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Predictive Capability for Strongly Correlated Systems:

Mott Transition in MnO, Multielectron Magnetic Moments, and Dynamic Effects in Correlated Materials

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3. Predictive Capability for Strongly Correlated Systems

Abstract

There are classes of materials that are important to DOE and to the science and technology community in general, generically referred to as strongly correlated electron systems (SCES), which have proven very difficult to understand and to simulate in a material-specific manner. These range from actinides, which are central to the DOE mission, to transition metal oxides, which include the most promising components of new spin electronics applications as well as the high temperature superconductors, to intermetallic compounds whose heavy fermion characteristics and quantum critical behavior has given rise to some of the most active areas in condensed matter theory. After decades of study from a variety of often quite approximate viewpoints, a material-specific, predictive capability for certain classes of these correlated electron systems is being achieved. This accomplishment has been based on (1) new theoretical innovations, (2) coupling of experts in many-body theory with electronic structure practitioners, (3) development of novel computational algorithms to solve the resulting equations, and (4) feedback from increasingly detailed experimental studies. These new capabilities are arising at a time when there are extensive and novel experimental probes to provide data for a *theory-computation-experiment feedback loop* that enables the most rapid progress, and also when extended computational power is available for solving the resulting numerical problem.

The objective of the proposed cooperative research team is to assemble the required expertise into a coherent team and focus on the application of these new methodologies to the specific issue of Mott transitions, multi-electron magnetic moments, and dynamical properties correlated materials. The goals are (i) to provide specific, detailed understanding of the complex correlation effects in strongly correlated systems, with specific emphasis on our compound of choice – MnO – through the application and further development of formal methods and numerical algorithms, and (ii) to make available efficient and accurate computer codes to materials modelers which can then be used more widely for strongly correlated systems. Success in this undertaking will have clear impact by moving the community toward the longer term goal of opening up the entire periodic table to materials simulations with predictive capability.

4. CRT Management Plan

Rationale for this Team. Due to the difficulty in addressing the strongly interacting many-body problem for a large number of electrons as in the case in solids, research on SCES has long been the purview of many-body theorists dealing with model Hamiltonians because of the need to reduce the number of degrees of freedom to the minimum necessary to confront the issues of interest. Weakly correlated materials, on the other hand, have been found to be handled very well by density functional based methods. The number of degrees of freedom in DFT-based methods is small enough that material-specific characteristics can be treated in great detail. With the advance in computational power coupled with theoretical and algorithmic advances, it has been realized in the past decade that synthesis of these approaches is becoming a viable proposition.

The Predictive Capability for Strongly Correlated Systems (PCSCS-MnO) Cooperative Research Team constitutes a diverse but complementary set of researchers who are all working towards the broad common goal of studying strong correlation effects in real materials and who have specific interest and expertise in the properties of transition metal oxides including MnO. These include leading practitioners of DFT, especially those whose research has a significant concentration on the development of correlated band theories and dynamical response functions, experts in the development and exploitation of many-body techniques (especially Monte Carlo simulations for obtaining thermodynamic properties), and leaders in the optimization and sampling of many-body wavefunctions. An outcome of recent collaboration amongst members of this team are forefront international LDA+DMFT efforts that include very successful steps toward combining chemical realism with treatments of electron correlation beyond the mean-field level. The CRT also includes researchers who have developed fundamentally new approaches to the strong correlation problem: the generation and application of Wannier functions which provide an optimal basis set and first principles values for the Hamiltonian matrix elements and interaction energies of complex materials; renormalization group related approaches which systematically reduce basis sets to a more tractable size; and novel methods, e.g. continuum diffusion and auxiliary field Quantum Monte Carlo, to solve the resulting Hamiltonians. This broad-based group, focused on certain aspects as described in this document, has produced efficient computational theories of strongly correlated electron systems that have predictive power and is poised to produce breakthroughs on the difficult, and important, MnO problem.

4.1 CRT Organization and Operation: This PCSCS-MnO CRT will be led by project coordinators Pickett and Scalettar. Subteams will be organized to address two separate but complementary thrusts, as well as a more specific crosscutting “signature problem” that will involve a majority of the CRT members in various ways. Subteam leaders will be responsible for the coordination of research efforts toward integrated goals.

These co-Principal Investigators will meet twice each year, once at the CRT stand-along coordination meeting and once at the March APS meeting. In addition, each team will produce a short progress report every four months. Contact at this relatively short time scale is essential to ensure the short-term synergy envisioned within the research subteams, and to assess the latest opportunities for collaborations across the subteams. Presentations of major accomplishments will be given in the semi-annual coordination meetings. Responsibility for overall supervision of the CRT activities will rest with the Principal Investigators, Pickett and Scalettar

The research focuses and the subteam members in this CRT are given in the following list. The manner in which the participants contribute is provided in the scientific narrative.

Signature Problem. *The Mott Transition in MnO.*
Leaders: Pickett, Zhang, Krakauer, Umrigar.
Members: nearly all members of the team will contribute to the study of MnO across the Mott transition, see Sec. 5.1.

Thrust A. *Multielectron Magnetic Moments.*
Leaders: McMahan, Scalettar, Savrasov.
Members: Gubernatis, Jarrell, Krakauer, Kuneš, Pickett, Martin, Scalettar, Zhang, ...(to complete)

Thrust B. *Dynamical Behavior of SCES.*
Leaders: Jarrell, Eguiluz, Ku.
Members: Eguiluz, Gubernatis, Krakauer, McMahan, Savrasov, Scalettar, Schulthess, Zhang.

Several crosscutting efforts are planned that are not evident from this list. These will be described in the technical sections of the proposal.

Resources Allocation. The plan is to provide 50% support for six postdoctoral researchers for this team. Each will be shared by at least two members and visits with other members will be encouraged. An especially suited graduate student may be considered as well. For the allocation of postdoctoral researchers, the set of eight lead PIs propose possibilities based on the work put forward in this plan, and all participate in the discussion (email). Assignments will be arrived at by a consensus (a substantial majority); shared experience of this group suggests decisions can be reached in this way. In case of a lack of consensus, the lead PIs will break the deadlock.

The remaining funds will be allocated, roughly equally, to coordination meetings and extended (longer than one week) inter-institution travel by the PIs and their students and postdocs. The cost of coordination meetings will be ascertained by the committee (below) and these costs and the meeting facilities will be discussed by all lead PIs, consensus determining the final decision. For travel support to the meetings, the lead PIs will propose a level of support and a maximum number of persons who can be supported, with the condition that those supported be reasonably distributed over the team. Research visits between various institutions in the team will be determined on a first come, first served basis, subject to reasonable distribution. Suggestions will be solicited from the team regularly.

Committees. Three working committees will perform essential tasks for this CRT. A *Coordination Meeting Committee* of Eguiluz, Savrasov, and Zhang will be in charge of planning the annual coordination meeting and the single evening coordination meeting held in conjunction with the March APS meeting. A committee in charge of coordinating *Computational Resources* will be headed by Jarrell and Umrigar. A third *Code Sharing Committee* to coordinate the readying of codes for sharing will be headed by Pickett, Kuneš and Umrigar.

Communications. Email communication will be the primary mode of day-to-day contact between the CRT participants, as well as organizational discussions. This team has found

that this has worked well in the recent past. An important communication and notification avenue will be a web page, which also has worked well with these team members, that will be extended and overseen by Scalettar. The purpose is to facilitate communication among all the CRT members, and to make available in one place much of the information a team member has frequent or occasional need for. This website will include immediate questions/discoveries of special joint interest, the progress reports, the coordination meeting presentations, as well as shared codes. The current URL is
http://leopard.physics.ucdavis.edu/rts/cmsn/index.html

4.2 CRT Synergy: In developing predictive approaches to strongly correlated materials, electronic structure calculations provide the materials-specific platform from which more accurate treatments of the electron-electron interactions are launched. The LDA+DMFT method is one formalism from which very significant recent progress has been made. In this approach the full band structure, or (so far) the physically relevant energy range downfolded into a smaller Hilbert space, is incorporated into a Green's function whose self-energy (computed with, e.g. QMC) includes temporal, but not spatial, fluctuations. This state-of-the-art approach has successfully illustrated some aspects of the Mott transition and the Kondo resonance in materials such as a few transition metal oxides and Ce, Pr, and Nd. The auxiliary field quantum Monte Carlo method of Zhang and Krakauer also uses for its basis the LDA (or LDA+U) single particle states. The diffusion Monte Carlo method, used by Umrigar and Hennig, starts with the orbitals obtained by DFT, but then reoptimizes them to reduce the fixed-node error.

However, several important formal and computational challenges remain. The three focus areas of this project will bring together their respective contributors' expertise to address these challenges, and then to integrate further the solutions into a coherent whole. The resulting methodologies are expected to be applicable to a wide range of correlated materials whose importance derives from basic-science and high-technology considerations which are central to this project. Each thrust area includes significant diversity of formal approach and computational algorithms, which will ensure both cross-fertilization as well as essential comparisons of results.

For our 'signature problem' we have chosen a glorious challenge (the Mott transition) in a specific material (MnO). The issues involved here are broad enough to engage much of the activities of this CRT, but on a compound with simple enough crystal and electronic structures that new and computationally intensive methods can be applied. Static correlated mean field methods have been applied recently (by a large collaboration involving several team members), capturing much of what can be learned from the static approach. There remain aspects of correlated band theories that need to be explored.

4.3 Teaming With Experiment: Advanced Photon Source at ANL and the Advanced Light Source at LBNL, and the neutron spectrometry carried out at ORNL (particularly the Spallation Neutron Source coming online in 2006). We have close connections with the diamond anvil cell group of Choong-Shik Yoo at Lawrence Livermore National Laboratory, where some of the most interesting aspects of the magnetic and structural evolution of MnO under pressure are being studied. **This must be fleshed out. Larson. who else?**

4.4 Availability of Computational Resources: Umrigar and Hennig have access to local computing facilities at the Cornell Theory Center, the Cornell NanoScale Science & Technology Facility. and to the supercomputers at Sandia National Laboratory, and the Ohio State Supercomputer Center (Clusters of 512 Itanium processors and of 512 Pentium processors, Cray X1), the National Energy Research Scientific Computing Center (6080 IBM SP3 processors and 712 Opteron processors) and NCSA (Altix of 1024 Itanium processors).

Jarrell has grants of time on TeraGrid machines at the San Diego Supercomputer Center as well as larger machines of similar (IA-64) architecture at the National Center for Supercomputer Applications and Argonne National Laboratory.

Ku has unlimited access (at the moment) to the parallel machines of CDIC (Center for Data Intensive Computing) and CMPMSD (Condensed Matter Physics & Materials Science Department) at BNL.

Pickett has applied for access to the 3.1 TFLOPS IA-64 Intel Cluster at NERSC, and is assessing the viability of using the 4.6TFLOPS Blue Gene machine at SDSC. Both are now part of the TeraGrid.

Others?

4.5 Development and Sharing of Codes: Progress in many areas of the physical sciences has been accelerated greatly by sharing of computational expertise and user-friendly codes (*viz.* drug design). The Hartree-Fock and DFT-based electronic structure methods are excellent examples, with applications extending from basic materials research to industrial laboratory use. This CRT will clean up certain research codes that are of some broad interest and use, and make them available to the scientific community. Specific plans are outlined in Sec. 7.

4.6 Acronyms used globally in the narrative. EP: electron-phonon. LDA: local density approximation. DMFA/DMFT: dynamical mean field approximation/theory. QMC: quantum Monte Carlo. AFQMC: auxiliary field QMC. VMC: variational Monte Carlo. DMC: diffusion Monte Carlo. TMO: transition metal oxide. RIXS: resonant inelastic xray spectroscopy. XES: xray emission spectroscopy. LAPW: linearized augmented plane wave. FPLO: full potential local orbital. STM: scanning tunneling microscopy. NCT: numerical canonical transformation. WS: Wannier state. ARPES: angle-resolved photoelectron spectroscopy.

5. Scientific Narrative

5.1 Our Signature Problem: Computational Theory of the Mott Transition in MnO

Scientific Questions. For fifty years the metal-insulator transition in correlated electron systems has been one of the central themes[1] of condensed matter physics. This has been a consequence both of the complexity of the fundamental issues, as well as the continued discovery of new materials in which strong interaction effects play a key role. For the specific case of the half-filled single band Hubbard model with nearest-neighbor hopping on a bipartite lattice, the behavior around the insulator-to-metal transition with accompanying loss of local moment, is reasonably well understood. In the Hubbard model, the competing tendencies arise solely from the kinetic and potential energies (bandwidth W and repulsion U respectively) in the Hamiltonian, favoring itineracy and localization respectively. Real materials, however, have additional degrees of freedom that, as is becoming clear only recently, give rise to a rich variety of possible transitions.

MnO is a transition metal monoxide (TMO) with open $3d$ shell that qualifies as one of the simpler realizations of a Mott insulator. It is, most certainly, a multiorbital system with the accompanying complexities of the tenfold degeneracy, but the half-filled $3d$ states under ambient conditions lead to a spherical spin-only moment. Applying pressure to such a system leads to a number of possibilities, including insulator-metal transition, moment reduction, volume collapse if a first-order transition (electronic phase change) occurs. These changes may occur simultaneously, or sequentially over a range of volumes. Any of these may be accompanied by a structural phase transition, that is, a change in crystal symmetry, but an isostructural volume collapse may occur as well. The $3d$ band width W of such a Mott insulator is very susceptible to applied pressure, and is one of the main determining factors of the strength of correlation effects.

While "closed subshell" MnO may seem to be one of the simpler $3d$ monoxides, it is actually not at all simple, moreover it is not typical of a $3d$ monoxide. The half-filled shell aspect is what makes it atypical, as shown for example by Saito *et al.*, who compiled[2] effective parameters for this system from spectroscopic information. An effective intra-atomic Coulomb repulsion energy as defined by them, for example, is roughly twice as large as for the other $3d$ monoxides. The complexity that should be expected can be considered in terms of the energy scales that are involved in the electronic structure and magnetism of these oxides. These include the $3d$ bandwidth W, an intra-atomic Coulomb repulsion strength U, an intra-atomic $d-d$ exchange energy (Hund's rule J), the crystal field splitting $\Delta_{cf} = \varepsilon_{e_g} - \varepsilon_{t_{2g}}$, and the charge transfer energy $\Delta_{ct} \equiv \varepsilon_d - \varepsilon_p$ (the difference in mean Mn $3d$ and O $2p$ site energies). In the magnetically ordered antiferromagnetic (AFM) state, there is further symmetry lowering and ligand field subsplittings involving $3d-2p$ hybridization. All of these scales evolve as the volume decreases, making the pressure-driven Mott transition a challenging phenomenon to describe.

Our Ambitious Goal, described in the following two subsections, is to provide the first comprehensive study of the Mott transition in a real strongly correlated material, using MnO as the prototype.

Computational Techniques and People. A wide variety of theoretical approaches and numerical techniques will be applied to this system at the relevant volumes (pressures): correlated band theory; LDA+DMFT for single-particle Greens functions, energetics, and spectrum, carried out in both all-electron and minimum basis (downfolded) versions; LDA+DCA for magnetic correlations; AFQMC study of correlated ground state wavefunctions; VMC and DMC study of correlated ground state and excited (particle-hole) wavefunctions). This effort will directly involve nearly all members of our team, and will greatly benefit from our close relationship with high pressure experimentalists and x-ray and neutron spectroscopists.

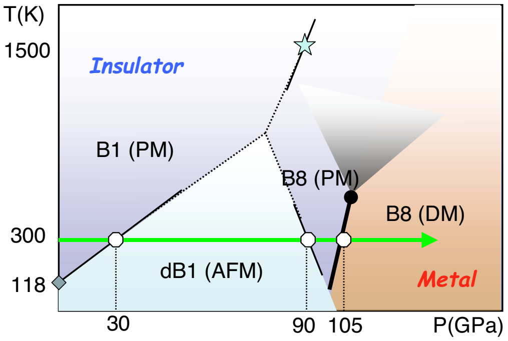

Figure 1: (Color online) The conceptual phase diagram of MnO based on recent high pressure work at Lawrence Livermore National Laboratory [3, 4]. The thick phase line signifies the first-order Mott transition which simultaneously accompanies the loss of Mn magnetic moment, a large volume collapse, and metalization. This transition should end at a critical point (solid circle). The gray fan above the critical point signifies a region of crossover to metallic behavior at high temperature. Only the distorted B1 (dB1) phase is magnetically ordered.

5.1.1 Preliminary Studies. The current experimental information, mostly at room temperature, on the behavior of MnO under pressure is summarized in Fig. 1. Resistance measurements provided the first evidence of the Mott transition in MnO near 100 GPa [3]. Recent x-ray diffraction and emission spectroscopy measurements of the crystal structure and magnetic moment by Yoo and collaborators[4] (which include members of this PCSCS-MnO CRT) have clarified the behavior. Around 90 GPa there is a structural transformation from the distorted B1 (rocksalt) phase to the B8 (NiAs) structure. This structure change is followed at 105 GPa by the Mott transition, consisting of a simultaneous volume collapse and moment collapse signifying a qualitative change in the electronic structure of the compound. A related phase diagram is seen in the lanthanide and actinide volume collapse transitions, with "metalization" defined in terms of the f spectral weight, and is a central consideration in our Thrust A.

On the theoretical side, little has been learned about how the Mott transition occurs in a real multiband TMO. The numerous energy scales listed above, and the S=$\frac{5}{2}$ moment on Mn arising from the five $3d$ electrons, allow for many possibilities for how the moment might disintegrate as the effective repulsion decreases. The high pressure limit is clear: a nonmagnetic $3d-2p$ band metal in which kinetic energy considerations overwhelm potential energy. This is the competition that is studied in the (simplified) Hubbard model. The multiband nature has attracted little attention until recently, when for example the question of possible orbital-selective Mott transitions[5, 6] have aroused interest. One can imagine one scenario of a cascade of moment reductions S = $\frac{5}{2} \rightarrow \frac{3}{2} \rightarrow \frac{1}{2}$ before complete destruction of magnetism.

In preliminary work involving many members of this PCSCS-MnO team[7] the electronic structure, magnetic moment, and volume collapse transition of MnO under pressure has been obtained from four different correlated band theory methods [local density approximation + Hubbard U (LDA+U), pseudopotential self-interaction correction (pseudo-SIC), the hybrid functional (combined local exchange plus Hartree-Fock exchange), and self-interaction corrected local spin density (SIC-LSD) method]. Each method treats, in its own way, correlation among the five Mn $3d$ orbitals (per spin), including their hybridization with three O $2p$ orbitals in the valence bands and their changes of these with pressure. The focus was on comparison of the methods, so calculations were confined to the rocksalt structure (neglecting the observed transition to the NiAs structure in the 90-100 GPa range). Each method predicted a first-order volume collapse, but with variation in the predicted volume and critical pressure. Accompanying the volume collapse was a moment collapse, which for all methods is from high-spin to low-spin ($\frac{5}{2} \rightarrow \frac{1}{2}$), not to nonmagnetic as the simplest scenario would suggest. The specific manner in which the transition occurs varies considerably among the methods: pseudo-SIC and SIC-LSD give insulator-to-metal, while LDA+U approach give insulator-to-insulator and the hybrid method gives an insulator-to-semimetal transition. Projected densities of states above and below the transition were used to analyze the character of each transition, revealing that in some cases the rhombohedral symmetry of the antiferromagnetically ordered phase clearly influences the character of the transition. The surprises uncovered by this broad collaboration provide an improved understanding of the types of complications that may occur in a multiband system that have no analog in single-band models.

5.1.2 Proposed Work This signature problem is specific enough, with sufficient tested codes either in hand or nearing readiness, that a fairly definite timeline can be laid out. Since this topic is an application that uses theory, algorithms, and codes that are used also in at least one of our two thrusts (Sec. 5.2 and 5.3), we defer discussion of details of the theory, algorithms, and codes to those sections, and simply relate in this subsection how they will be applied to our signature problem. Most references to the literature will also be deferred to those sections. The items labeled 2005 and 2006 represent results from recent or preliminary work, *i.e.* they are completed. Items labeled 2007 are entirely in-hand, and in some cases are in prepration now. Some items labeled 2008 or 2009 represent new capabilites at that time. Thus the Mott transition in MnO is not only our signature problem, but MnO will be used as the testbed for extensions of our codes as they become available. This list of other strongly correlated electron systems is long and there is great variety in the methods that are used; it is a credit not only to this team's expertise but also to its synergetic activities that we believe the following extensive programme is not only viable, but very practicable to carry out.

2005. Aside from aspects discussed above, MnO is an appropriate choice of application for this topic because of the recent experimental work recently done on MnO, culminating in the (still somewhat schematic) phase diagram shown in Fig. 1. The relevant crystalline phases are known (NaCl and NiAs). The pressure range (hence volume range) is known. And the fact that there is a substantial moment collapse is evident from the data, although nothing in detail about the character of the collapse is known.

2006. The work of the large collaboration described briefly above, in applying four correlated band theory methods to MnO under pressure, has been completed.[7] This work will serve as a guide for what to look for in the DMFT calculations. The LDA+U work on MnO has been extended[8] even more recently. Specifically, it has been established that the character of the collapsed state is *in*sensitive to the value of U within reasonable limits, while it is much more sensitive to the exchange (Hund's) parameter J than common knowledge would suggest. The value of U has been calculated with the capability built into the LAPW code Wien2k, giving the value U=5.6 eV, quite close to the value we have been using (5.5 eV). The volume dependence of U will be calculated and incorporated into further studies. Exploration of these LDA+U predictions will continue through 2007.

2006. Calculations of the ground state energy, guided by density functional generated wavefunctions, have been carried out after further optimization of the wavefunctions for MnO molecules using the AFQMC method. This code has been adapted to treat periodic systems.

2007. An all-electron LDA+DMFT code, put together by team member Jan Kuneš in consultation with several other PCSCS-MnO team members, is working and providing the single-particle spectrum of NiO, a sister TMO to MnO. This code is all-electron in the band structure sense: the crystal Greens function includes not only the correlated orbitals (ten $3d$ orbitals on each Mn atom) but also the six O $2p$ orbitals and any other conduction orbitals that are relevant. This all-electron capability will enable a realistic comparison with spectroscopic data, because there is a strongly dispersive, nondescript (that is, not clearly associated with any single atomic orbital) conduction band that dips though the upper Hubbard bands and hybridizes with them. Initial emphasis will be on changes in the spectrum as the volume is reduced, *viz.* when and how does the Mott gap disappear? This study will be done for both the NaCl and the NiAs structures.

2007. For a variety of reasons (to test downfolding strategies, to evaluate influence of reduced Hilbert space vs. computational efficiency, etc.) we will address MnO with less than the all-electron basis. The first choice will be the minimum basis Mn $3d$ orbitals only. DMFT+DCA codes will be applied to (1) compare with all-electron results, and (2) simulate the antiferromagnetic spin correlations, and (3) evaluate the effects of these correlations on properties.

2007. VMC/DMC study of AFM MnO. The correlated multi-configuration wavefunction for both ground state and electron-hole excited states will be optimized to obtain energetics, and thus the optical gap. The optimized wavefunction will provide the characteristics of states; for example, the CI coefficients will reveal the amplitudes of the various configurations that are incorporated into the wavefunction. (See Thrust A for further description of these methods.)

2007. AFQMC study of solid MnO. Building on our success with TiO and MnO molecules, we will first apply the planewave and pseudopotential approach to the MnO solid (rocksalt and NiAs structures). As we gain feedback from these results and other complementary calculations of the team, we will augment or substitute the plane-wave approach with our generic basis code, using a more efficient downfolded basis. The goal of this application of AFQMC is to complement the LDA+U, DMFT, and DCA approaches with correlated wavefunction ground-state results, for the range of volumes and pressure where the Mott transition occurs.

2008. Refine the LDA+DMFT(QMC) free energy functional with the goal of achieving predictive capability for structural energy differences of correlated electron systems, with MnO as the testbed. Free energies have been calculated in material-specific applications for lanthanides by team members McMahan and Scalettar using QMC, and for actinides by team member Savrasov using more efficient and approximate atomic solvers. Current forms of the free energy functional contain approximations that bear refinement, and require extension as the full Coulomb operator is implemented into the QMC codes.

2008. Wannier function study of the Mn moment under pressure. The symmetrized Wannier function representation of MnO will be used (Ku) to analyze magnetic interactions in compressed MnO, and to search for unusual mechanisms that could compete with Hund's coupling and that might account for the unexpected spin-flip seen in LDA+U studies by members of our team (Kasinathan, Koepernik, Kuneš, Pickett), whose recent work shows an unexpected sensitivity to the strength of the Hund's coupling on Mn. Ku will also address the question with the new maximally localized Wannier function capability that was applied to manganites.[15]

2008. Phonons in MnO from LDA+U. Using the frozen phonon method, calculations of phonon frequencies and eigenvectors will be carried out for MnO (magnetically ordered, if such solutions exist) for high symmetry Q points and a sequence of volumes extending through the Mott transition. Substantial changes are anticipated at the insulator-metal transition. Of great interest will be the change that occurs at the magnetic collapse ($S=5/2$ to $S=1/2$), which in the LDA+U prediction occurs between two insulating phases.

2008. Phonons in MnO from AFQMC and VMC/DMC. It is a straightforward matter to obtain the zone center vibrational frequencies and eigenvectors from each of these methods. (We currently have no plans here, or for the previous item involving LDA+U, to include the internal electric field and hence obtain the LO-TO splitting of modes. While this splitting and the related Born effective charges would indeed be interesting, we do not expect the information would justify the investment of time in extra coding.) Results at zone boundary points, while conceivable using supercells, would be expensive. These results will be used to 'calibrate' the accuracy of the LDA+U frequencies, and provide guidelines for DMFT frequencies to follow (which would be at high temperature in the spin-disordered phase).

2009. Thermodynamic theory of the Mott transition in MnO. In this third year the focus will be on finalizing the free energy functional and predicting, on the basis of DMFT(QMC) calculations, the volume(s) at which transitions occur, and the amount of volume collapse at each transition. A likely scenario, based on what knowledge there is currently of the phase diagram (experiment and LDA+U), is that there is an NaCl→NiAs structural transition, followed by a moment-collapse transition which may or may not coincide with the insulator-to-metal transition. DCA calculations will be carried out as allowed (the computational expense is much greater) to assess the effect of spin fluctuations on the transition.

5.2 Thrust A: Multielectron Magnetic Moments

Scientific Questions. This research thrust focuses on the many degrees of freedom presented by $3d$ or $4f$ atoms with their highly degenerate localized orbitals. Although moment formation and the Mott transition are relatively well understood for the single band Hubbard model on selected lattices, there are few realizations of any Hilbert space this simple in real materials. (Li_xNbO_2 is one realization of a single-band system, on a triangular lattice, which has been under study by members of this team[9].) The multiband (equivalently, multiorbital) nature introduces essential new physics into the correlated electron problem, *viz.* Hund's rules. The multiorbital aspect is well accounted for in DFT-based methods (LDA and correlated band methods such as LDA+U), but the spin degree of freedom in such mean field pictures is classical, and also constrained (at least locally) to be simply up or down.

A series of key unanswered questions about the electron correlation driven transitions in compressed $3d$ (transition metal oxides, TMO) and $4f$ (lanthanide metals) systems concerns the role of multielectron Hund's rules moments: how and when do these moments disassemble or quench, what happens to the separate spin and orbital components, when do Kondo-like screening effects come into play, and how do all of these features relate to the large-volume-change Mott or delocalization transitions and more generally to the observed structural sequence in lanthanides?

The types of behavior that can now be envisioned in TMOs was summarized in Sec. 5.1. Most interesting of the results from correlated band theory calculations versus volume is that (i) moment reduction can result from spin compensation (an orbital doubly occupied, both up and down) but also by spin cancellation (all five $3d$ orbitals occupied giving a spherical density, but some flipped giving a highly anisotropic spin density), and (ii) the magnetic space group can be important (*i.e.* symmetry reduction by magnetic order can determine the spin configuration).

In spite of great progress on early lanthanides using the LDA+DMFT approach, especially by team members McMahan and Scalettar, the compressed $4f$ metals still present many puzzles. Beyond the analogous questions from the TMOs (what spin arrangement is favored) one may further ask what is required to address the Kondo volume collapse question. Requirements include (i) LDA+DMFT calculations of the bare $4f$ moment from $\langle J^2 \rangle$, (ii) the screened moment from magnetic susceptibility, and (iii) the juxtaposition of these results with reliable structural energy differences as a function of compression. LDA+DMFT structural energy differences have recently been demonstrated using a two-pole approximation to the self-energy.

One issue to address is how our numerically precise but approximate treatments of the self-energy compare against earlier LDA+DMFT(QMC) results for Ce, Pr, and Nd in the absence of intraatomic exchange (these results provide a standard). Then simulations will move on to the case where the full Coulomb operator is treated. With each level of capability we will address also the later rare earths (Sm,Eu,Gd,...) with the objective of understanding the gradual disintegration of Hund's rule coupling, which sometimes (in the $L = S, J = |L - S| = 0$ ions Sm^{2+}, Eu^{3+}) lets the moment *begin to appear* before eventual collapse at (high) pressure. State-of-the-art Cowan-Kotani codes (see Sec. 5.2.2) will be developed and employed to provide a material-specific interpretation of the signature of the moment in RIXS data, to be provided by our collaboration with the high pressure group of C. S. Yoo (LLNL). This effort extends earlier PCSCS work Ce, Pr, Nd (LDA+DMFT),[10, 11] on Gd,[12, 13] and on EuN (LDA+U).[14]

The size of the "basis set" in a given system determines both the aim of the research effort and the scale of the computational effort. For the time-dependent LDA+U code (Eguiluz, Kuneš, Pickett) with spin treated classically and colinearly, it is possible to handle 40-atom cells as they have done recently for $\mathrm{Na}_x\mathrm{CoO}_2 \cdot y\ \mathrm{H}_2\mathrm{O}$. For all-electron LDA+DMFT studies of MnO (Kuneš, McMahan, Pickett, Scalettar), the primitive two atom cell studied over the necessary range of pressures already requires substantial computational effort, although several atoms per cell can be handled as this project gathers steam. This strong dependence on basis set size drives our planned extensions of recent improvements[15] in systematic Hilbert space reduction (Ku, White), from the all-electron LDA starting point to the minimum (but not subminimum!) set of hybridized orbitals (Wannier functions) that captures the low energy degrees of freedom.

Computational Techniques and People. This thrust addresses several aspects of multiorbital characteristics of correlated systems. Both charge and spin dynamical response functions provide a valuable window into the microscopic behavior of a correlated system, and close comparison of our calculated response function with direct measurement by nearby experimentalists (Eguiluz with Larson, ORNL) will provide the synergy necessary to obtain verification of calculational methods and move the understanding forward rapidly.

This team has a broad and complementary suite of methods and codes for addressing the behavior of multiorbital atoms and their moments: correlated band methods (LDA+U and SIC-LDA); dynamical response in the LDA+U method, a technique that is unique to our team and will provide full dynamical response functions; LDA+DMFT, from minimum basis to all-electron, with real-frequency spectra obtained from maximum entropy methods developed by team members (Gubernatis, Jarrell); DMC/VMC evaluations of optimized correlated many-body wavefunctions; wavefunction-guided AFQMC simulations. The methods and the important computational algorithms are described in following sections.

5.2.1 Preliminary Work.

- LDA+U correlated band theory. The LDA+U method provides (it is said) static version of the DMFT approach. It is the primary way of investigating Hubbard-type intra-atomic interactions at T=0 in a material-specific way. It is routinely implemented in a rotationally invariant way. This is found to be important in rhombhedral MnO (the AFM II phase). And unlike DMFT carried out above the ordering temperature, the LDA+U method describes correlation effects that can be strongly tied to the local environment, and also is sensitive to long-range order. These aspects lie at the core of the ability of the LDA+U approach to describe (and some cases *predict*) spin-, charge-, and orbital-ordering.

Recent results from work of several team members (see Sec. 5.1 for more detail) reveal that this static-correlation method can lead to unexpected internal spin arrangements, *viz.* a d^5 Mn^{2+} ion in which every orbital is singly occupied, but some are up and others are down: S=1/2 or S=3/2 instead of the S=5/2 moment under ambient conditions in MnO. The result for the Mn^{2+} moment versus volume from a broad collaboration involving four correlated band theories is shown in Fig. 2, where the first order transition and S=5/2 to S=1/2 "collapse" is predicted by all four methods. More recent work by team members (Kasinathan, Koepernik, Pickett) has revealed an unexpected sensitivity of the spin configuration of the Mn^{2+} ion to the strength of the Hund's rule parameter J in LDA+U calculations. In addition to the most widely understood tendency toward pairing of spins (magnetism), J also carries the information relating to the off-diagonal in orbital Coulomb repulsion, that is, the anisotropy (the F_2 and F_4 Slater integrals). This off-diagonality may be more important than has been expected, and this question will continue to be pursued by this group. *Johannes, Kasinathan, Koepernik, Kuneš, Pickett*

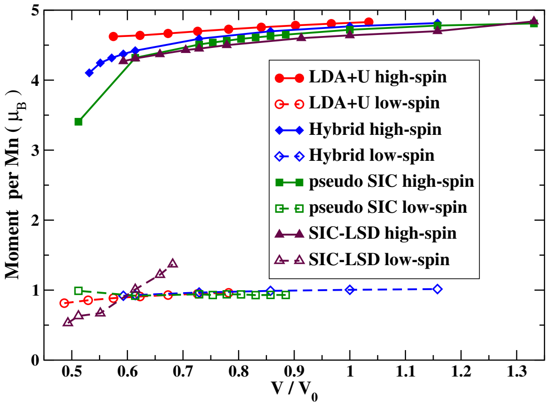

Figure 2: Calculated moment on each Mn site in antiferromagnetic MnO as a function of volume for the various functionals. All the methods predict a distinct collapse (first order) of magnetic moment with decrease in volume. At large volumes, the high spin state with S = 5/2 (single occupancy of each of the $3d$ orbitals) is realized while the low spin state with S = 1/2 is favored for smaller volumes. Note: the computational methods calculate the 'Mn moment' is inequivalent ways, so small differences have no significance.

• The correlations present statically in the LDA+U method have been incorporated into a self-consistent theory and code for dynamical response built on LDA+U (as opposed to LDA, previously developed and proven in many systems (*viz.* MgB_2[16]). With the value of U obtained from Wien2k, this code represents a parameter-free (hence often designated *ab initio*) method for the dynamical response of correlated materials. *Eguiluz, Kuneš, Pickett*
• Realistic *all-electron* LDA+DMFT calculations and, at a later stage their cluster generalizations (dynamical cluster approximation, DCA), based on material-specific local density approximate (LDA) input are on the threshold of being able to answer these questions and thereby address exciting new experimental developments.[4, 17, 12] We use 'all-electron DMFT' to designate the treatment of Hubbard interactions within a full LDA basis set. *Jarrell, Kuneš, McMahan, Pickett, Savrasov, Scalettar*
• DMC computations, based on optimized wavefunctions, are now at the stage where they can, and will during this project, provide an entirely new theoretical probe of strongly correlated TMOs. Extending the CHAMP (Cornell-Holland Ab-initio Materials Package) suite

of codes
http://www.tc.cornell.edu/˜ cyrus/champ.html
Umrigar and Hennig will carry out correlated wavefunction studies of MnO and related TMOs during this project. In order to get highly accurate energies from DMC it is essential to optimize the many-body wave functions. For the last 15 years, the standard method for doing this has been the *variance minimization method* as prescribed by (PCSCS team member) Umrigar *et al.*[18] because many fewer Monte Carlo samples are required than when using *naive* energy minimization. However, although variance minimization is very efficient at optimizing the Jastrow parameters it is not quite as effective at optimizing the parameters(CI coefficients, LCAO coefficients and exponents of basis functions) in the determinantal part of the wave function that can affect the positions of the many-body nodes. However, in recent years, starting with the work of Fahy [**?**] and Nightingale [**?**] there has been a breakthrough in methods for performing energy minimization. These methods have already been superceded by yet better methods. At the present time, there are three highly efficient methods for energy optimizing many body wave functions [**?**, **?**, 22, 23], all of which were invented by the authors of CHAMP. Using these new methods it has been found to be possible to systematically reduce the fixed-node error and thereby for the first time get truly reliable energies from DMC for molecules. We plan, as part of this proposal to extend this capability to periodic solids.

For periodic systems it is important to also perform finite-size extrapolation to get accurate results. The recent advance by team member Martin and collaborators[24] has been found to increase efficiency.

One of the virtues of QMC methods is that they can make good use of massively parallel computers. An earlier version of CHAMP was found to run on 2000 processors of Sandia's ASCII-Red machine with a parallel efficiency around 95%. Current versions of the code are being run at the Ohio State Supercomputer Center (512 node Itanium clusters and 512 node Pentium clusters, and the Cray X1), at NERSC (6080 IBM SP3 processor machine and the 712 node Opteron cluster) and at NCSA (Altix shared memory machine with 1024 Itanium processors). Recently, at NERSC, it has been run on as many as 1000 processors; this number is limited only by queue availability.

- AFQMC applications. Due to recent advances in codes and successful applications by team members Zhang and Krakauer, a goal is to apply the phaseless AF QMC method in several different capacities (direct *ab initio* calculations, as a benchmark tool, or interfaced with band theory approaches to study realistic *models*). The method has been applied successfully to TiO and MnO molecules, and the corresponding periodic solids provide the present challenge: very little correlated wavefunction study of any material-specific nature has been attempted for transition metal oxides. Both magnetic energies within a given structure, and structural energy differences, will be studied with the AFQMC codes. As we gain feedback from these and complementary calculations of other team members, we will apply also our generic basis code and also compare with a more compact and numerically efficient downfolded basis. Our intention is to bring AFQMC into the suite of codes we have available (*viz.* LDA+U, DMFT, DCA) to learn how to understand and describe correlation effects in TMOs in an *ab initio* material-specific manner.

5.2.2 Proposed Work.

• The LDA+U approach so far provides the only explanation[25, 26] for the charge ordering[27] (and antiferromagnetism) at x=1/2 in Na_xCoO_2. As reflected in the program of the recent *First Intl. Workshop on the Physical Properties of Lamaller Colbatates* (July 2006, Orsay), there is strong interest in understanding the potassium counterpart $K_{0.5}CoO_2$. It shows a very similar set of transitions as temperature is reduced: K ion ordering; charge and spin ordering; transition to a tiny gap insulator. However, its LDA Fermi surface is different enough[28] that Fermi surface nesting cannot be responsible in both materials, leaving correlation as the leading candidate. The LDA+U method will be applied to $K_{0.5}CoO_2$ to study its small magnetic moment, and to compare with that of $Na_{0.5}CoO_2$.

The LDA+U method will also be extended in a more exacting study of EuN. This system is Eu^{3+} f^6, $S = 3, L = 3, J = 0$ nonmagnetic at ambient pressure. Recent experience of team members working on MnO indicate that the solutions (metastable 'excited states' can be obtained as well as the ground state) are, unexpectedly, dependent on the value of the Hund's parameter J in the physical range of J. (Since it is only weakly screened from its atomic value, it can be calculated with a relatively small uncertainty.) This J-dependence will be pursued to establish whether this is a factor in the difficulty that has been encountered in obtaining the correct total angular momentum J=L+S. ...to be completed...

• Response Functions in LDA+U ....(to be written)...

• LDA+DMFT. The proposed work in this segment will begin testing this and other precise but approximate treatments of the self-energy against earlier LDA+DMFT(QMC) results for Ce, Pr, and Nd in the absence of intraatomic exchange, and then move on to the case with the full Coulomb operator. We will also carry out calculations on later rare earths (Sm,Eu,Gd,...) with an objective of understanding the gradual disintegration of Hund's rule coupling, which sometimes (J=0 ions Sm^{2+}, Eu^{3+}) lets the moment begin to appear (before eventual collapse). State-of-the-art Cowan-Kotani[29, 30] codes will be developed and applied (Scalettar, McMahan, Pickett) to provide a material-specific interpretation of the signature of the moment in resonant inelastic x-ray scattering (RIXS). These exact diagonalization approaches can treat the full complexity of the Coulomb operator and also disentangle the spin and orbital contributions to the total moment. As mentioned above, this effort extends earlier PCSCS work Ce, Pr, Nd (LDA+DMFT),[10, 11] on Gd,[12, 13] and on EuN (LDA+U).[14]

One of the essential tasks in a full description of multielectron moments is to treat properly correlations allowing *all* of the on-site degrees of freedom, namely to include the full rotationally invariant Coulomb operator as described by all three ($3d$) or four ($4f$) Slater integrals. This and the ability to accurately calculate structural energy differences will require significant improvements in existing impurity solvers. The issue of whether or not magnetic correlations are also playing a role in these systems can be addressed by moving beyond DMFT to the DCA. Finally, to truly understand these systems, new (x-ray emission spectroscopy [4, 12]) and older (magnetic susceptibility) experimental diagnostics for the moments need to be understood and analyzed by these theoretical techniques.

The *Anderson impurity model* (AIM) approach, which describes a single correlated site (e.g., a Mn atom) in a sea of valence electrons (e.g., surrounding O atoms), is a natural guide for generalizing DMFT to multiorbital correlated atoms. The AIM has been extremely useful in analyzing photoemission data, [31] and more recently XES data[32] and RIXS results.[30] As the Mn($3d$)-O($2p$) hybridization in this MnO example grows under compression, the model is capable of providing important insights into many of the critical questions raised earlier, such as how the orbital and spin components of the Hund's rules moments may evolve differently and the role of screening by the valence electrons. This particular use of AIM calculations for multielectron moments has received little attention and is the first task of this approach. Such calculations can still be challenging for exact diagonalization techniques for d and f shells near half filling, and may require insightful approximations or other (e.g., Lanczos) solutions.

The second stage of this effort is to incorporate the core holes, and evaluate the Kramers-Heisenberg formula with calculated initial, intermediate, and final states in order to analyze the experimental XES and RIXS diagnostics for the focus materials of this proposal. In particular a side peak in XES data is used as a diagnostic for the multielectron moment, and it is hoped to understand to what extent this measurement probes orbital, spin, or total moment, and to what extent it is sensitive to the bare or screened moment.
Scalettar, Pickett, McMahan, ⋯

The LDA+DMFT method offers a far more chemically realistic approach to the materials discussed in this proposal. However, there remain challenges in including the full multipole character of the Coulomb operator in these techniques, which along with the spin-orbit interaction is critical to a faithful treatment of multielectron moments. Recent work on Am, however, has provided a step forward, although in doing so a rather approximate two-pole treatment of the self-energy was used.[33] The first goal in this subthrust is to scope out the compression behavior of such target materials as MnO using LDA+DMFT with the usual Hubbard U (monopole part of Coulomb operator). Equivalent calculations for a number of compressed rare earth metals have already been carried out.[11]

The more challenging subsequent tasks are to include the full Coulomb operator along with spin-orbit, and have an impurity solver which is sufficiently precise to yield reliable structural energy differences. The idea is to monitor the evolution of the Hund's rules moments (orbital, spin, possible collapse and/or screening) and to juxtapose this behavior with the structural evolution. The Am work by team member Savrasov[33] has already demonstrated one direction to pursue. This subthrust benefits from having three different LDA+DMFT implementations amongst the investigators. The effort is sufficiently new and difficult, that we view these initial and different implementations as a strength, enabling us by cross comparisons to zero in on an optimal algorithmic and computational strategy.
Kuneš, Pickett, Scalettar, Savrasov, McMahan, ⋯

• LDA+DCA. Both of the previous subthrusts preclude the ability to treat magnetic order, and yet the phase diagram Fig. 1 for the signature problem of the Mott transition in MnO, suggests a room temperature compression path which passes into and then out of a region of antiferromagnetic order *before* reaching the Mott transition. It seems clear that an examination of magnetic ordering behavior will also be essential to understand this problem, and this requires moving beyond DMFT to the DCA. The added layer of complexity suggests doing initial calculations here for model few band systems, before attempting LDA+DCA. *This will require rewriting by Mark as to what he wants to do. It is not even clear that DCA*

in a problem with the full Coulomb operator is feasible.
Jarrell, Scalettar, Gubernatis, $\cdots$.

- AFQMC. The AFQMC method and codes have been extended. We demonstrated the accuracy of the new phaseless ground-state auxiliary-field quantum Monte Carlo (AF QMC) method [36, 37] for the transition metal oxides TiO and MnO molecules, using a plane-wave basis [38]. This was one of only a few QMC calculations of any type for TM oxides. We also implemented the new method for any generic 1-particle basis [39]. Using Gaussian basis sets, we achieved excellent accuracy in a variety of first-row atoms and molecules (within a few mHa of full-CI and high-level coupled-cluster methods for total all-electron energies, binding energies, ionization potentials, and electron affinity). A systematic study on post-d elements Ga-Br and In-I was carried out,[**?**] **what reference is this?** and the calculated ionization potentials and electron affinities were in excellent agreement with experiment (to within chemical accuracy).

We also tested the method in describing bond stretching, which mimics different levels of electron correlation. The ability of a computational method to deliver uniform accuracy as bonds are stretched/broken will be very important for the proposed work, because of the need to accurately distinguish structural differences. In H_2O, as bonds are stretched to increase the effect of correlation, our method exhibits [39] better overall accuracy and a more uniform behavior than the coupled-cluster CCSD(T), which is a gold standard in quantum chemistry (but which is computationally costly, with an N^7 scaling). Similar preliminary results have been obtained for other systems. For example, as the bonds are stretched across a metal-insulator like transition in a chain of 50 hydrogen atoms, the method gives the equation of state in agreement with exact DMRG results [**?**] to within 0.003eV/electron.

Together with our earlier plane-wave studies, we have now applied the phaseless AF QMC method to close to 100 systems. (We are also presently studying the ferroelectric well-depths in solid $BiScO_3$.) Thus, while further testing and development of the new AF QMC method will have to continue, we believe it is at the state where applications can become a focus.

5.2.3 Computational Challenges.

It is appropriate here to review the computational issues that are involved in the *DMFT(QMC) generally* (which is used by several team members: Jarrell, Scalettar, McMahan, Savrasov, Kuneš, Pickett), and the cluster generalization DCA(QMC) used most extensively by Jarrell and collaborators. At the most basic (and somewhat naive) level, Monte Carlo calculations are inherently parallelizable: a Markov chain of events is followed to obtain statistics, and these statistics can be accumulated by chains running on individual processors. As long as the necessary updates can be done on a single processor, efficiency in parallelization can be expected to be high. In parallelizing DCA(QMC) the bottlenecks can be (a) memory limitations, which increases as the square of the number of sites in the cluster, (b) updates of the Green's functions, which can be quite fast if it can be done in cache but suffers when main memory must be accessed (as this is done very often), and (c) surprising perhaps, but when the Monte Carlo sampling is implemented very efficiently over many processors, the warmup step (to 'thermalize' the system) can become an issue.

The AFQMC calculations are very demanding, requiring very large computer allocations and human resources. Each AF QMC calculation is like hundreds to thousands of looselycoupled (imaginary)-time-dependent DFT calculations. We then extrapolate with multiple calculations for convergence with respect to basis size, Trotter error, supercell size, etc. For TMOs, for example, often at least a $2 \times 2 \times 2$ supercell is needed, giving several hundred valence electrons. (We are presently also implementing a hybrid approach using plane-wave representation of the Coulomb kernel for localized basis sets, which may yield additional speed-ups.)

We now have several versions of the AFQMC code, which interface with a number of standard quantum simulation software packages (mostly manually at present). For example, our plane-wave code interfaces with ABINIT and OPIUM, while our localized-basis code interfaces with NWCHEM, GAMESS, GAUSSIAN, etc. Our codes are all parallelized with MPI and run efficiently on multiple platforms. As our method matures, we will seek to implement the various standards (e.g., on I/O format) which are being developed by the quantum simulations community, and work towards making the code and the interfaces more user-friendly. This will facilitate code-sharing within the community.

5.3 Thrust B: Dynamic Effects in SCES.

Scientific Questions. Although the metal-insulator transition can be regarded as a quasi-static manifestation of changes in correlation effects (*viz. dc* conductivity), most phenomena in strongly correlated materials are manifest in the dynamics of the system. Historically, 'dynamics' in this usage has meant electronic excitations or fluctuations, and that certainly lies at the heart of the correlation problem. The last decade has shown however that an additional dynamic interaction must be incorporated before data on SCES can be given a proper interpretation, and therefore is a requirement for any predictive capability. This additional effect is the lattice dynamics. Lattice coupling in manganites can be a determining factor in what the system becomes at a given doping level[95]; lattice coupling to carriers in cuprates is evident in the $La_{2-x}Ba_xCuO_4$ (LBCO) system at x=1/8, in phonon dispersion of the three heavily studies cuprate families and, many think, in the quasiparticle dispersion near the Fermi level,[94] and becomes involved in the pairing interaction[97]; recent data[110] point to lattice entropy as essential for understanding the volume collapse in Ce. For these reasons we conclude that a predictive capability for SCES must include lattice dynamics as well as electron dynamics. Fortunately, recent developments (within our team especially, but also elsewhere in the community) make it possible to make serious inroads on the phonon participation issue as our treatment of dynamics of electronic correlation becomes more quantitative and efficient. Both types of dynamics will involve several members of our PCSCS-MnO team.

The peculiar Na_xCoO_2 system provides a clear challenge and opportunity at this time, with considerable experimental data now available and with no hint of consensus on the correct theoretical picture. The triangular lattice aspect is of central interest, of course. The system is correlated in the large x regime, and seemingly weakly correlated for $x < 0.5$, but there is not even any good indication of the appropriate value of U. The extensive LDA+U work by the PCSCS-MnO team will be extended to LDA+DMFT. The problem at low energy is a three-band t_{2g} one, with some small but important symmetry-breaking ($t_{2g} \rightarrow a_g + e + g'$). A second thrust concerns investigations of embedded Co clusters and is a natural extension of our earlier work on transition metal oxide molecules. The implementation of localized bases in QMC developed by the PCSCS-MnO team now allows a more efficient simulation of solids, using down-folded or model Hamiltonians, embedded cluster methods, or conventional periodic boundary conditions.

Theoretical interest in the lattice involvement in the behavior of SCES has been sharpened by recent theoretical indications that electronic correlations may greatly enhance the effective EP coupling, and therefore may account for the phonon involvement in recent data (noted above) and structural transition of LBCO at x=1/8. Heretofore the more prevalent picture had been that strong interactions tend to depress EP coupling strength. In the newer scenario, the electronic interactions result in band narrowing[97] which enhances the effective EP coupling, driving the system to the polaron regime even for moderate EP couplings. In the earlier picture, correlation suppresses the charge response and thereby the coupling. EP coupling is known to contribute to phase separation and spin and charge ordering in some heavy fermion systems and the cuprates, and almost certainly is involved in the complex phase diagram of plutonium. There has been recent progress in both experiment and theory. The phonon dispersion in the δ-phase of Pu has just been measured for first time using newly developed inelastic x-ray scattering scattering techniques[98], with results agreeing quite well with the *predictions* of (PCSCS-MnO team member) S. Savrasov *et al.*[96] Evidence for the importance of EP coupling is even more pronounced in the cuprates. Analysis of experiments in the high-temperature superconductors undoubtedly shows that electron-phonon interactions play an important role in the properties of these materials. Similar effect are seen in the manganites[106], where *e.g.* Raman experiments show a softening of certain phonon modes with doping[107].

A Pressing Development: Phonons in the Lanthinides and Actinides. The Kondo volume collapse, characterized by the discontinuous isostructural phase transition between the γ and α phases of Ce, has recently been modeled impressively well by PCSCS-MnO team members McMahan and Scalettar,[10] but still stimulates controversy. Recent LANL neutron scattering data presented by Jeong *et al.*[110] suggests that lattice entropy accounts for 40% of the entropy change at the Ce collapse, rather than it being purely electronic with $\delta S \approx log(2J+1)$ as theory has suggested.[108, 10] The question is fundamental: is the moment fully screened away in the α phase and completely bare in the γ phase; if not and the lattice is involved, the physics is much richer and more complicated to describe, and the observed entropy change of $log(6)$ ($J = 5/2$) is coincidental. Pr also has a volume collapse transition, and that same analysis leads to $\delta S \approx log(9)$ which implies a localized Hund's rule moment ($L = 5, S = 1, J = 4$), but only as long as the lattice contribution is negligible.

Computational Techniques and People. A capability unique to our team is the calculation of dynamical response functions based on the LDA+U treatment of correlation...... (complete when this section is written)...

5.3.1 Preliminary Results.

• LDA+U-based Dynamical Response. **Description can go here, or in the analogous position in Sec. 5.2.**

• LDA+DMFT(DCA)+Phonons. To address some of these problems, we have developed a new class of massively parallel QMC cluster solvers which are able to treat the many time scales presented by the combined correlated electron and phonon system. **We need some computational nitty-gritty here. What new algorithms? computational expensive aspects. What is in place (Preliminary work)? What needs to be done and will be done (Proposed research)? MPP?!** By the third year we expect that these computations will be extended to real materials applications based on an LDA starting point (thus, an all-electron LDA+DCA capability). We propose to do this in two stages. First, within a simple periodic Anderson model DMFA/DCA calculation we will study the role of different phonon modes. When the computational techniques are perfected, we will add realistic phonon modes, calculated from first principles, to the LDA+DMFA calculations.

The electronic dispersion in several cuprates, as measured by ARPES spectra [99, 100, 101], shows a kink at an energy (about 70 meV) very close to phonon modes measured by neutron scattering. This data suggests that the quasiparticle couples very strongly to either the phonons or some collective spin excitation. Furthermore, a peculiar isotope-effect was recently measured in the cuprates [101]. When the in-plane ^{16}O ions are replaced with O^{18} ones which results in a shift in frequency of the hard oxygen modes, the quasiparticle dispersion also shifts at high energy.

• Real space understanding of excitons via local Wannier state (WS) picture. In collaboration with an ORNL experimental effort of studying charge excitations below the gap in NiO and CoO, we have developed a real space WS-based picture for visualization of the formation and interplay of excitons via particle-hole pairs. This formulation allows an intuitive understanding of the observed strong anisotropy and q-dependence of the measured spectrum. Based on the new framework, the observed nodal directions can be easily understood as a result of the point group symmetry (a new selection rule), and shown to be very sensitive to a weak symmetry breaking resulting from the AFM order. This new realization has led to the suggestions of a new way of conducting experiments that probe the wave functions of the low-energy states in SCES in general.

5.3.2 Proposed Work.

• Lattice coupling incorporated into Hamiltonian downfolding. Ku and White will extend further their recent developments in downfolding, focusing on the 1/8 doped cuprates in addition to the undoped materials. The novelty they have introduced is to go beyond the usual 'non-interacting down-folding', instead incorporating the interaction already at the downfolding level. New work will include implementation of their new numerical canonical transformation method to (i) obtain a low energy Hamiltonian in more systematic fashion, (ii) to renormalize the non-relevant interactions, and (iii) expose the role of interactions around ground states in different (competing) phases. The objective is to identify the low energy states that form the quasiparticle in collaboration with Jarrell and Scalettar, and then to carry out a systematic study of the material dependence of the various cuprate families. **A few more specifics here.**

• LDA+DMFT+Phonons. Applications will focus primarily on the high temperature superconducting cuprates. These materials are characterized by strong electronic correlations which has caused many investigators to assume that the superconductivity is purely of electronic origin. However, analysis of high resolution ARPES[99, 100, 101] experiments, neutron scattering [102, 103, 104] and STM [105] data in the high-temperature superconductors establish that EP interactions play an important role in the properties of these materials. Therefore one fundamental question to be addressed is: how does strong electron-electron interaction interplay with strong EP coupling? In order to address this question, we have modified the codes discussed above **Codes and modifications are not yet discussed...** to include breathing and buckling modes identified by neutron scattering experiments on the cuprates [103, 104]. We will use these codes to address the effect of phonons on the ARPES spectrum and quasiparticle dispersion, the phase diagram and especially pairing, and the neutron and other two-particle spectra of the cuprates.

We will explore first whether the kink revealed by ARPES is due to the coupling to a collective spin excitation already present in the simple Hubbard model, as was suggested by Kakehashi and Fulde [111] using another quantum cluster formalism. Our new codes allow us to explore this question systematically on significantly larger clusters. We will add the phonon dynamics to see how the spectrum changes. We will investigate the isotope effect by employing calculations with different phonon frequencies.

The temperature-dependence of the spectra is also of great interest. Finite temperature ARPES in weakly doped cuprates exhibit a wide quasiparticle (QP) peak at the nodal points, which is difficult to explain with purely electronic models [112, 113]. Both self-consistent Born approximation (SCBA) [114] and exact diagonalization [115] in t-t'-t"-J model capture the QP dispersion but yield a sharp nodal QP peak. DCA calculations without phonons [116] also exhibit a sharp nodal peak. We propose to investigate the temperature dependence of the QP linewidth when phonons are considered. Preliminary calculations based on SCBA indicate a strong broadening with increasing temperature even for moderate electron-phonon coupling [117]. This result would be of crucial importance for interpreting many of the experimental features observed in ARPES, such as the long controversy regarding the chemical potential shift upon doping [113].

Our preliminary results (Jarrell's group) suggests that the inclusion of EP coupling may significantly enhance the pairing interaction, but suppresses the superconductivity T_c due to the formation of polarons. We propose to investigate the T_c dependence in detail, both as a function of electron-phonon interaction and phonon frequency, for realistic for cuprates Breathing and Buckling modes. We intend to study the interplay of the phonon frequency and the antiferromagnetic exchange J since both these parameters define low energy scales and are of comparable magnitude in real systems. *Electron-Phonon coupling and Neutron Spectra of the Cuprates. As discussed above, neutron scattering has been an important probe of the phonon and spin dynamics of the cuprates. We recently modified our codes to calculate both the spin and phonon structure factors. We will calculate $S(k, \omega)$ of both spin and phonons, and study the softening of the phonon modes as the system is doped, as well as the change in the phonon dispersion and density of states. We will also calculate the phonon Debye-Waller factor. *Jarrell, Krakauer, Savrasov, Scalettar, Zhang*

We will calculate the phonon spectra to facilitate comparisons with neutron scattering experiments underway at the SNS and also determine the Raman, and ARPES spectra. Significant code improvements in the treatment of phonons via QMC will facilitate these studies.

*AFQMC calculations.***Does part of this belong here, with fleshing out of course.** The simplest form of the phaseless auxiliary-field method is the constrained path Monte Carlo (CPMC) approach, which exists in both ground-state [34] and finite-temperature [35] forms. This is applicable to "simpler" model systems such as the Periodic Anderson Model or the Holstein-Hubbard model. In parallel with our DCA and DMFT efforts, the CPMC method can be applied in the first stage to investigate phonons. For systems with more realistic interactions, our implementation of the phaseless AF QMC method with a general, localized basis allows us to efficiently model ground-state properties, using down-folded Hamiltonians, embedded cluster methods, or conventional periodic boundary conditions. In principle it remains straightforward to include lattice distortions and electron-phonon interactions in this framework. We have also formulated the basic idea for generalizing the phaseless approximation to finite temperatures, and plan to develop and implement it. **(connection with cluster impurity solver — need to discuss with Mark, Richard and others to see if there's interest and if connection is worth emphasizing)**

Downfolding Hamiltonians and Interfacing QMC codes with Electronic Structure (Jarrell, Krakauer, Ku, Savrasov, White, Zhang) At the beginning of the 2003 CMSN project, the DMFT/DCA codes using QMC solvers were able to simulate single-band models with local (Hubbard) interactions. In the past two years, we have developed multi-band, multi-orbital codes which are able to treat an arbitrary number of (downfolded) bands and a lesser number of correlated orbitals per site. These codes will now be integrated with the self-energy based electronic structure codes to study more realistic systems. The new AFQMC approach has a similar capability to provide input self-energies including electronic correlations into band structure codes. Our expertise in optimized Wannier functions and the first-principles derivation of effective Hamiltonians in reduced Hilbert space will facilitate this connection of QMC to density functional theory.

5.3.3 Computational Challenges.

6. Global Computational Issues and Challenges

We have discussed some of the computational challenges which will be involved in solving this CRT's "signature problem." Other, more general challenges arise in porting our methods and codes to other strongly correlated systems. We describe those issues, and our proposed resolution of them, here.

A. Building a common data format for QMC and DMFT codes. Taking our cue from electronic structure codes, we accept that there will always be a variety of DMFT codes. Because of that, and the desirability of being able on occasion to transfer data between codes, we are undertaking the task of standardizing this transfer of data. ...to be completed...

B. Ensuring the stochastic criterion for QMC simulations. It was noted some time ago[70] that even cleverly constructed QMC algorithms may encounter problems with stochasticity: the simulation may get stuck in some subregion of phase space for which the algorithm for making the MC moves does not provide a stochastic sampling of the space. In our recent all-electron LDA+DMFT(QMC) codes, this problem was encountered for a transition metal monoxide, where the flipping of a single electronic spin in a multielectron moment was found to be inhibited by the algorithm for MC updates. The preliminary fix, still undergoing testing at the time of writing this document, is to explicitly include such single-spin reversals on an intermittent basis. The point to be made here is that this project is addressing new problems with very little or no precedent (behavior of multielectron magnetic moments, and how they disintegrate as the interaction strength decreases). We expect to encounter ......

C. Developing criteria for the 'convergence' of QMC algorithms. Although powerful and indeed irreplaceable, QMC algorithms are notoriously computationally intensive and the results of necessity contain statistical noise. As a result, there is a crucial question of when the results are converged. The analogous situation has long been studied for electronic structure code, where the approach to convergence is not statistical but nevertheless not always easy to specify.

D. Numerical canonical transformation. Central to the NCT method is the use of symbolic representation of 2nd quantized operators that allow manipulation of the effective Hamiltonian without explicitly employing numerical Fock space that scales exponentially. In addition, this makes the method free from the finite site lattice effects common to the many-body calculations. Objects for representing and manipulating the "Hubbard X operators" will be encapsulated in C++ objects. The main computation effort appears to lie in sorting the operators into normal orders and in ordering terms (in a bi-tree) for fast addition of new contributions. Fortunately, almost all of these operations are perfectly parallelizable and thus will benefit greatly from distributed memory structure of modern supercomputers and clusters.

7. Sharing of Codes

To promote the use of our research by the research community, we have the goal of making the following capabilities available to knowledgeable users.

A. *Diffusion Monte Carlo with optimized wavefunctions.* The CHAMP suite (Cornell-Holland Ab-initio Materials Package) is already available for use *http://www.tc.cornell.edu/ cyrus/champ.html* and is already used by several electronic structure groups worldwide. Extensions will be made available as they pass the necessary tests.

B. *All-electron LDA+DMFT*. The basic codes are, in several respects, already in place, with the DMFT(QMC) code for solving the DMFT equations and calculating the real-frequency spectrum undergoing final testing. This code has been been constructed by Jan Kuneš, former PCSCS postdoc with Pickett and Scalettar. The underlying QMC code was taken from Krauth,[71] made publicly available when the early review of DMFT[71] was published. This code was speeded up and generalized to handle multiorbital systems.

The LDA underpinning will be provided by the IFW Dresden-conceived, constructed, and supported[72] code *Full Potential Local Orbital* (FPLO). The basis set consists of atomic orbitals; as such, the basis is physical and non-orthogonal. This latter feature requires the handling of an overlap matrix within the DMFT algorithm, which is presently undergoing debugging and testing.

The anticipated capabilities of the code include: (i) total electron number N(μ,T) given the chemical potential μ, or conversely $\mu(T)$ given N; (ii) local r.m.s. moment $\mathcal{M}$ and its orbitally decomposed components; (iii) real-frequency spectrum and its orbitally decomposed contributions, evaluated with MaxEnt algorithms; (iv) free energy $F(T)$.

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