steering based on runtime analysis of output or other available data, not trivial extensions as that to three dimensions or simple addition of potential terms.

```
Input parameters
   options for writing data to file. code verification.
   options for runtime control of program.
        amount and kind of noise to add.
        type of solution search to be performed.
   which form of potentials to use for matrix elements
   values of parameters for the potentials
        coulomb energies U
        hopping parameters t
        onsite energies e
        factor for relative spin polarization
        exchange J parameter for lda+u potential
   hess and serene power series coefficients
   size of the lattice
   total up and down spin counts
   method for obtaining a starting guess for solution densities
        anti-ferromagnetic
        flat
        random
        alteration of or continuation of previous interations
   mixing method
        simple mixing: percent of new densities to mix with the old
        convergence dependent mixing: linear dependency factor.
   convergence methods and parameters
        run time directed search type
        mixing type
```

```
          convergence acceleration type
          eigensolver parameters
     exit control parameters
          maximum number of iterations
          error control
```

Additions to this list would include

```
     choice of eigensystem package
        single precision
        double precision
        complex
        ARPack like routine intenally configured to provide
        a simulated annealing environment for solution
        identification in the much less than half filled
        case or, to in general examine the lowest eigenstates.
     convergence to local minima scheme like that due to Broyden
     a general solution storage scheme (database)
        choice of detail
        interface with crystal structure manipulator
     precompile routine that stripes unneeded loops from a program.
        simply require that software capability upgrade
        which slows things up always implies addition of code never
        subtraction or rearrangement, then tag the additions by line
        number.  This is usually possible.
     generate something that others can add to and that will
     monopolize the small but increasingly influential user market.
```

.

Of particular interest is the assignment of the hopping parameters. To do this both the primitive cell structure and that of the underlying Bravais lattice are needed. However, once the functional form of this these parameters is determined for neighbors of orbitals in a single primitive cell, only the bravais lattice type is needed to determine the hopping between all neighboring orbitals in the lattice. Thus we will speak of a lattice of primitive cells and in general a spin density n would be indexed as $n_{spin_{orbital_{atom_{cell}}}}$. Only the 2 dimensional case is modeled here and the underlying lattice of cells is "square". Under these conditions the following file structure for inputing constant hopping parameters t can be reliably setup by hand. The following is an example for 2 atoms in a primitive cell each with 2 orbitals. Only hopping to the neighbors of orbitals in the cell located at lattice position $(0,0)$ are needed. Note that neighbors may lie outside the primitive cell.

```
 2               number of atoms in the (0,0) cell
 2               number of orbitals on atom 1 in the (0,0) cell

 5               number of neighboring cells atom 1 orbital 1 interacts with
```

```
 0 0            x,y coordinate of first cell (neighbors in same cell here)
     1          number of atoms in that first cell to interact with
        2       number of orbitals on the first atom to interact with
            t   index to obtain the hopping parameter for the first orbital
            t   index to obtain the hopping parameter to the second orbital

-1 0            x,y coord of second cell (a cell next to the (0,0) cell)
     2          number of atoms in that cell to interact with
        2       number of orbitals to interact with on the first atom
            t   index to obtain the hopping parameter to that first orbital
            t   index to obtain the hopping parameter to the second orbital
        2       number of orbitals to interact with on the second atom
            t
            t

             etc.
```

The form of this input file facilitates the setting up of the hopping matrix. For setup of the Hamiltonian matrix for a general crystal structure it is ideal from the view point of the target program but would then require a user interface to create it. In the absence of this interface, differences in parameter requirements between the one orbital and the two orbital cases, necessitated a construction of two separate input files.

Allocation of memory for the initial data is provided as it is input. Additional space must be allocated for results of previous iterations. This is done to allow comparisons between the results of the present iteration and that of previous iterations.

Having constructed the single particle Hamiltonian matrix, described in the previous section eigenstates are obtained This is accomplished with a "Lapack" routine downloaded from $http:\backslash\backslash gams.nist$, a National Institute of Science and Technology web site. It is a single precision routine but easily distinguishes the difference between the energies of different solutions. The single precision of the machine on which this code was run was $\sim 10^{-6}$. The smallest per electron energy difference observed was $\sim 10^{-4}$. During the early iterations when the eigensystems being obtained are far from converged computional accuracy may be sacrificed for the sake of computational speed. The package used provides for this. The number of eigenvectors to be obtained may also be specified.

When densities are obtained from the eigenstates only the N states with the lowest eigenvalues are used, where N is the number of electrons. Each eigenvector is a single electron state. Components of the eigenvector, when squared, are the occupancies, for that electron state, on the different orbials in the lattice. Each electron state is spread over the entire lattice. Recalling that we have made a mean field approximation wherein all potential felt by electron not due to the entirely local is the same as that for all other electrons in the system. Thus the electron eigenstates are independent. Square the same component of each electron eigenstate in the system and add together. the result is the total electron density on a particular orbital. The presence of orbitals which have a fractional occupancy is of some concern. The whole idea of using a supercell here is to obtain the actual densities of the orbitals not just the total energy of a system. However, this parial occupancy is in the spirit of modeling valence orbitals as tightly bound and is to some extent correct in general. One of the goals of LDA modifications is to obtain model solutions for which the occupancy of these valence electrons is descretized to a more reasonable degree. Again, the number of the eigenstates for up and down spin are each fixed and computed separately.

Computation, of potentials in the Hamiltonian matrix, directly from the output densities results in chaotic behavior. The feedback is too strong so a fractional amount of the new densities is added to the old densities and this new guess used as input to setup a new matrix.

Before these densities are mixed a root mean square distance comparison is made between input and output densities to determine when the solution is sufficiently converged.

When a solution is obtained the results, including the values of all input parameters are output to file. Densities of a converged solution are exhibited numerically in array form. The actual density values which usually fall between 0 and 1 have been multiplied by 100 and truncated to integers for appearance. There is one array for each orbital, for spin on that orbital and these densities for the atom as a whole If there is more than one atom per site they are each exhibited separately. The sums and differences of the up and down spins are also exhibited.

These same densities appear as Mathematica density plots arranged on a single page. Our model system has periodic boundary condition so these plots are repeated once in both x and y directions to facilitate pattern recognition. That is each plot is doubled. The 8×8 lattice appears as a 16×16 density plot.

The total energy per electron are display as is that for up and down spin electron separately. Eigenvalues of the occupied state are summed and a per electron energy obtained.

Also computed are Fourier transforms. The Fourier transform of the densities on an 8×8 lattice is again an 8×8 lattice but of complex coefficients $c(k_x, k_y)$ from wihich the density at any site $r = (r_x, r_y)$ can be reconstructed as the linear combination $\sum_k c(k)e^{i\vec{k}\cdot\vec{r}}$. When the system is stongly coupled ($U >> t$) and when the total numbers of up and down spins are unequal, the solutions become more complex. Their spatial symmetry and periodicity need to be analyzed and compared numerically. The transform is useful here as the more symmetric solution require for their reconstructionl fewer fourier coefficients. For example the components $c(k_x, k_y)$ of a lattice of random values would again be random. However, the transform of the up spin densities of the anti-ferromagnetic case would consist of but a single non zero real coefficient, $c(5, 5)$ appearing at position $(5, 5)$ in the fourier space lattice. More commonly one thinks of k_x, and k_y as ranging from 0 to 2Π in which $c(5, 5)$ is written as $c(\pi, \pi)$. The up spin density of an anti-ferromagnetic lattice at site (x, y) is 1 if $x + y$ is odd and 0 otherwise. Similarily a flat lattice of all $1's$ has a single nonzero real value at $c(1, 1)$ i.e. $k^{\vec{=}0}$. Some complex components may be required even for highly symmetric solution. This is the case for a $\sqrt{2} \times \sqrt{2}$ symmetry where in there is periodicity along both the 45^o diagonals with the period being $\sqrt{2}/2$ the boundary periodicity of of the lattice. In general most of the symmetry behavior is exhibited by the $c(k_x, k_y)$ for $k_i \leq n/2$ for an $n \times n$ lattice of densities. This is due to the periodic boundary condition and indicates that observation of some interesting spin orderings may only be possible on larger lattices.

Computation of solutions for larger systems is feasible. The eigensystem for say the 758×758 matrix of a 16×16 real space cell by 2 orbital system can be obtained in under a minute. It has been determined on the basis of a few dozen parameter sets that the low energy physical solutions converge in the fewest iterations and in addition require less old/new density mixing. Also, observation of a converging solution after only a few iteration shows that the character of a particular solution is determined very early on in the iterative proceedure. Thus a highly converged solution can, if desired, be obtained quickly by use of a Broyden convergence scheme [6] it is also observed that the solution obtained is highly dependent on the initial guess, and one must try several starting points or adopt some other scheme for finding good (low energy) solutions.

VI. CONVERGENCE BEHAVIOR OF SOLUTIONS

Unfortunately even though characteristics of a ground state solution in our model system, may resemble those of a real material; the iterative procedure by which the solution is obtained definitely does not model nature's dynamical behavior. Thus, although there is always a ground state solution a self consistent iteration (SCI) may not obtain this state. Now the fact that the solution of a SCI is a fixed point means that each solution can be viewed as a local minimum with respect to its occupied eigenstates or any other of its characteristics for that matter. A SCI starting from a small perturbation of these states for a given solution will result in convergence to that same solution. Referring to perturbation of any set of eigenstates or densities as adding noise we now examine the solutions and convergence behavior of the model for the single orbital case model in a range of U values low enough for which the different solution densities are clearly identifiable.

The SCI procedure for the half-filled single orbital case results in a handful of solutions. From random starting densities, the occurrence vs energy distribution of these solutions favors those of low energy.

For all values of U the AF solution was the solution of lowest total energy. The general characteristics of the solutions for larger U and related problems in the multi-band case will be discussed later.

As relates to the adding of noise, it was observed that the level of noise which can be added during a SCI which has converged to within some fixed distance, without altering the final solution result, is larger for those SCI converging to lower energy solutions.

The forms of these convergence dependencies shows that, at any stage of convergence, if one is converging to a solution with an energy sufficiently above ground energy, adding sufficient noise will more likely than not result in convergence to a different solution with lower energy.

Not surprising. However, if "sufficiently above" majorizes more states than can be randomly searched through in a reasonable time we much either make an educated guess at the correct final solution and verify it by convergence in a single iteration or in some other way direct the iterative procedure.

The following dependency of convergence rate on energy of the converged solution suggests that, at several stages of convergence, a selection be make, from several trial additions of noise, based on succeeding observed convergence rates.

VII. A FEW TRIAL RUNS

The code is written so as to allow multiple atoms and orbitals. First it is tried for the simple LDSA, one atomic type, one orbital. The 4 nearest neighbor hopping parameters are set to -1. The on site energy ϵ_o set to 2. U is varied from 1 to 10. The lattice size is 8×8 and the number of up and down spins ($n \uparrow, n \downarrow$) both equal to 32. The mixing parameter set to .1 that is .1 new densities .9 old densities. Computations are single precision. The convergence distance is set to 10^{-4}. For all values of U total occupancy, $n \uparrow + n \downarrow$, was the same on every site so the spin $n \uparrow$ densities can be inferred from the $n \downarrow$ densities. Fifteen different solutions were found. Five exhibited a $\sqrt{2} \times \sqrt{2}$ symmetry. A couple had $\sqrt{2} \times \sqrt{1}$. Two others had a spin wave $\times 8$ symmetry. A couple with $\sqrt{2} \times \sqrt{2}$ were quasi anti-ferromagnetic. The lower the total energy, the larger were the regions with AF behavior. Of course the most popular was the 8×8 AF case. The AF solution always had the lowest total energy but given the range of total energies for all the solution there were several with energies which were very close. For U in the range $3-5$ these close solutions occurred nearly as often as the AF case and exhibited the property that $| n \uparrow - n \downarrow |$ had a wave like nature. Visually, different solutions were most easily distinguished by the $| n \uparrow - n \downarrow |$ plot. Below $U = 3$ the AF case appeared less often and above $U = 5$ AF dominated.

A similar set up with 2 orbitals per site and $U(\alpha, \beta)$ values of $U(1,1) = 1$, $U(1,2) = U(2,1) = 2$, and $U(2,2) = 4$ had uniform total density equal to 1 on each site. The total spin density on orbital 2 was suppressed and nearly flat. The $n \uparrow$ pattern on orbital 1 was the same as the the $n \downarrow$ pattern on orbital 2 and vis versa.

For the single orbital case I compared my results with the results generated by an existed suite of routines by Warren Pickett which model the Self Interaction Corrected LDA. Both exhibited several non AF solutions for intermediate values of U with the AF solution being dominant. Also the general appearance of the small eigenvectors was the same tending to be flat as were the energies and distribution of eigenvalues.

SOLUTION CHARACTERISTICS VS LATTICE SIZE

Aside from aiding program verification, observing behavior of solutions as a function of lattice size saves time. It is useful to the comparison for per electron energy for a fixed set of model parameters. If, for example, the ground state is determined to be AF, with constant magnetization for lattice sizes 4x4 and 8x8, it is probably enough going to be the same for a 16x16. On the other hand, if the difference, in energy for two solutions of different character but same lattice size, is smaller than the energy difference, of two solutions of character both similar to one of those but each on a different lattice size say 8x8 and 10x10, (and the result looks interesting) one might do well to try a 12x12.

VIII. BLOCK SUPERCELL METHOD

One can simulate the behavior of a 16×8 lattice by allowing eigen solutions with complex components and imposing a phase shifts on the periodic solutions of each of the adjacent 8×8 super-cells. We thus have Block like solutions which are different for different amounts of shift. Physical quantities must be averaged over these different solutions. A quantity of interest in a bulk 2D crystal is a function of the crystal momentum but is usually expressed as a function of energy. Thus when one averages the quantity over the system; it is done by integrating against $g(\epsilon)d\epsilon$, rather than $dk_x dk_y$. Given the dispersion relation $\epsilon(k_x, k_y)$ this density of energy states $g(\epsilon)$ for each fixed $\epsilon(k_x, k_y)$ is thus the integral of $1/|\nabla\epsilon(k_x, k_y)|$ over that differential area (paths) in k space with energy $\epsilon(k_x, k_y)$. If this area becomes finite for some value of ϵ then $g(\epsilon)$ blows up and the value ϵ is a Van Hove singularity.

The integration is performed for a continuous dispersion relation by breaking the k space surface into a mesh of triangles. The corners of the triangles are lifted off the k plane into the 3D space $(k_x, k_y, \epsilon(k_x, k_y))$ forming a new mesh of triangles which approximates the surface $\epsilon(k_x, k_y)$ and is exact at triangle corners. The value of $\epsilon(\vec{k})$ at a k point not a triangle corner is obtained in an obvious way. Integration in 3D k space to obtain $g(\epsilon)$ has been detailed [7]. For the 2D case the form of the reciprocal lattice vectors and centers of gravity of the triangle is a bit different and obtaining a result is simplified by fewer summations.

Assume that in k space the corners $\vec{0}, \vec{1}, \vec{2}$ of a triangle are ordered with respect to energy ϵ. The gradient on this triangle with respect to energy is everywhere the same and is a linear combination of the linearly independent vectors reciprocal to $\vec{1} - \vec{0}$ and $\vec{2} - \vec{0}$ say b_x and b_y respectively. The gradient then is $b_y(\epsilon(\vec{1}) - \epsilon(\vec{2})) + b_x(\epsilon(\vec{2}) - \epsilon(\vec{1}))$. Along any line on the triangle perpendicular to the direction of this gradient the value of ϵ is constant. Pick one. Also pick a fixed energy band of finite width $\Delta\epsilon$. The approximate contribution of this triangle to the integral form of $g(\epsilon)$ is just the area of the $\Delta\epsilon$ band about ϵ projected onto the k space plane. The area of the band is approximately $\Delta\epsilon$ time the length of the constant ϵ line on the triangle. To project onto the k plane divide by the magnitude of the gradient. The formula for the length of the line depends on whether ϵ on the line lies between $\epsilon(\vec{0})$ and $\epsilon(\vec{1})$ or between $\epsilon(\vec{1})$ and $\epsilon(\vec{2})$. Sum over all triangle on which a fixed value of ϵ appears and you have the value of $g(\epsilon)$ for a particular value of ϵ. Just watch out for singularities. Cannot divide by zero.

For a fixed choice of $\Delta\epsilon$, $g(\epsilon)$ has been evaluated for evenly spaced energy values for ease of use. Now consider the case where the integration to obtain $g(\epsilon)$ is not over k space but over k space weighted by a function $A(k_x, k_y)$. In this case the weight used on a $\Delta\epsilon$ band will be the approximation obtained by choosing the value of A at the center of the line of constant ϵ. This value is obtained by making a triangular approximation to A as was done with ϵ. If ϵ is near a singular point or if A changes significantly along the constant ϵ line, refine the triangular mesh.

I coded up this method of obtaining $g(\epsilon)$ and tested it for $\epsilon(\vec{k}) = \vec{k} \cdot \vec{k}$ and obtained the expected linearly increasing $g(\epsilon)$ which flatten to a constant once $\vec{k}$ reached the nearest zone boundary. At present I am using one super-cell with $\vec{k} = 0$ case, no Bloch boundary conditions.

This concludes my thesis.

APPENDIX A: SAMPLE OUTPUT

This appendix contains sample output of the program plus.f90. The various parameters input to the program are show along with the converged solution. The set up here is one atom per cell with two orbitals on each of these atoms. What is provided is that which was disscused in section V The solutions for these samples include:

Only eigenvalues for the occupied states are listed. The total energy contribution obtained by summing of eigenvalues of occupied states is of the same order of magnitude as that obtained by computing the numerical value of the Hamiltonian. However, as discussed the actually values for each differ.

The accompanying plots of lattice densities are repeated in both the horizontal and the vertical directions. That is, the lattice size is $8x8$ but the plots are $16x16$.

The following output with accompanying plot is typical of results starting the iterations from anti-ferromagnetic densities. The ordering of spin on each orbital is clearly not random but still very disordered. For each spin the total density on the atom is nicely ordered.

```
 1 iteration itdump dump info site ixdump iydump
 35  1  1
 1  query, include noise, iaddnoise iterations
 20  query every iaddnoise iterations
 0  print first hamiltonian and densities for first iteration and exit (0,1)
 1  include the hopping parameters
 0  off diag electrostatic term(0,1)
 1  include standard electrostatic term(0,1)
 1  include the onsite (external) term (0,1)
 0  include lda with 4/3 power  (0,1)
 0  include lda with 4/3 power, h&s  sum
 1  include lda as hess and serene sum  (0,1)
 1  include the u for lda+u repair  (0,1)

 3   the number of potentials (uvalues) to input
 8.00000  8.00000  8.00000  uvalues

 6  6           nx   ny
 32  32    spinup  spindown

 .100000        amix  mixing

 1.000000E-04   densities have converged when
 1  eigen solver demands a tolerence
 1.000000E-05  superseeded by eigenfactor1
 1.000000E-04   tolerance set to eigenpackage/distance
 1000   maximum number of interations
-1   a 0 gives random wvfn, a -1 gives AntiFerro
 .250000   factor of U to substract 2nd term in plus u

 6   number of hopping parameters
-1.00000 -1.00000 -1.00000 -.000000 -.000000 -.000000

 1   number of atoms in cell
 2   number of orbitals
 .200000   factor of zeta term in lda

 10    polynomial coefficiet for hess serene
 .000000
-1.32532
-.300919
 3.27475
-13.7277
 29.0402
```

```
 -34.1589
  21.9011
 -7.11752
  .917821


                          onsite energies
  1.00000  1.00000


-4.61847 -3.15307 -2.90953 -2.49704 -2.33625 -1.44551 -1.10551  -.99525
 -.85575  -.78333  -.52980  -.05477   .17062   .52969   .78863   .90721
  .92385   .99501  1.08575  1.10630  1.11594  1.27451  1.44882  1.66882
 2.03638  2.11946  2.31204  2.55502  2.75405  3.01683  3.17858  3.55369



-4.64424 -3.50771 -3.29101 -2.96723 -2.73967 -1.90119 -1.61694 -1.29967
-1.19454  -.93759  -.77879  -.66829  -.29897  -.13352   .11941   .35814
  .54411   .69501   .81760   .83322   .89731   .97608  1.10786  1.20339
 1.35395  1.41464  1.78009  1.99458  2.27127  2.67215  2.88063  3.16552


totaleigenenergy =   .177540     .383030    -2.795041E-02
                       total      upspin      downspin
total kinetic    =  -.842187    -.903523    -.780851
total electro    =   7.13600     7.14658     7.12542
total onsite     =   1.00000     1.00000     1.000000
total lda        =  -6.70941    -6.70941    -6.70941
total_plusu      =  -1.72014    -1.62814    -1.81214
total energy     =  -1.13574    -1.09450    -1.17698

distance =   9.578531E-05     1.257147E-04

Converged in   616  iterations.
***

***
```

The highly symetric solution have more degenerate or nearly degenerate eigenstates.

The long variable names aid variable organization and help to prevent conflict in that large pool of memory shared by the supporting subroutines.

Implementation of the needed solution search requires a linked list tree implementation of this structure falls within Fortran90 capability or do as a c++ subroutine.

APPENDIX B: CODE LISTING

The following fortran90 code listing is not exhaustive.

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