Transition Metal Materials: A First Principles Approach to the Electronic Structure of the Insulating Phase

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1 Introduction

The role of first principles methods in the calculation of material properties has been growing steadily in recent years. Advances in the underlying theory have improved reliability while algorithmic and computer hardware improvements have led to faster calculations on more realistic model systems. In simple metals, semiconductors and inorganic materials such calculations now underpin our understanding of the electronic structure and bonding. In contrast, attempts to apply first principles methods to highly correlated systems have been fraught with difficulties. Until recently almost all calculations were based on the independent electron approximation as embodied in the local density approximation (LDA) to density functional theory (DFT). When the LDA is used to describe the magnetically ordered, insulating ground states of materials such as NiO and La_2CuO_4 a non-magnetic, metallic ground state is obtained [1]. Initially this was thought to be a failure of the independent electron approximation and proof positive that such highly correlated systems could not be described using band theory. It is now apparent that this is not the case. The failure of the LDA was due to its approximate treatment of the exchange interaction. Indeed a variety of approaches have now been developed to introduce better descriptions of the on-site exchange interaction [2, 3, 4].

In the current work we approach this problem from a different point of view. The key to this approach has been the realisation that the magnetically ordered insulating ground state may often be described by a single determinant wavefunction and may therefore be accurately represented using the Hartree-Fock approximation (HF) which, by definition, contains the exact exchange interaction. In this short article the background to this approach will be outlined (section 2), with results for the pedagogical system NiO explored in detail (section 3). Recent results for superexchange coupling (section 4), orbital ordering (section 5) and of electron doping effects (section 6) will also be presented. Some conclusions and points for further discussion will be presented in section 7.

2 The Independent Electron Approximation

The independent electron approximation used in almost all current first principles theory of the electronic structure in periodic systems (for some exceptions see [5, 6]) consists of solving the time independent N-electron Shrödinger equation;

$$(-\frac{1}{2}\sum_i \nabla_i^2 + V_{en} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r_i}-\mathbf{r_j}|})\Psi(\mathbf{r_1},\mathbf{r_2},\mathbf{r_3},\ldots,\mathbf{r_N}) = E\Psi(\mathbf{r_1},\mathbf{r_2},\mathbf{r_3},\ldots,\mathbf{r_N}) \tag{1}$$

by assuming that each electron moves independently in a mean field potential V_{eff}, that is;

$$H\psi_i = \left(-\frac{1}{2}\nabla^2 + V_{en} + V_H + V_{eff}\right)\psi_i = \varepsilon_i\psi_i \tag{2}$$

Conventionally the electron-nuclear interaction (V_{en}) and the classical (Hartree) electron-electron interaction (V_H) are separated from V_{eff}. The N one electron orbitals which result (ψ_i) are occupied by the N-electrons of the ground state.

In the DFT approach V_{eff} is a local potential which is an unknown functional of the charge and spin densities. In practice the LDA approach approximates the functional locally using the computed exchange-correlation energy density of the homogeneous electron gas. Thus some fundamental properties of the exchange and correlation interactions of the homogeneous electron gas are built into the effective mean field potential. If the exact functional were known the self consistent solutions of equation 2 would yield the exact

ground state densities and energy. It is important to understand that even in this limit the "orbitals" which solve equation 2 (or antisymmetrised products thereof) do not approximate the many body wavefunction of equation 1. The orbitals correspond to a fictitious non-interacting system; their role in the theory is to parameterise the variation of energy with respect to the ground state densities.
The Hartree-Fock (HF) approximation is an alternative independent electron theory based on an equation similar to equation 2. In this approximation the many body wavefunction is approximated as an antisymmetrised product of one electron functions, that is;

$$\Psi(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, \ldots, \mathbf{r_N}) = A(\prod_{i=1}^{N} \psi_i(\mathbf{r_i})) \tag{3}$$

Within this approximation the optimal one electron functions are the self consistent solutions of equation 2 with V_{eff} replaced by the explicit non-local exchange interaction between the single particle orbitals;

$$V_{eff}\psi_i(\mathbf{r_1}) = \int d\mathbf{r_2} V(\mathbf{r_1}, \mathbf{r_2})\psi_i(\mathbf{r_2}) = -\sum_j \int d\mathbf{r_2} \frac{1}{|\mathbf{r_1} - \mathbf{r_2}|} \psi_j(\mathbf{r_2})\psi_i(\mathbf{r_2})\psi_j(\mathbf{r_1}) \tag{4}$$

The explicit Coulomb and exchange interactions between electrons in the single particle orbitals are computed and (by definition) the correlation interaction is excluded. For non-periodic systems with small numbers of electrons powerful techniques for evaluating the effects of correlation exist and are widely used. For periodic systems the effects of correlation may be estimated using correlation functionals based on the DFT approximation. Some results of this procedure are presented below. In systems where the band gap is small, or closes, the exact exchange interaction is a poor approximation to the electron-electron interactions. In these cases an LDA treatment of the exchange potential is preferable.
The failure of the LDA to describe adequately the ground state of the highly correlated oxides despite the fact that the ground state is well approximated by a single determinant wavefunction is now understood. Within the LDA the potential felt by each electron is computed from a functional of the total electron densities. For the density functionals in common use this leads to eigenvalues which are relatively weak functions of the particular orbital

occupancy. The effects of the orbitally dependent potential will be examined in detail in the next section.

3 Nickel Oxide

Nickel oxide (NiO) crystallises in the rock salt structure. At temperatures below 525 K the spins on the open-shell Ni-ions order antiferromagnetically in the so called AFII structure shown in figure 1.

Figure 1: The cubic rocksalt structure of nickel oxide. In the AFII phase neighbouring planes of Ni ions in the (111) direction (right panel) are coupled antiferromagnetically.

A band theory of NiO which neglects electron-electron interactions must yield a metallic ground state - the Fermi energy falling within the Ni d-band. The system may however be considered as an ionic materials consisting of Ni^{2+}-d8 ions octahedrally coordinated to closed-shell O^{2-} ions. In figure 2 the electronic structure of the NiO d-band is characterised from this ionic point of view taking into account only intra-site interactions.

Figure 2: The energy levels of a Ni^{2+} ion in an octahedral field - see text for explanation.

In this picture the orbital energies of the Ni^{2+} (d^8) ion are dominated by *intra-site* effects; the (averaged) diagonal (U) and off-diagonal (U′) Coulomb interactions and exchange (J) determine the orbital energies shown in the figure. The orbitals are split into triply (t_{2g}) and doubly (e_g) degenerate sets. A direct consequence of these intra-atomic interactions is that the unoccupied e_g orbital is split from the occupied states by a gap of order $U >> J$. There is fairly direct experimental evidence for this ionic picture of the electronic structure of NiO. The optical adsorption spectrum has a series of lines due to the rearrangement of the d-electrons within the $3d^8$ multiplet (the Frenkel excitons). The fact that these excitations are also observed in Ni-doped MgO and that the spectrum does not depend on Ni concentration is compelling evidence for localised nature of these states [7]. Within the Hartree-Fock approximation the dominant intra-site exchange and Coulomb interactions which determine the qualitative nature of the ground state in NiO are evaluated as explicit interactions between the single particle orbitals. Furthermore one expects the correlation corrections to the ground state wavefunction to be relatively small as the first excited states are rather high in energy. We therefore expect a reasonable first order description of this system to result from a simple independent electron theory based on the HF approximation. The effects of inter-site interactions in the periodic material may be taken into account by solving the periodic-HF equations. One expects such inter-site effects to be relatively small.

Figure 3: The electronic density of states of NiO for the ferromagnetic (upper panel) and antiferromagnetic phases (lower panel) computed within the Hartree-Fock approximation

Figure 3 contains the density of states (DOS) of NiO computed in the HF approximation for both the ferromagnetic and antiferromagnetic phases. The DOS demonstrates that the simple ionic picture of strongly correlated NiO may be recovered naturally in a band theory. Comparing the ordering of the t_{2g} and e_g minority and majority spin states we see that the simple ionic picture of figure 2 is preserved. The d-subbands are broadened by inter-site interactions but the dominant energy scales are determined by the intra-site interactions. The operation of the superexchange interaction can be seen in the narrowing of the e_g band in the antiferromagnetic state.
It is significant that the insulating nature of the ground state does not depend on the state of magnetic order. The on-site interactions depend on the existence of a *local moment* and not the ordering of the moments. The gap in the eigenvalues between the valence (O-2p) band the conduction (Ni-$e_g \downarrow$) band is approximately 14 eV. This is, as one would expect, very much larger than the experimental band gap ($\sim$4 eV) and reflects the large effects of relaxation and correlation on the transfer of an electron between valence and conduction bands (ie: the eigenvalue gap reflects the unscreened U while the optical band gap is due to a screened U[7]). The band gap can be studied within this formalism by creating explicit electron addition and removal states; this problem will be analysed further in section 6. The development of efficient and reliable software for applying HF theory to periodic systems (the CRYSTAL package [8, 9]) has allowed detailed studies of transition metal materials

to be made [10, 11, 12, 13]. The structurally simple monoxides, MnO and NiO, exemplify many of the important features of these calculations.
MnO adopts the same rocksalt structure as NiO (figure 1) with an electronic structure based on the Mn^{2+}-d^5 ion. The computed lattice constants for MnO and NiO are compared to experimental data in table 1. In general the HF approximation overestimates the lattice constants of ionic compounds by some 1-2%. This systematic trend is well known and is due to the neglect of intra-site correlation, which leads to an overestimation of the size of the ions [14]. This tendency, and the local correlations which correct for it, have recently been analysed is some detail [15, 16]. The computed lattice constants of MnO and NiO are $\sim$ 2% larger than those observed indicating that the bonding in these materials is described on a similar footing to that of the simple oxides [14].

	lattice constant (Å)	
	calculated	experimental
MnO	4.526	4.445
NiO	4.264	4.168

Table 1: The predicted lattice constants of MnO and NiO in the AFII phase compared to experimental data

The relative energies of the AFII, AFI (antiferromagnetic order in the (100)-direction) and ferromagnetic spin arrangements are reported in table 2 [11].

	E-E_{ferro} milli-eV/cell	
	AFII	AFI
MnO	-23	0.8
NiO	-66	23.8

Table 2: Energies of the AFI and AFII spin arrangements relative to the ferromagnetic state. The energies are evaluated at the computed lattice constant of the AFII structure

In both materials the observed ground state (AFII) is found to be the lowest energy state indicating that the qualitative features of the superexchange interaction between the localised d-electrons (via the O-2p orbitals) are correctly described. The AFI phase, which is not observed, is unstable with

	Computed	Observed
MnO	90.47	90.62
NiO	90.08	90.1

Table 3: Deviations from ideal cubic angles (90 degrees) of the crystal axes in the AFII state due to magnetostriction

respect to both ferromagnetic and AFII phases. The energies of various spin states can be used to estimate the local spin-spin interactions, and via an Ising model, the Néel temperatures (T_N) in these systems. In MnO and NiO respectively the estimated T_N are 94 and 392 K. The absolute magnitudes of the spin interactions are not very well described while the relative magnitude of the coupling compares favourably to the observed T_N of 116 and 525 K [11].

The interaction of spin and lattice degrees of freedom has an important and well characterised consequence in the cubic monoxides. There is a rhombohedral distortion of the unit cell due to magnetostriction in the AFII phase. The ordering of spins in alternate planes results in a reduction of the exchange repulsion between these planes and thus a thus a contraction of the lattice along the (111) direction (figure 1). This is usually expressed as an inclination of the cubic crystal axes; computed [11] and observed [17, 18] values are compared in table 3. The rather close agreement suggests that spin-lattice interactions may be computed with some confidence.

The detailed analysis of the ground state properties of the transition metal monoxides given in this sections demonstrates that band theoretic methods based on an adequate description of the intra-site exchange interactions provide a qualitatively correct description. Ground state properties such as lattice structure, spin couplings and spin-lattice interactions may be computed with some confidence. In the next section we examine the behaviour of the exchange interaction in another class of materials in which strong net ferromagnetic interations have been observed.

4 Superexchange Interactions in Chromium Cyanides

The reliable calculation of the relative magnitudes and, in particular, the signs of spin interactions is a vital first step towards an understanding of spin dynamics and lattice-spin interactions such as spin polarons. In most of the magnetic insulators known the dominant magnetic interaction seems to be via the superexchange mechanism which leads to antiferromagnetic coupling. The recently discovered light magnetic materials based on the parent compounds, $KM^{II}[Cr^{III}(CN)_6]$ (with M = V, Mn, Ni) provide an important test for any theoretical approach as the ground states display strong interactions producing both antiferromagnetic and ferromagnetic coupling. The structure of these materials can be rather complex but is based upon a particularly simple framework with MN_6 and CrC_6 octahedra arranged on a cubic rocksalt lattice. The basal plane of this structure is displayed in figure 4.

Figure 4: The basal plane of the cubic materials $KM^{II}[Cr^{III}(CN)_6]$ (with M = V, Mn, Ni)

Two possible spin arrangements have been examined in these systems [19]. The ferromagnetic state in which unpaired spins at the Cr^{III} and M^{II} are aligned parallel and the ferrimagnetic state in which the spins of differing magnitude are antiparallel. The computed energy differences between these states states are presented in table 4 [19]. A breakdown of the total energy difference into kinetic-, exchange- and Coulomb- (electron-electron and electron-nuclear) energy contributions is also given.

M	d-configuration	total	exchange	kinetic	coulomb
V^{II}	t_{2g}^3	120	270	-75.6	-74.5
Mn^{II}	$t_{2g}^3 e_g^2$	21.5	34	7.89	-20.4
Ni^{II}	$t_{2g}^6 e_g^2$	-49	-204	152	3.0

Table 4: Magnetic ordering energies, E_{ferro}-E_{ferri} (milli-eV/cell) computed in optimised geometries; a positive energy favours the ferrimagnetic state. The Coulomb energy contains electron-electron and electron-nuclear interactions.

A distinct trend emerges from these calculations; the V compound has strong antiferromagnetic interactions, the Ni compound has ferromagnetic interactions and the Mn compound is intermediate with weak antiferromagnetic coupling. This trend has recently been observed in the somewhat more complex materials realised experimentally. In materials based on the formula $A_3^{II}[Cr^{III}(CN)_6]_2.nH_2O$ with (A=Mn, Ni) the Mn material has a ferrimagnetic ground state with T_N=50-60K whereas the Ni compound is ferromagnetic with T_N=90K [20, 21, 22]. A critical temperature of 315K has been observed in the antiferromagnetically coupled amorphous compound $V^{II}_{0.42}V^{III}_{0.58}[Cr(CN)_6]_{0.86} \cdot 2.8H_2O$ [23]. As in the simple monoxides the observed trend in the magnetic coupling strength is reproduced at this level of theory.

The origin of the strong variation in the magnetic coupling with the substituted cation can be analysed within the calculations and understood in terms of a simple model. The various d-electron configurations of these cations (table 4) interact with the Cr^{III} ion in the t_{2g}^3 state via the CN group. In the V compound the interaction, $V(t_{2g}^3)$–NC–$Cr(t_{2g}^3)$, is dominated by the need for the t_{2g} orbitals to be orthogonal in the ferromagnetic state. This results in a strong relative stabilty of the ferrimagnetic state. In the Ni compound the t_{2g} are spin paired and the interaction is $Ni(e_g^2)$–NC–$Cr(t_{2g}^3)$; the e_g and t_{2g} orbitals have small overlap via the CN group and the effects of the orthogonality constraint are correspondingly weak. The remaining interaction is the indirect exchange integral via the CN orbitals which favours the ferromagnetic state. In the Mn compound the Mn-ion has both e_g and t_{2g} orbitals occupied and the competing effects tend to cancel yielding a weakly ferrimagnetic state.

Studies of the chromium cyanides show that the variation of magnetic coupling with orbital occupancy pattern of transition metal ions may be reproduced within band theory once an adequate description of the exchange interaction is adopted. In the next section a case study of $KCuF_3$ is presented in which an understanding of the interaction between the orbital-occupancy, lattice and spin degrees of freedom is required in order to describe the ground state electronic structure.

5 Orbital Degeneracy and Lattice-Spin Interactions: $KCuF_3$

The interaction of spin and lattice degrees of freedom in the transition metal monoxides has been discussed above. In these materials changes in the occupancy pattern of the localised orbitals on a site often requires considerably less energy than transferring electrons between sites. In certain materials orbital ordering can occur in which local occupancy patterns interact and form phases with long range order [24, 25]. This interaction is a mechanism for strong coupling between the lattice and electronic degrees of freedom. The orbital ordering in $KCuF_3$ has recently been studied within an *ab initio* formalism [26]. This material crystallises in the distorted perovskite structure shown in figure 5.

Figure 5: The distorted perovskite structure of $KCuF_3$

The undistorted structure consists of near cubic array of CuF_6 octahedra. Locally the distorted structure consists of each octahedron being extended along a and contracted along b - or vice versa. Adjacent distortions are orthogonal to each other (figure 5). A convenient order parameter for this symmetry breaking is the fractional coordinate of the F-ion along the Cu-Cu bond (X_F=0.5 in the undistorted structure).

The origin of the distorted geometry can be understood by considering the electronic structure from an ionic point of view. The Cu-ions are in the Cu^{2+}-d9 oxidation state and thus in the high symmetry perovskite arrangement the degenerate Cu-e_g orbitals are partially filled. One expects that a breaking of this degeneracy will result in a lowering of the energy due to a Jahn-Teller-like interaction. The degenerate state is not amenable to a single determinant description. This description may, however, be appropriate for the symmetry broken state in which there is a well defined local orbital occupancy and a significant band gap. Analysis of the computed charge and spin densities in this state indicates that the ionic picture is appropriate [26]. The unpaired spin on the Cu-site alternates between non-degenerate combinations of the local d-orbitals - the orientations of these orbitals mirroring the locally distorted geometry.

The distortion energy per unit cell of $KCuF_3$ as a function of the lattice distortion is displayed in figure 6.

Figure 6: The distortion energy of $KCuF_3$ as a function of X_F. The upper curve is computed within the Hartree-Fock approximation while in the lower curve a DFT estimate of the correlation energy has been included.

The predicted equilibrium distortion occurs at a fractional coordinate close to that observed (X_F(obs)=0.46). The inclusion of a DFT estimate of the correlation energy increases the well depth slightly and increases the equilibrium distortion to be in slightly better agreement with experiment.
The magnetic structure of $KCuF_3$ is also of great interest as it is highly anisotropic. The antiferromagnetic interactions along the crystallographic c-direction are several orders of magnitude larger than the weakly ferromagnetic interactions in the ab-plane. In the undistorted phase one would expect isotropic antiferromagnetic interactions in a,b and c directions mediated by the superexchange mechanism discussed in section 4. In order to understand the weak magnetic coupling in the ab-plane the energy difference between planar ferro- and antiferromagnetic states as a function of the lattice distortion have been computed [26] and are plotted in figure 7.

Figure 7: The energy difference per formula unit (eV) between the planar ferro- and antoferromagnetic phases as a function of X_F

As the fluorine ion moves away from the bond centre its ability to mediate the superexchange interaction is rapidly destroyed and the in-plane magnetic coupling weakens. As in the compound $NiCr(CN)_6$ (section 4) the residual coupling is due to the indirect exchange integral and is therefore ferromagnetic.
Using the energy differences to parameterize an Ising model of the magnetic interactions indicates that the computed coupling is considerably smaller than that observed experimentally [26]. The development of techniques for computing the absolute magnitudes of magnetic couplings reliably is the subject of current research [27, 28].
The case study of $KCuF_3$ is of great importance as it demonstrates that the interaction between orbital occupancy, lattice and spin degrees of freedom may be studied with some confidence within a single determinant band theory in which the local exchange interactions are treated accurately.

6 Excitation of the ground state: hole doping in $LiNiO_2$

The discussion in previous sections establishes an independent electron description using an accurate exchange interaction as a reliable tool for studying the ground state properties of many transition metal materials. In some systems this is not surprising as it is clear that a single determinant description is physically reasonable and in others, such as $KCuF_3$, the systems spontaeneously breaks symmetry to a state in which this description is appropriate. In systems where there are many configurations which might contribute to the ground state wavefunction one expects the effects of explicit correlation to be large and for the single particle description to break down. This problem is particularly acute when one wishes to compute the energy of excited states. Although progress has been made on this using techniques which do not attempt to compute the wavefunction directly [29, 30] it is largely an unsolved problem.

In this context the system $Li_xNi_{1-x}O$ is of particular interest as it allows perturbations of the ground state electronic structure of NiO to be probed by chemical means - each Li^+ ion substituted for a Ni^{2+} ion adds a hole to the system. There is therefore an approximate correspondence between the ground state electronic structure of the Li-doped compounds and the electron removal states in NiO. Despite the potential complexity of the excited state recent calculations [31, 32] have demonstrated that the ground state of the doped material is reliably described within a single determinant formalism.

In section 3 we presented the density of states of NiO (figure 3) which shows a broad O-2p valence band above the Ni-d states. This eigenvalue spectrum implies that the first ionisation state of NiO consists of a hole in the O-2p band. There is evidence for this point of view from resonant photoelectron spectra [33, 34] and cluster studies [35]. The computed ground state spin density of NiO is compared to that of the doped material, and $Li_{0.125}Ni_{0.875}O$, in figure 8 [31]. The Ni^{2+} sites are clearly visible in the spin density. The d8

Figure 8: The spin density in the 100 basal plane of NiO (upper panel) and of the symmetry broken state in $LiNi_7O_8$ (lower panel)

electronic structure discussed in section 3 is apparent with the unpaired e_g

Figure 9: The O-p contribution to the conduction band density of states of NiO and $Li_{0.125}Ni_{0.875}O$

orbitals prominant. There is little or no spin density present on the essentially closed shell oxygen ions. Upon Li-doping an unpaired orbital is created which spontaeneously localises on a single O site - the p-like spin density in the lower panel of figure 8). At this level of theory it is not possible to be certain that the localisation of the hole state is the correct ground state. The accurate description of an alternative state with the electron delocalised over several oxygen sites requires a multideterminental approach. Our confidence in the HF prediction of the localised state is increased by the accompanying lattice distortion which results in significant stabilisation. The Li^{+} ion relaxes away from the O at which the hole has localised and towards the neihbouring O^{2-} ion. At the equilibrium displacement of 0.27 Åthe energy of the state is lowered by 0.27 eV. There is further evidence for the localised state from calculations on clusters [36] and dielectric loss measurements [37]. A very similar trapping of the doped hole is observed in hole addition states in NiO [32].

The spectroscopy of this state is also of great interest. The conduction band density of states for $Li_{0.125}Ni_{0.875}O$ is compared to that of NiO in figure 9. Upon substitution of Li the empty O-p states of NiO are largely unaltered. However the localised hole state splits away from the conduction band and appears in band gap below the conduction band edge by some 2.5-3.5 eV depending on the doping concentration [31]. This state corresponds closely to the observed X-ray adsorption spectra from the oxygen K-edge [33].

$LiNiO_2$ is an important system as it allows one to examine the hole doping of NiO within a ground state formalism. In the doped states we find analogues of excited states which one anticipates will be very difficult to describe within an independent electron formalism. A spontaeneous symmety breaking results in a localised state of well defined orbital occupancy which may be described using a single determinant wavefunction. The relaxation energy which accompanies the symmetry breaking, cluster, dielectric loss and spectroscopic studies support this qualitative picture of hole doped state.

7 Conclusions

Considerable progress has been made in understanding why independent electron, band theoretic approaches to the ground state electronic structure of "highly correlated" transition metal materials have been, in the past, unsuccessful. An accurate treatment of the exchange interaction results in a reliable description of ground state properties in many systems. The tendency of long range Coulomb interactions to generate symmetry broken states in periodic materials means that a single determinant description is often appropriate even for states with apparently complex electronic structre. The performance of this theory in a wide range of materials has now been documented and its reliability established. The theory is implemented in the widely used CRYSTAL software [9].

8 Discussion

Question: Prof. A.S. Alexandrov

The excited states, which you have described, are of course small polarons stabalised by the Li distortion. I am wondering how one can get a metallic conductivity with a polaron level shift as large as 3.5 eV ?

Answer:

Yes I think that the hole doped states are small polarons. The 2.5-3.5 eV is a shift in the Hartree-Fock eigenvalue of the O-p state. This is not the energy energy barrier to polaron transport which would be better approximated by the relaxation energy of 0.27 eV. This is a more reasonable energy scale for the known transport properties.

Question: Prof. C.N.R. Rao

Can your calculations account for differences between low and high spin states in solids eg: Fe(II) or Cu(III) ?

Answer:

The UHF calculations have a bias towards the high spin state as the magnitude of the correlation energy is greater in the low spin state. Often the crystal field splittings are large enough to dominate correlation effects and the correct state is obtained.

Question: Prof. J. N. Murrell

Your message has been that single determinant wave functions provide a good basis for understanding many properties of many solids. However, we know from molecular calculations that this approximation as it stands leads to significant errors in many properties and one needs to add correlation to get generally satisfactory results. There are also many molecular systems for which the single determinant is not even a good first approximation. Why should we find solids to be simpler systems to deal with than molecules ?

Answer:

This is a very important feature of these *ionic* materials. The highly symmetric environment and long range Coulomb forces tend to separate the orbitals into well defined subsets with a significant gap between occupied and unoccupied states. Hence, the ground state of NiO is rather well described by a single determinant while one could easily imagine a covalently bonded molecular complex for which this approximation would be poor. In this sense certain solids are "simpler systems" than many molecules. This is not always true and the accurate treatment of explicit correlation for solids is one of the main challenges facing solid state physics at present.

Question: Dr. RL Johnston

Is there a simple explanation for the observed distortion in $KCuF_3$ rather than an alternative tetragonal distortion ?

Answer:

The ordering of the Cu-orbitals and resultant movement of the F-ions allows the energy gain of removing the degenerate state at the Fermi energy at a cost of short range repulsions between pairs of Cu- and F-ions. A tetragonal distortion of the lattice involves a strain energy which seems certain to be higher than the short range repulsions.

Question: Prof. DE Logan

The theoretical Néel temperatures you report clearly agree well with experiment and yet, if I have understood you correctly, they are obtained by an effective mapping onto an underlying Ising model with material parameters extracted from what amounts to an unrestricted Hartree Fock calcuation. I would have thought this to be a rather crude approximation, as indeed it would be for, say, the Hubbard model. Can you comment on why such a procedure appears to work well in your case ?

Answer:

Yes, that is the procedure applied and indeed the Néel temperatures in NiO and MnO are rather close to that observed experimentally - about 30% too low. The procedure is rather crude and the mapping of the UHF energetics onto an Ising model is indeed unsatisfactory - if only becasue the definition of $< S^2 >$ is problematic. More recently explicitly correlated cluster calculations have been used to examine the exchange coupling, J. In this work it was found that UHF theory underestimates J rather systematically - by a factor of 2-3 [27, 28].

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