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Charge and Spin Fluctuations in the Density Functional Theory

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Abstract

We introduce a conceptual framework which allow us to treat charge and spin fluctuations about the Local density Approximation (LDA) to the Density Functional Theory (DFT). We illustrate the approach by explicit study of the Disordered Local Moment (DLM) state in Fe above the Curie Temperature T_c and the Mott insulating state in MnO.

1 Fluctuations and Density Functional Theories

Fluctuations are strangers to Density Functional Theories, whether quantum [1] or classical [2]. In what follows we shall analyze the burden of this remark and argue that the lack of formal provision for including fluctuations into such theories is an handicap worth overcoming.

1.1 Two free energy paradigms of many body theory

In fig. 1 we list side by side the principal, well known, formulae of the Landau-Ginzburg-Wilson (LGW) and the Kohn-Sham (KS) type of approaches [3, 1] to problems with many interacting degrees of freedom.

Evidently, Landau's advice [4] is to make up a free energy functional $F^{MF}[\varphi]$ of some variable field, order parameter, $\varphi(\vec{x})$ and minimize it. This

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is the mean field approximation. If this is not good enough one is to exponentiate $F^{MF}[\varphi]$. Namely, make all predictions of the theory be functional averages with respect to the probability distribution $\frac{1}{Z} e^{-\beta F^{MF}[\varphi]}$. When evaluating the functional integrals, as in finding the partition function Z , one often proceeds using the saddle point method. This requires the expansion of $F^{MF}[\varphi]$ about its minimum, at φ_{MF} , in powers of the deviations $\delta\varphi(\vec{r}) = \varphi(\vec{r}) - \varphi_{MF}(\vec{r})$ and then performing the functional integral.

Evidently, this approach to the problem is a theory of fluctuations *par excellence*. It is a particularly powerful method when the most significant fluctuations can be identified by physical intuition. Although statistical mechanics problems are the most frequent examples of this approach the many-electron problem is often cast into the above form using the Hubbard-Stratanovich transformation [5].

By contrast in density functional theories there are no fluctuations of the field $\varphi(\vec{x})$ about the mean, $\bar{\varphi}(\vec{r})$, or some other standard $\varphi_{MF}(\vec{r})$. It is always the average field $\bar{\varphi}(\vec{r})$ that occurs. Even in an exact theory one is to minimize the exact functional $\Omega[\bar{\varphi}]$. Unlike the previous approach in which $F^{MF}[\varphi]$ remains of the same form (usually a simple polynomial in φ and $\vec{\nabla}\varphi$) as progressively better approximations are sought, density functional theories require more and more complicated functionals, $\Omega[\bar{\varphi}]$, as the level of approximation is improved. On the other hand the mathematical task of minimizing $\Omega[\bar{\varphi}]$ remains the same. Indeed, it is the relative simplicity of the minimization procedure compared with doing functional integrals, and the availability of a vast arsenal of numerical techniques for doing it that are the principal virtues of this approach [1].

Our purpose in this talk is to suggest a way of including fluctuations, in the above sense, into the density functional theory approach to the inhomogeneous many electron problem and thereby bring physical intuition to bear on the problem of going beyond the Local Density Approximation.

1.2 The method of summing over constraints

Recalling the conventional density functional argument, summarized in fig. 1, we note that the spectacular achievement of replacing the immense complexity of fluctuations in Fock Space by a minimization problem has been bought about at the price of introducing an effective potential functional $v^{eff}(\vec{r}, [n])$ which is, to say the least, difficult to fathom beyond the Hartree approximation.

Our proposal is to let $v(\vec{r}, [n])$ fluctuate in accordance with our physical

intuition and identify the predictions of the theory with averages over an appropriate ensemble of such fluctuations.

To lay the formal foundations for such a scheme we must return to the origin of the Gibb distribution function $\hat{\rho} = Z^{-1} \exp\{-\beta\hat{H}\}$. As is well known it may be obtained by minimizing the generalized grand potential [6]

$$\Omega[\hat{\rho}] = \text{tr} \left(\hat{\rho} \left(\hat{H} - k_B T \ln \hat{\rho} \right) \right) \quad (1)$$

with respect to arbitrary variations in the density matrix $\hat{\rho}$ defined in an appropriate many-body Hilbert space. We shall now present an alternative to the above procedure which will turn out to be useful. Although we shall make no effort to be rigorous we hope that our arguments are persuasive.

Let us look for a density matrix $\hat{\rho}(\{\mu_i\})$ such that an arbitrarily selected set of operators $\{\sigma_i\}$ have a prescribed expectation value

$$\text{tr} (\hat{\rho}(\{\mu_i\}) \sigma_i) = \mu_i. \quad (2)$$

Clearly, such density matrix can be found by minimizing $\Omega[\hat{\rho}]$ in eq. 1 subject to the constraints in eq. 2. Then the grand potential associated with the prescribed set of averages $\{\mu_i\}$ is

$$\Omega(\{\mu_i\}) = \Omega[\hat{\rho}(\{\mu_i\})] \quad (3)$$

and the probability that the system takes on a particular set $\{\mu_i\}$ is

$$P(\{\mu_i\}) = \frac{1}{Z} e^{-\beta\Omega(\{\mu_i\})} \quad (4)$$

where

$$Z = \prod_i \int d\mu_i e^{-\beta\Omega(\{\mu_i\})} \quad (5)$$

and $\int d\mu_i$ is a generalized symbol for summation or integration as follows from the nature of the averages $\{\mu_i\}$.

Evidently, the above procedure should be exact. It merely breaks up the full task on the left hand side of fig. 1 into two parts: solving the problem with constraints and then summing over the constraints with appropriate weights.

The next move in our derivation is now clear: we should deploy the density functional argument for converting the many body problem defined by the density matrix $\hat{\rho}(\{\mu_i\})$ to an effective, self consistent one electron problem in place of the conversion depicted in fig. 2. Naturally, such reasoning

leads to a Kohn-Sham type of Euler-Lagrange equation for the constrained problem:

$$\left(-\nabla^2 + v^{eff}(\vec{r}; [n(\vec{r}; \{\mu_i\})])\right) \varphi_n(\vec{r}) = \epsilon_n \varphi_n(\vec{r}) \quad (6)$$

$$n(\vec{r}; \{\mu_i\}) = \sum_n |\varphi_n(\vec{r}; \{\mu_i\})|^2 f(\epsilon_n(\{\mu_i\})) \quad (7)$$

where it is assumed that the averages $\{\mu_i\}$ are unique functionals of $n(\vec{r})$, and hence it makes sense to search for a infimum of $\Omega[n]$ among functions $n(\vec{r}; \{\mu_i\})$ which correspond to the set of prescribed averages [7]. Of course, technically such problems would be solved by the method of Lagrange multipliers. Moreover, one may wish to consider the spin polarized version of the above theory where Ω depends on $n_\uparrow(\vec{r})$ and $n_\downarrow(\vec{r})$ separately. However, we leave such details to the next section where particular instances of our scheme will be discussed. What matters here is that the *gedanken* calculation prescribed by eqs. 6, 7, and the recipe that after each iteration the calculated charge density $n_{cal}(\vec{r}; \{\mu_i\})$ has to be projected back into that part of function space which is consistent with the constraints, may have a solution. Clearly, if it does, the grand potential defined in eq. 3 is given by

$$\Omega(\{\mu_i\}) = \Omega[n(\vec{r}; \{\mu_i\})] \quad (8)$$

and hence we have recovered the statistical description of eqs. 4, 5.

In short we have arrived at the following sensible prescription for including fluctuations into the density functional theories:

- i. Carry out density functional calculations for a system with a selection of constraints;
- ii. Calculate averages over the ensemble of constraints, in other words fluctuations, using Gibbsian weights defined eqs. 4, 5 and 8.

Consequently, to introduce fluctuations about the Local Density or Local Spin Density Approximation we should carry out the step in i.) using the LDA or LSDA. Clearly, this is a very flexible scheme whose power depends on finding the constraints which correspond to the physically relevant fluctuations. In what follows we present explicit examples of how it works.

2 The Hubbard Alloy Analogy Approximation

Although our aim is to carry out the above program on the bases of first principles calculations, as a first primitive example we wish to consider a

simple model. It is defined by the one orbital per site Hubbard Hamiltonian [8]:

$$H = - \sum_{\langle ij \rangle, \sigma} t_{ij} c_{i, \sigma}^\dagger c_{j, \sigma} + \frac{U}{2} \sum_{i, \sigma} c_{i, \sigma}^\dagger c_{i, \sigma} c_{i, -\sigma}^\dagger c_{i, -\sigma} \quad (9)$$

where i and j refer to lattice sites, σ the projection of the electronic spin along the z-axis, $c_{i, \sigma}^\dagger$, $c_{j, \sigma}$ are the usual creation and annihilation operators, t_{ij} is a hopping integral and U is an on-site repulsive interaction parameter.

A way of tackling this problem is to define the Greens function:

$$G_{\sigma\sigma}(ij; t) = -i \langle T \{ c_{i, \sigma}(t) c_{j, \sigma}^\dagger(0) \} \rangle \quad (10)$$

where T is the usual time ordering operator, derive its equation of motion and solve it by decoupling the two particle average which appears in such an equation as an inhomogeneous term. Namely, we make the following approximation

$$\langle T \{ c_{i, -\sigma}^\dagger(t) c_{i, -\sigma}(t) c_{i, \sigma}(t) c_{j, \sigma}^\dagger(0) \} \rangle \approx n_{i, -\sigma}(t) G_{\sigma\sigma}(ij; t). \quad (11)$$

If we further assume that

$$n_{i, -\sigma}(t) = \langle c_{i, -\sigma}^\dagger(t) c_{i, -\sigma}(t) \rangle \quad (12)$$

we are dealing with the usual Hartree-Fock approximation [8]. The seminal suggestion of Hubbard [9, 10, 11] was that one should not set $n_{i, -\sigma}(t)$ equal to the average occupation number but allow it to fluctuate between the values 0 and 1. Although such classical fluctuation can not make up for the error introduced by the decoupling in eq. 12 it turns out that they represent a considerable improvement on the Hartree-Fock approximation which, like the Density Functional theories of the previous section, does not allow for any fluctuation in the potential an electron sees. Briefly, Hubbards alloy analogy prescription was to solve the Greens function equation:

$$\sum_l [(\epsilon - \epsilon_0 + U n_{i, -\sigma}) \delta_{il} + t_{il}] \tilde{G}_{\sigma\sigma}(lj; \epsilon) = \delta_{ij} \quad (13)$$

which follow from eq. 12 [8], for a fixed set of occupation numbers $\{n_{i, \sigma}\}$ and consider the average of $\tilde{G}_{\sigma\sigma}(ij; \epsilon)$ over an ensemble of configurations $\{n_{i, \sigma}\}$ as the approximation for the one particle Greens function defined in eq. 10 e.g.:

$$G_{\sigma\sigma}(ij; \epsilon) = \langle \tilde{G}_{\sigma\sigma}(ij; \{n_{i, \sigma}\}; \epsilon) \rangle. \quad (14)$$

This recipe was completed by the assumption that the occupation numbers $\{n_{i,\sigma}\}$ are independent random variables and hence it is sufficient to carry out the average in eq. 14 within the well tried Coherent Potential Approximation (CPA) [12].

As is well known the above scheme leads to a splitting of the Hartree-Fock band for $U > zt$, where z is the number of nearest neighbours and hence zt is the bandwidth. As a consequence, for a half filled band and large enough U ; there will be a gap at ϵ_F as shown in fig. 3. This state is widely regarded as a good description of a Mott insulator [9, 10, 11, 13].

Clearly, we have recalled the above example to illustrate how including charge fluctuation about the Hartree-Fock solution can lead to qualitatively new results and dramatically new insights. The remainder of this contribution will be devoted to discussing the first tentative steps towards implementation of the above scheme for describing charge and spin fluctuations about the LDA [13].

3 Fluctuations about the Local Spin Density Approximation within the SCF-KKR-CPA

Let us consider a simple explicit version of the fluctuations discussed in Sec. 1. To begin with let us constrain each site to be in one of four possible states: excess charge with overall spin up ($+\uparrow$), excess charge with overall spin down ($+\downarrow$), charge deficit with overall spin up ($-\uparrow$) and charge deficit with overall spin down ($-\downarrow$). This means that at a site i and for spin projection σ there will be four possible charge densities

$$\bar{n}_{i\sigma}^\nu(\vec{r}) = \bar{n}_{i\sigma}^{+\uparrow}(\vec{r}), \bar{n}_{i\sigma}^{+\downarrow}(\vec{r}), \bar{n}_{i\sigma}^{-\uparrow}(\vec{r}), \bar{n}_{i\sigma}^{-\downarrow}(\vec{r}). \quad (15)$$

As for as the statistical sum over constraints (see eqs. 4 and 5) are concerned we shall work in the mean field approximation and hence assume that each site i is in one of the four states with probabilities:

$$P(\nu) = P(+\uparrow), P(+\downarrow), P(-\uparrow), P(-\downarrow) \quad (16)$$

independent from the states of the other sites. This implies that the effective potential at \vec{R}_i for an electron with spin σ will be a functional of $\bar{n}_{i\sigma}^\nu(\vec{r})$, and, through the non-local Hartree contribution, the average $\bar{n}_{i\sigma} = \sum_\nu P(\nu) \bar{n}_{i\sigma}^\nu(\vec{r})$ e.g.:

$$\bar{v}_{i\sigma}^{eff,\nu}(\vec{r}) = v^{LD}(\vec{r} - \vec{R}_i; [\bar{n}_{i\uparrow}^\nu, \bar{n}_{i\downarrow}^\nu; \bar{n}_{i\uparrow}, \bar{n}_{i\downarrow}]). \quad (17)$$

We now seek to solve for the electronic structure for each complete set of constraints $\{n_{i\sigma}^{\nu}(\vec{r})\}$ and average the energy and other observables over all constraints using the mean field theoretic weight

$$P(\{\nu_i\}) = \prod_i P_i(\nu_i). \quad (18)$$

As is well known from the theory of disordered systems a useful general quantity to average is the electronic Greens function. In our case this is the Greens function which satisfies the Kohn-Sham equation:

$$\left[-\nabla^2 + \sum_i \bar{v}_{i\sigma}^{\epsilon}(\vec{r} - \vec{R}_i) \right] \bar{G}_{\sigma\sigma}(\vec{r}, \vec{r}'; \epsilon) = \delta(\vec{r} - \vec{r}') \quad (19)$$

for particular configuration $\{n_{i\sigma}^{\nu}(\vec{r})\}$ and potential functional defined in eq. 17. The quantity of general interest from which many useful properties like the averaged total energy [14] can be calculated is the averaged Greens function:

$$G_{\sigma\sigma}(\vec{r}, \vec{r}'; \epsilon) = \langle \bar{G}_{\sigma\sigma}(\vec{r}, \vec{r}'; \epsilon) \rangle \quad (20)$$

where $\langle \dots \rangle$ stands for average with respect to the distribution given in eq. 18.

A well tried method for dealing with electrons in a random crystal potential for which the potential wells on different sites fluctuate independently is the Coherent Potential Approximation [14]. Fortunately, this method has been implemented for such muffin tin type, crystal potentials as one usually studies in connection with density functional theory. The procedure is called the KKR-CPA method [15, 16, 17]. It was developed for dealing with the electronic structure of substitutional metallic alloys but it turns out that its numerical techniques for implementing the Self Consistent Field Korringa Kohn Roštoker Coherent Potential Approximation (SCF-KKR-CPA) algorithm are ideally suited for describing the internal, many body, fluctuations we are concerned with here.

Note that according to our recipe, so far, eq. 19 has to be solved self-consistently before averaging. Of course the KKR-CPA proper, being a strictly one electron theory, is not designed to deal with this complex problem. However, within the spirit of the mean field theory implied by eq. 18 the order of averaging and self consistency can be interchanged. The resulting theory is the SCF-KKR-CPA algorithm. As we shall illustrate presently it facilitates the practical consideration of a large class of problems we care to pose within the general framework in Sec. 1. In particular the following procedure is fully tractable:

1. start with a set of charge distributions $\bar{n}_1^\nu, \bar{n}_\downarrow^\nu$ and the corresponding probabilities $P(\nu)$ listed in eq. 16;
2. calculate the effective potentials $\bar{v}_{i\sigma}^{eff,\nu}(\vec{r})$ using the Local Density prescription indicated in eq. 17;
3. placing the above potential on a lattice according to the probability distribution in eq. 19 solve for the partially averaged Greens functions $\langle G_{\sigma\sigma}(\vec{r}, \vec{r}'; \epsilon) \rangle_{i,\nu}$ using the KKR-CPA scheme;
4. from the partially averaged Greens functions in 3.) calculate the local charge densities

$$n_\sigma^\nu(\vec{r}) = - \int d\epsilon f(\epsilon) \text{Im} \langle G_{\sigma\sigma}(\vec{r}, \vec{r}'; \epsilon) \rangle_{i,\nu} \quad (21)$$

for $\nu = +\uparrow, +\downarrow, -\uparrow$ and $-\downarrow$;

5. repeat the procedure until convergence in $\bar{n}_{i\sigma}^\nu(\vec{r})$.

Note that during the above self contained part of the calculation the probabilities $P(\nu)$ are given and not changing. To complete the theory one must specify them by returning to eqs. 4, 5 and 18 for inspiration.

For example one could determine them by requiring that the free energy $F = \langle H \rangle - ST$ is at a minimum with respect to variations in the set $\{P(\nu)\}$. We hasten to add that most of the possibilities remain unexplored. In the explicit examples we shall treat in the next section all four states $\nu = +\uparrow, +\downarrow, -\uparrow, -\downarrow$ are taken to occur with the same probability. Evidently this correspond to a high temperature state which is fully disordered with respect to the fluctuations considered.

To summarize the arguments in this section we note that we have set out perhaps the simplest version of our program of introducing fluctuations about the LDA by considering LDA states with constrains and summing over, albeit in an approximate - mean field theoretic - fashion over these constraints. The question is what can we expect to learn from this particular scheme.

In general one of the possible outcomes of the above self consistent procedure with $P(\nu) = \frac{1}{4}$ for all ν is that all four charge densities $\bar{n}_{i\sigma}^\nu(\vec{r})$ converge to the same one \bar{n}_σ . In this case we learned very little. This circumstance is entirely analogous to the case of spin polarized calculations where the self consistency procedure converges to a symmetric, paramagnetic, state. We have allowed the system freedom to fluctuate, for times long compared with

the inverse bandwidth ($\frac{\hbar}{W}$), but such fluctuations turned out to be unstable and in the ergodic limit disappeared.

A more interesting possibility is the case where n_{σ}^{+1} goes to n_{σ}^{-1} ($= \bar{n}_{\sigma}^1$) but $\bar{n}_{\sigma}^1 \neq \bar{n}_{\sigma}^{\downarrow}$. Now, the spin symmetry, on the time scale of $\frac{\hbar}{W}$, is broken. Of course it is restored in the ergodic limit as is evidenced by the fact that $P_{\uparrow} = P_{\downarrow} = \frac{1}{2}$. Namely, there are as many up sites as down sites and hence the system is paramagnetic. This is the Disordered Local Moment (DLM) state to be discussed in the next section.

An other interesting possibility is that n_{σ}^{+1} converges to $n_{\sigma}^{+\downarrow}$ ($\frac{1}{2}n_{\sigma}^{+}$) and n_{σ}^{-1} converges to $n_{\sigma}^{-\downarrow}$ ($\frac{1}{2}n_{\sigma}^{-}$). In this state the local charge fluctuates between $\bar{n}^{+} = \sum_{\sigma} \bar{n}_{\sigma}^{+}$ and $\bar{n}^{-} = \sum_{\sigma} \bar{n}_{\sigma}^{-}$. We shall refer to it as the Disordered Local Charge (DLC) state. Clearly, the Mott-Hubbard state in Sec 2 is an example of this interesting circumstance.

Naturally further cases could be considered but given the explicit examples to be discussed in the next section these two will suffice.

4 The Disordered Local Moment states of Iron

While the Density Functional theory in the Local Spin Density Approximation (LSDA) gives a good account of the magnetic ground state of most metallic magnets [18] it fails miserably in predicting the Curie temperature T_c . As is well known this is because in LSDA at finite temperature the local magnetization does not fluctuate in its direction, as it would in the Heisenberg Model, and hence the entropy is only that associated with the thermal excitation of electron-hole pairs. The scheme outlined in the previous section ideally suited for incorporating the missing fluctuation into the theory.

The principles of introducing Heisenberg Model like fluctuations into an electronic theory based on the Hubbard Model were discovered by Hubbard [19, 20] and independently by Hasegawa [21]. The way these notions can be implemented into the Density Functional Theory, along the lines of our arguments in this paper, are due to Pindor et al [22], Oguchi et al [23] and Györfy et al [24]. In short one constrains the magnetization in each unit cell to lie along a set of selected directions $\{\hat{e}_i\}$ where \hat{e}_i is a unit vector associated with the i^{th} unit cell:

$$\bar{m}_i = \hat{e}_i \left| \int d^3r \bar{m}_i(\vec{r}) \right|. \quad (22)$$

Then, density matrix is given by

$$n(\vec{r}) = n_0(\vec{r})\mathbf{1} + \mu(\vec{r})\vec{\sigma} \cdot \hat{e}_i \quad (23)$$

where σ^x , σ^y and σ^z are the usual Pauli spin matrices and $\mathbf{1}$ is the unit matrix. Moreover, the local effective potential has the form

$$v^{eff} = \frac{1}{2}(v_\uparrow + v_\downarrow)\mathbf{1} + \frac{1}{2}(v_\uparrow - v_\downarrow)\vec{\sigma} \cdot \hat{e}_i \quad (24)$$

where v_\uparrow , v_\downarrow are the potentials seen by \uparrow and \downarrow spin electrons respectively in the frame of reference where the axis of spin quantization is along the local direction vector \hat{e}_i . For reasons of symmetry it turns out to be the case that in the disordered state it is sufficient to consider only directions which are up and down with respect to a common axis of quantization \hat{e}_z . Namely,

$$\hat{e}_i = \pm \hat{e}_z \quad (25)$$

and hence the potential for an electron with spin projection along \hat{e}_z is v_\uparrow and v_\downarrow with equal probabilities, $P_\uparrow = P_\downarrow = \frac{1}{2}$ and the same is true for a spin down electron. Thus we neglect the charge fluctuations and study the simple binary case of two states per site only. Averaging over all orientational configurations using the SCF-KKR-CPA we find the partially averaged Green's functions $\langle G_{\sigma\sigma}(\vec{r}, \vec{r}'; \epsilon) \rangle_{i\uparrow}$ and from this we calculate the local charge densities $\bar{n}_\sigma^\uparrow(\vec{r})$ and $\bar{n}_\sigma^\downarrow(\vec{r})$. From these we recalculate effective potential v_\uparrow^{eff} and v_\downarrow^{eff} and proceed to self consistency. At the end we calculate the local moment

$$\mu_\uparrow = -\frac{1}{\pi} \int d\epsilon f(\epsilon) \int_{\Omega_i} d^3r \sum_\sigma \sigma \text{Im} \langle G_{\sigma\sigma}(\vec{r}, \vec{r}'; \epsilon) \rangle_{i\uparrow} \quad (26)$$

with a similar expression for μ_\downarrow . Clearly on account of symmetry $\mu_\uparrow = \mu_\downarrow = \bar{\mu}$. If the above procedure converges to a finite $\bar{\mu}$ there is a local moment in the paramagnetic state. Otherwise, there is no moment in the above sense and the paramagnetic state is a Stoner state [18, 19, 20, 21]. In Fe, Co and Ni we found a moment in the DLM state in agreement with experiments. In fig. 4 we show μ for these three metals as a function of temperature. The temperature dependence is due to the Fermi factors in eq. 26 and in the formulae for calculating the various partially averaged charge densities. Namely, it is the consequence of thermally excited electron-hole pairs. Thus the temperature where the calculation converges to $\bar{\mu} = 0$ is T_S the Stoner temperature. As expected it is very much larger than

T_c . Györfly et al [24] also investigated the stability of this DLM state to symmetry breaking changes in P_{\uparrow} and P_{\downarrow} . They found a Curie temperature T_c of 1250K. For a mean field theory this is in very satisfactory agreement with the experimental value of 1044K.

5 Towards a theory of Mott-Hubbard Insulators

As is well known LDA predicts that the 3^d transition metal oxides MnO, FeO etc are paramagnetic metals in sharp contrast with the experimental facts, according to which they are antiferromagnetic insulators. A way out of this dilemma is suggested by the fact that the spin polarized LSDA calculations based on the observed, type II, antiferromagnetic structure gives a gap at the Fermi energy [25]. However, this exchange gap is too small and in any case these systems are insulators above the Neel temperature T_N . Evidently, to land credence to the suggestion one must investigate the DLM state, which should describe these systems above T_N , to see whether the gap survives the loss of magnetic long range order.

Terakura et al [25] have performed the first DLM calculation for MnO within the first principles framework of a non-self consistent KKR-CPA calculation. They used v_{\uparrow} and v_{\downarrow} potential functions from their antiferromagnetic ground state calculation. The density of states they found for the DLM state is shown in fig. 5. Clearly, there is a hint of a gap but it is hardly convincing. We have repeated their calculation and found roughly the same result (shown in fig. 6). In fact we have investigated the Bloch Spectral Function, $A^b(\vec{k}, \epsilon)$, and found a smeared but nevertheless well defined Fermi Surface surrounding the Γ point. Thus, we conclude that, for the set of non self consistent potentials we used, the DLM state appears to be a metal.

On the other hand Hubbards suggestion, in his original paper, was that the insulating gap is due to charge fluctuations. That both charge and spin fluctuations may play a role was stressed by Cyrot [13]. In short the above first principles attempts do not exhaust even the readily tractable possibilities offered by our treatment of fluctuations within LDA. We are currently engaged on including charge fluctuations. Such procedures may be regarded as first principles versions of Hubbards original model calculations [9, 10, 11]. They will easily accommodate such charge transfer gaps as favored by Zaanen et al [26] and Anisimov et al [27] and will not be limited by the relative weakness of exchange splitting in these systems.

Our hope is that through the 90's the possibilities of including fluctuation

into the Density Functional Theory to improve on the LDA will be fully explored.

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Figure Captions

Figure 1. Two energy paradigms.

Figure 2. The conventional Density Functional Method.

Figure 3. The Hartree Fock and the split Hubbard bands for one band Hubbard model.

Figure 4. The magnetic moment μ in the DLM state as a function of temperature found in Fe, Co and Ni.

Figure 5. (a) Total state densities of MnO (in states/Ry/MnO) in the ferromagnetic state, (b) in the antiferromagnetic states of the first kind, AF I, (c) of the second kind, AF II, and (d) in the paramagnetic state. The vertical lines denote the Fermi level. (after Terakura et al [25]).

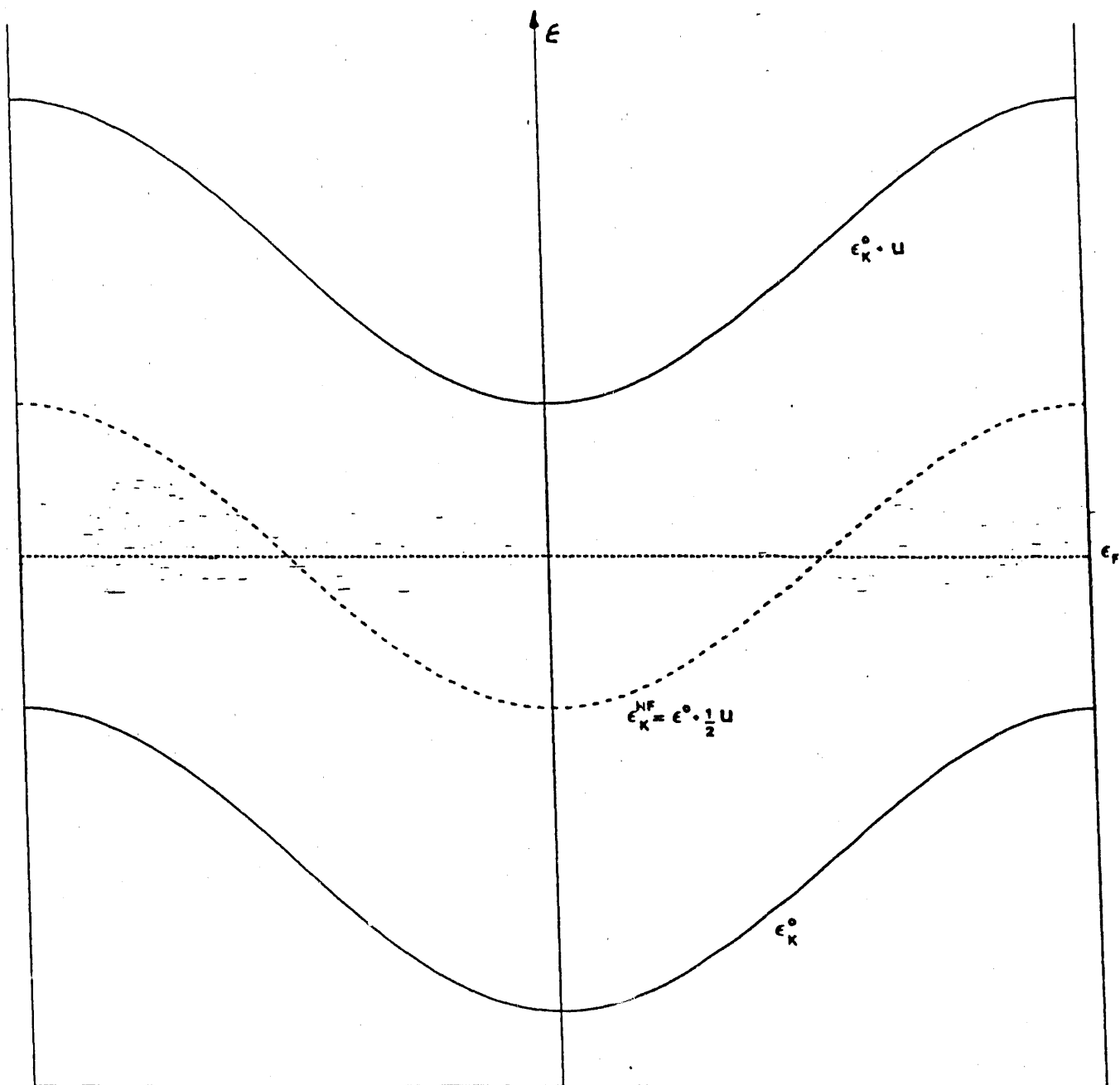
Figure 6. The Density of States of MnO. The vertical line denotes the Fermi level. (our DLM calculations).

| Landau-Ginzburg-Wilson Functional Integral representation | Kohn-Sham Density Functional Theory |
|---|---|
| $\delta F^{MF}[\varphi] = 0$ $Z = \int d\varphi e^{-\beta F^{MF}[\varphi]}$ $F = -k_B T \ln Z$ <p>difficult functional integrals but simple $F^{MF}[\varphi] =$ $= \int d^d z [\nabla\varphi ^2 + \alpha \varphi ^2 + \beta \varphi ^4 + \dots]$</p> | $\delta F^{MF}[\varphi] = 0$ $\delta F^{EXACT}[\varphi] = 0$ <p>simple minimization but hard to find corrections to LSD</p> |

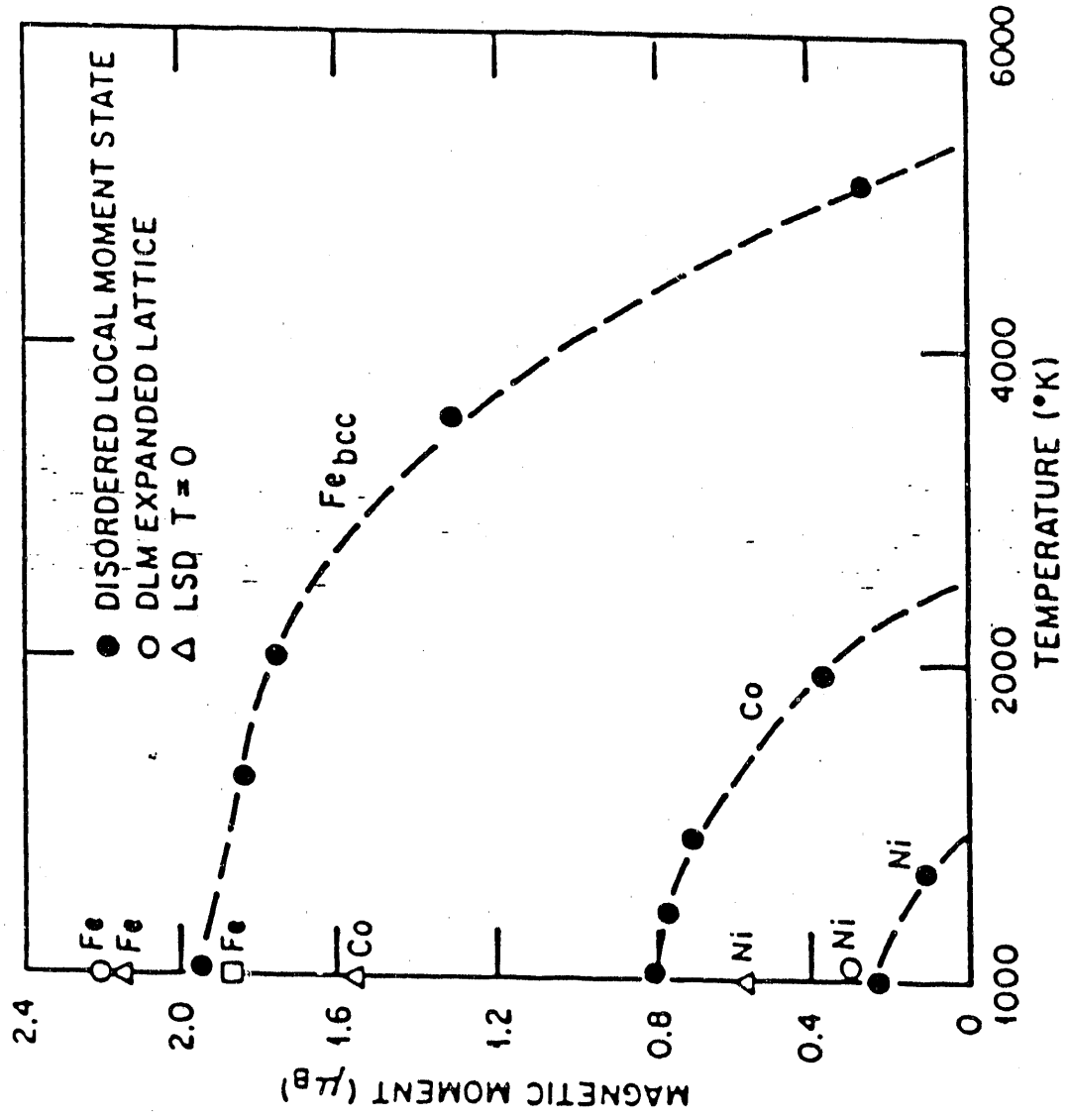
Figure 1: Two energy paradigms.

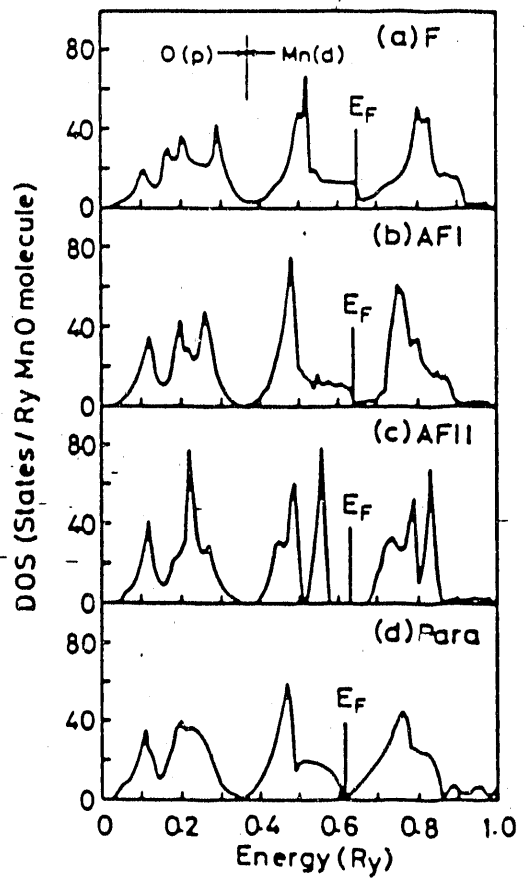
$$\left. \begin{aligned}
 \hat{\rho} &= \frac{1}{Z} e^{-\beta \hat{H}} \\
 Z &= \text{tr} \{ e^{-\beta \hat{H}} \} \\
 \Omega &= -k_B T \ln Z
 \end{aligned} \right\} \xrightarrow{DFT} \begin{aligned}
 \delta \Omega[n] &= 0 \\
 (-\nabla^2 + v^{\text{eff}}(\vec{r}; [n])) \varphi_n &= \epsilon_n \varphi_n \\
 n_0(\vec{r}) &= \sum_n |\varphi_n(\vec{r})|^2 f(\epsilon_n) \\
 \Omega &= \Omega[n_0]
 \end{aligned}$$

Figure 2: The conventional Density Functional Method.



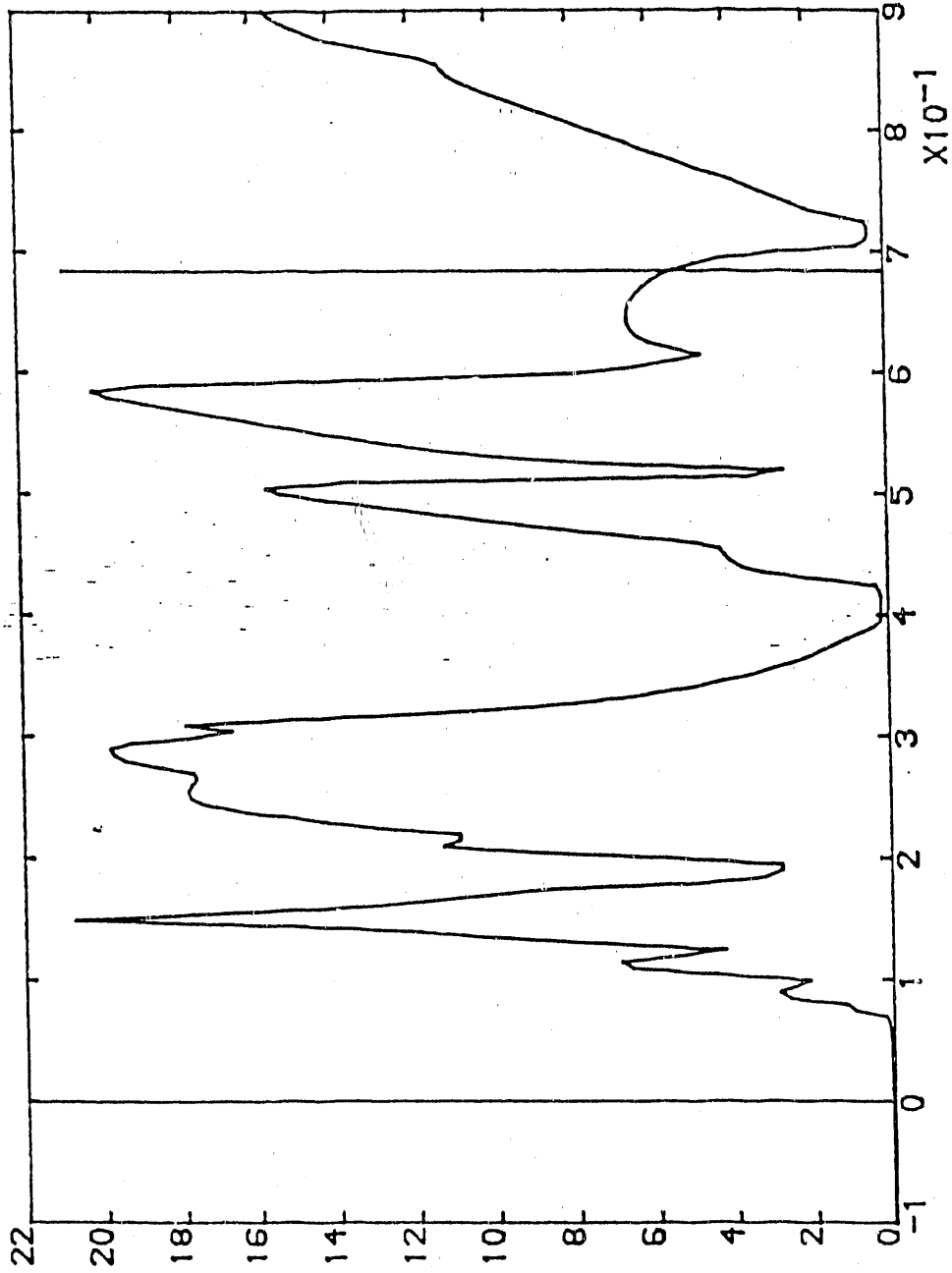
LOCAL MAGNETIC MOMENTS IN THE PARAMAGNETIC STATE





DLM1 MnO DOS total

DLM1MNO
DLM1MNO



DOS(e)

energy

END

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