

Quantum Impurity Models as Reference Systems for Strongly Correlated Materials: The Road from the Kondo Impurity Model to First Principles Electronic Structure Calculations with Dynamical Mean-Field Theory

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(Received September 2, 2004)

Dynamical mean field theory (DMFT) relates extended systems (bulk solids, surfaces and interfaces) to quantum impurity models (QIM) satisfying a self-consistency condition. This mapping provides an economic description of correlated electron materials. It is currently used in practical computations of physical properties of real materials. It has also great conceptual value, providing a simple picture of correlated electron phenomena on the lattice, using concepts derived from quantum impurity models such as the Kondo effect. DMFT can also be formulated as a first principles electronic structure method and is applicable to correlated materials.

KEYWORDS: quantum impurity models, correlated electrons systems, dynamical mean field theory, density functional theory, first principles electronic structure methods

DOI:10.1143/JPSJ.74.147

1. Introduction

Strongly correlated materials pose conceptual and computational challenges. To understand this class of materials and compute their properties, we need a starting point which goes beyond free fermions and includes in addition correlated local degrees of freedom, namely impurity models.

Quantum impurity models, have a rich history dating back to the Kondo effect, i.e., the increase in resistivity upon addition of a small amount of magnetic impurities to a metal.¹⁾ To explain this phenomena, Professor Kondo considered the simplest prototype of a quantum impurity model (QIM), the model that now bears his name. A general QIM model is defined by a few quantum mechanical degrees of freedom coupled to a continuum of extended states. In the Kondo model the spin of the impurity plays the role of the local degree of freedom, while the conduction electrons to which it is coupled by the exchange interaction plays the role of the extended states (bath of excitations).

The Kondo model and its extensions have had a tremendous impact in condensed matter theory. Generalizations to higher spins and different kinds of conduction electrons media have been constructed and studied. Mesoscopic electronic devices such as quantum dots offer new physical realizations, where the parameters of the QIM can be controlled to unprecedented accuracy. These topics and others will be covered in other articles in this volume. The focus of this paper is another far reaching application of quantum impurity models: QIM serve as the simplest *reference systems* to describe lattice models via the dynamical mean field theory (DMFT) mapping.^{2,3)}

This perspective has given new insights into the strong correlation problem in general,⁴⁾ and more specifically into

the localization delocalization transition or Mott–Hubbard transition problem. It is now being used to construct a first principles approach to the calculation of physical properties of strongly correlated electron systems.^{5–7)} In this contribution, honoring Professor Kondo, we highlight some aspects of the dynamical mean field framework. We focus on the conceptual clarity that comes from viewing a correlated problem in terms of its associated local impurity model. Generalized quantum impurity models, built around sites, links and plaquettes (clusters with two and four sites), not only help us compute physical quantities of correlated materials, but also allows to understand intuitively their physical properties.

In §2, we introduce correlated electron systems and some concepts of DMFT. Section 3 addresses an extension of DMFT ideas to a first-principles electronic structure method. In §4, we sketch our understanding of the Mott–Hubbard transition in terms of a QIM defined on a site (the Anderson impurity model⁸⁾ and its Kondo limit¹⁾). Section 5 describes the metal insulator transition in Titanium Sesquioxide and its description in using a two site (link) QIM as a reference frame.⁹⁾ Section 6 describes the idea of a non-uniform breakup of the Fermi surface, in terms of a four site (or plaquette) impurity model, a connection discovered recently.¹⁰⁾ We conclude by highlighting some quantitative successes in the field of actinides and pose some general questions in §7.

2. Weakly and Strongly Correlated Electrons Systems, Density Functional Theory (DFT) and Dynamical Mean Field Theory (DMFT): Self Consistent Quantum Impurity Models as Reference Frames

In the last century, we have achieved an accurate theory of weakly correlated materials such as simple metals, semi-conductors and band insulators. Landau Fermi liquid theory describes the electronic excitations of those materials over a

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broad range of energy and length scales, in terms of a system of free fermions in a periodic potential and their bound states or collective modes. Our understanding of the excitations in these systems results from their *correspondence with the states of a simpler systems, that we understand*. The correspondence between the states of an interacting system and those of a system of weakly interacting Fermions that we can solve perturbatively provides the conceptual justification for thinking of a solid as a collection of free Bloch electrons in a periodic potential, and underlies the success of the “Standard Model” of solid state physics.

The second pillar, supporting our understanding of weakly correlated materials, is the density functional theory (DFT).¹¹⁾ In this approach the total energy and the charge density of the solid is obtained as a minimum of a density functional. Extremizing this functional gives rise to the Kohn–Sham equations which have the form of a single particle Schrödinger equation in a self consistent potential.

$$[-\nabla^2 + V_{\text{KS}}(\mathbf{r})[\rho]]\psi_{\mathbf{k}j}(\mathbf{r}) = \epsilon_{\mathbf{k}j}\psi_{\mathbf{k}j}(\mathbf{r}), \quad (1)$$

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}j} f_{\mathbf{k}j}\psi_{\mathbf{k}j}^*(\mathbf{r})\psi_{\mathbf{k}j}(\mathbf{r}). \quad (2)$$

$$V_{\text{KS}}[\rho] = V_{\text{crystal}} + V[\rho] \quad (3)$$

The first two equations *defines* the notion of the Kohn–Sham potential. It is the one body potential that added to the Laplacian produces a one particle Hamiltonian whose ground state density equals the the density ρ of the original physical Hamiltonian. $V[\rho]$ is a universal functional, the same for all solids.

While the functional form of $V[\rho]$ is not known explicitly, we have very good practical approximations of it, for example the celebrated local density approximation or LDA.¹¹⁾ The density functional theory gives us an adiabatic connection, a conceptual bridge, between the state of a system of fictitious non interacting particles with eigenenergies $\epsilon_{\mathbf{k}j}$, and the full many body Hamiltonian. While the Kohn–Sham spectra and the Kohn–Sham states cannot be interpreted as the spectrum for adding and removing a particle in the true interacting system (formally their only role is to give us a representation of the exact density in terms of the density of free particles), it turns out that in weakly correlated materials they are a good zeroth order approximation to the true excitation spectrum. Namely, the Kohn–Sham Green’s function is an excellent starting point for the computation of the single particle spectra and the optical conductivity in perturbation theory in the *screened* Coulomb interaction. The first order approximation is known as the GW method.¹²⁾

The success of this approach is due to the fact that the experimental spectra of many weakly correlated materials is close to the Kohn–Sham spectra. Hence the LDA+GW program provides a perturbative realization of Landau–Fermi-liquid ideas. In fact we can take this criteria as an operational *definition* of weakly and strongly correlated materials. Weakly correlated materials, are those for which the LDA+GW program offers a good description of their physical properties, while this construction fails for strongly correlated materials.

The physical properties of strongly correlated electron systems cannot be described, in a broad range of energies, in

terms of Fermi liquid theory and cannot be computed perturbatively in an expansion in the screened Coulomb interactions. Typically the spectra of strongly correlated materials do not remotely resemble the spectra of the corresponding Kohn–Sham system. Instead they contain excitations that resemble the excitations of open shell atoms broadened by the periodicity of the solid. These states have no analog in the Kohn–Sham theory, and require a non perturbative description, where the starting point has the correct atomic physics built in from the start.

Correlated electrons display a bewildering array of anomalies that cannot be accounted within the standard model of solid state physics. Their properties cannot be described in terms of rigid bands. These materials sometimes exhibit metallic resistivities that exceed the Mott–Ioffe–Regel limit (maximum metallic resistivity determined by the condition that the mean free path equals the wavelength of the electron), and display highly non local transfer of spectral weights in their photoemission and optical spectra as control parameters are varied. They easily become inhomogeneous under very small perturbations such as the introduction of disorder. They have very large linear and non linear responses. In simple terms, they do “big things”, such as high temperature superconductivity, giant volume collapses, colossal magnetoresistance, ultrafast non linear optical responses, gigantic thermoelectric powers and Kerr rotation angles. Surely, other useful and spectacular phenomena are going to be found among the myriad of ternary and quaternary compounds containing correlated materials.⁴⁾

The treatment of strongly correlated electron systems, requires a method, which unlike band theory, can also use atomic states as reference systems. The method has to be able to treat real space and momentum space, Hubbard bands, and quasiparticle bands, on the same footing. DMFT is the simplest framework satisfying these requirements. It can be viewed as a generalization of the Kohn–Sham theory to treat the physics of correlated electron systems.⁶⁾

The DMFT construction reduces the quantum many body problem to the evaluation of a quantum impurity model describing its atomic degrees of freedom in a dynamic bath which obeys a self consistency condition. This self consistent QIM is a simpler system which is used to understand and compute the properties of correlated materials, in analogy to the DFT reduction of the full many body problem to the Kohn–Sham system of particles in a static mean field potential.

A central object in the DMFT approach is the local Greens function. The concept of locality should be understood as a restriction to a finite region in space. This could be just a unit cell, or a cluster of cells, which formally can be treated on the same footing in the cellular DMFT approach or CDMFT.¹³⁾ Working in a tight binding basis, the local Greens function is written as:

$$-\langle T[c_\alpha(\tau)c_\beta^\dagger(\tau')] \rangle = G_{\text{loc},\alpha\beta}(\tau, \tau') \quad (4)$$

The indices $\alpha\beta$ are spin, orbital or cluster indices if a supercell notation is used. We start from a non interacting electron system in k space, defined by an overlap matrix and a Hamiltonian matrix $\hat{O}(\mathbf{k})$ and $\hat{h}^{(0)}(\mathbf{k})$. We then define an exact frequency dependent quantity, i.e., a “local self energy” $\mathcal{M}_{\text{int}}(i\omega)$, as the *local or k independent* function

such that added to the non interacting Greens function reproduces the exact local Greens function of the system. This resembles the same way the exact Kohn–Sham potential reproduces the exact density of the solid:

$$G_{\text{loc},\alpha\beta}(i\omega) = \sum_{\mathbf{k}} [(i\omega + \mu)\hat{O}(\mathbf{k}) - \hat{h}^{(0)}(\mathbf{k}) - \mathcal{M}_{\text{int}}(i\omega)]_{\alpha\beta}^{-1}, \quad (5)$$

$\mathcal{M}_{\text{int}}(i\omega)$ is a local quantity. To get a closed system of equations for it, requires a functional relation relating it to G_{loc} . This can be obtained from a quantum impurity model. From the QIM, we can derive an “exchange and correlation functional” $\Phi_{\text{xc}}[G_{\text{loc}}]$ ^{6,14)}

$$\mathcal{M}_{\text{int}}(i\omega)[G_{\text{loc},\alpha\beta}] = \frac{\delta\Phi_{\text{xc}}[G_{\text{loc}}]}{\delta G_{\text{loc}}} \quad (6)$$

which is akin to eq. (3) in density functional theory.

One can arrive at the DMFT approach by taking the atom, rather than the band as a reference system. This highlights the power and flexibility of the DMFT approach, and the concept of the DMFT “Weiss field”. Now we imagine focusing on one atom or a cluster of several atoms and the rest of the atoms act as the bath of the QIM, mathematically described by a Hybridization function $\Delta_{\alpha,\beta}(i\omega)$. The exact Weiss field, which when added the atomic degrees of freedom, reproduces the exact spectral function of the solid.

$$-\left\langle T[c_{\alpha}(\tau)c_{\beta}^{+}(\tau')] \right\rangle_{\Delta} = G_{\text{loc},\alpha\beta}(\tau, \tau'). \quad (7)$$

H_{at} is the Hamiltonian of the atom, and the average $\langle \dots \rangle$ is taken with respect to the QIM action:

$$S[\Delta] = \int d\tau d\tau' \sum_{\alpha\beta} c_{\alpha}^{+}(\tau) \left[\delta(\tau - \tau') \frac{\partial}{\partial \tau'} + \Delta_{\alpha\beta}(\tau, \tau') \right] c_{\beta}(\tau') + \int d\tau H_{\text{at}}(\tau), \quad (8)$$

An equation relating the exact Weiss field to the local Greens function, $\Delta = \Delta(G_{\text{loc}})$ and to the lattice structure constant offers an alternative formulation of the DMFT equations.

The dynamical mean field construction, mapping lattice models onto impurity models was originally designed to provide a solution to lattice models in the limit of infinite dimensions.¹⁵⁾ It is then very reassuring that with a cluster of two sites, DMFT produces very accurate results for static quantities in one dimension,¹⁶⁾ which is exactly soluble by the Bethe ansatz.

Finally, ab initio methods such as DFT and constrained DFT can be used to derive the on site Coulomb interactions and the hopping elements of a given material. DMFT can then be used for the solution of the model Hamiltonian. This approach has been applied to many d and f electron systems.^{5,7)}

3. Realistic DMFT

The ultimate goal of a theory of strongly correlated electron systems would be to achieve the same level of conceptual understanding, and predictive capabilities that we have for weakly correlated materials. In this section we discuss further ideas that promise to turn DMFT into a truly first principles method, that can be used to carry out controlled approximations of material properties. There are

situations where a first principles approach is absolutely necessary. For example, when we need to compute the total energy of the system or when it is not clear a priori what are the active degrees of freedom at a given energy scale and what is the value of the interaction strength parameters of the problem.

To apply Dynamical Mean Field Theory in this instance,^{18,19)} one rewrites the full many body problem in terms of a free electron system interacting with a Bose field describing the dynamics of the screened Coulomb interactions. One then defines the Greens function of the Bose field $W(x, x') = -\langle T\phi(x)\phi(x') \rangle$ and of the electrons $G(x, x')$, and writes down the Baym Kadanoff functional in terms of those fields.^{18,19)}

$$\Gamma_{\text{BK}}[G, W, \Sigma, \Pi] = -\text{Tr} \ln [G_0^{-1} - \Sigma] - \text{Tr}[\Sigma G] + \frac{1}{2} \text{Tr} \ln [v_{\text{C}}^{-1} - \Pi] + \frac{1}{2} \text{Tr}[\Pi W] + E_{\text{Hartree}} + \Phi_{\text{BK}}[G, W] \quad (9)$$

Φ_{BK} is defined as the sum of all two particle irreducible diagrams containing Bose and Fermi propagators, with the exclusion of the Hartree term. DMFT suggest a natural approximation to this functional by *truncation* of Φ_{BK} to include only *local* diagrams.¹⁹⁾ Different definitions of locality are available, including one which is independent of the choice of basis set.⁶⁾ The approach is *systematic* because the truncation the size of the supercell defining the concept of locality (as in the CDMFT approach) can be increased to improve the approximation.

This approximation results in a self consistent set of equations for the local Greens functions of the Fermi and Bose fields, which can in turn be formulated in terms of a QIM^{6,19)} once a basis set is prescribed. The algorithm delivers the local part of the Greens function, G_{loc} , and the local part of W , W_{loc} , providing a rigorous definition of frequency dependent local interaction once a basis set is introduced.⁶⁾ After the solution of this self consistent QIM model for the local Greens functions and self energies, non local corrections can be included perturbatively and we expect that the local spectral spectral functional provides a good starting point for the computation of the full self energy of correlated materials in the same way that the DFT provides a good starting point for the computation of the self energy in weakly correlated materials. This general program, has been fully implemented in a model Hamiltonian context.²⁰⁾ For related ideas on combining DMFT with GW and a partial implementations for an itinerant magnet, Ni, see ref. 22.

It is illuminating to examine earlier approaches to the combination of band theory and DMFT in the light of the functional approach described in this section. It is traditional to divide the electronic orbitals into two sets, light (L) and heavy (H). Only the the self energy of the heavy electrons is expected to be strongly frequency dependent suggesting the substitution: $\Sigma(r, r')(\omega) \approx V[\rho(r)]\delta(r - r') + \sum_{\mathbf{R},\alpha,\beta} \Sigma_{\alpha,\beta\mathbf{R}}(\omega)\Phi_{\mathbf{R}\alpha}(r)\Phi_{\mathbf{R}\beta}(r')$ into the functional (9). The rationale for that approximation, is that the self energy effects on the light electrons is approximated by a static exchange and correlation potential, and the frequency dependence of self energy of the heavy electrons is taken into account $\Sigma_{\alpha,\beta}(\omega)$ is extracted from an self consistent QIM and a

double counting correction is added to it to compensate for the exchange and correlation of the heavy orbitals already contained in the exchange correlation potential. $\Phi_{R\alpha}(r)$ are orbitals describing the heavy electron sector. For consistency W is taken to be non zero in the H sector only. It is important to stress that the quality of this approximation can be improved by enlarging the basis set describing the H sector. One further approximation consists of replacing the frequency dependent W by a static Hubbard U . With all these replacements, (9) becomes functional of the density and the local Greens function with the Hubbard matrix of local parameter which can be estimated from constrained DFT calculations or empirical data. This functional²¹⁾ has been successfully applied to the investigation of electronic and elastic properties of Plutonium. If the self consistency in the charge density is ignored, i.e., $V[\rho] \approx V[\rho_{\text{LDA}}]$ we recover the LDA+DMFT scheme suggested earlier.⁵⁾ This simplified approach can already reproduce the experimental spectra of a large number of correlated oxides.⁷⁾

Finally we mention that a spectral density functional can also be viewed as an exact theory,⁶⁾ by introducing an exact functional of the local W and G whose extremum yields the total energy of the solid. The DMFT functional is then viewed as a practical approximation to the exact spectral density functional, in the same spirit as the LDA functional approximates the exact density functional when one carries out applications to weakly correlated materials.

4. Temperature Driven Mott–Hubbard Transition: Single Site DMFT Study of the Frustrated Hubbard Model at Integer Filling

The early applications of (single site) DMFT to the frustrated Hubbard resulted in new insights into correlated electron materials.³⁾ It was found that in the strongly correlated metallic regime, both quasiparticle features and Hubbard bands are present in the spectra.²⁾ This conclusion was independently drawn from experimental observations by Fujimori.²³⁾ The evolution of the spectral function at zero temperature was elucidated afterwards. Within single site DMFT, the Mott transition takes place via the transfer of spectral weight from low to high energies.¹⁷⁾ The schematic phase diagram of the partially frustrated model, sketched after ref. 24, is drawn in Fig. 1. At low temperatures, there is some form of long range order. It depends in a very sensitive way on the details of the Hamiltonian. On the other hand, at high temperatures, the behavior in the normal state is more universal, and it is shared among many different materials. This universality²⁶⁾ justifies the applicability of single site DMFT to very simple models, such as the Hubbard model (with on site interaction U and hopping and bandwidth W), in the regime of the high temperature paramagnetic metal paramagnetic insulator transition, as long as the model is sufficiently frustrated.

Because of its simplicity and universality, the phase diagram in Fig. 1 is very instructive and provides considerable intuition into the behavior of many materials. It has a Fermi liquid regime at small U (corresponding to a QIM below the Kondo temperature) and a paramagnetic Mott insulating regime at large U (corresponding to a Kondo spin in an insulating bath). Two crossover lines, and the spinodal lines U_{c1} and U_{c2} intersect at a critical endpoint. The first

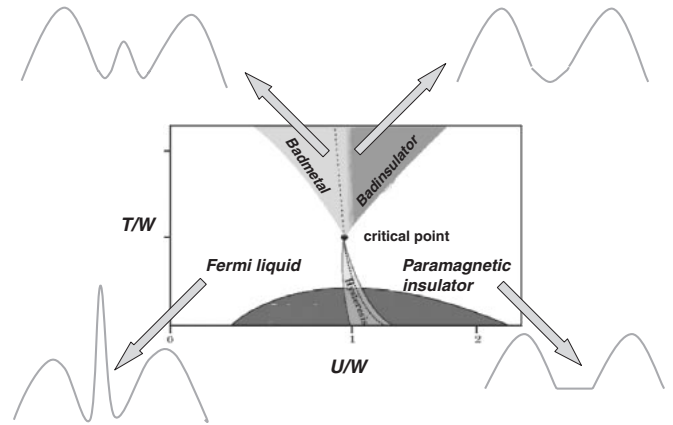


Fig. 1. Qualitative phase diagram (temperature T vs Coulomb repulsion U , in units of the bandwidth W of a partially frustrated Hubbard model at integer filling sketched after ref. 24. Above the ordered phase in red, there are four regions, a Fermi liquid, a bad metal, a bad insulator and a Mott insulator. One can interpret each regime in terms of the spectral function of the corresponding QIM, also sketched in the figure. The central peak, present in the Fermi liquid regime, is the Kondo resonance of the Anderson impurity model.

crossover regime occurs due loss of coherence, the Fermi liquid state then evolves into a bad metal (described by a Kondo impurity above its Kondo temperature). The second cross over takes place as thermal excitations rapidly smear the Mott–Hubbard gap leading to a bad insulator.²⁴⁾

The evolution of the electronic structure within DMFT made definite experimental predictions, such as a temperature and pressure driven transfer of spectral weight. This was observed in optical and photoemission spectroscopies. The DMFT phase diagram is consistent with many transport experiments. More system specific calculations, and more detailed experiments have recently provided more evidence supporting the validity of the qualitative DMFT picture as for example in ref. 25.

Besides the successes in accounting for considerable experimental data in many materials, the studies of the Mott phenomena in single site DMFT provide us with a new paradigm for thinking about strongly correlated electron materials. It is clear from both theory and experiment, that correlated materials at zero temperature have a complicated landscape which is very sensitive to chemical and structural details which require detailed modeling. The various minima in Fig. 2, can be studied by applying CDMFT on unit cells which are large enough to describe the relevant broken symmetry. On the other hand, the short distance (high temperature) properties of these materials, can be captured by a local approach, describing an effectively homogenous situation, which explores all the phase space above the various zero temperature minima, as sketched in Fig. 2.

The study of the Mott transition also highlights the difficulties that standard renormalization group approaches face, when dealing with strongly correlated materials. This is caused by the rapid changes in the nature of the relevant degrees of freedom as we vary parameters. The relevant low energy local degrees of freedom, at a given scale, on the other hand, appear naturally once we adopt a framework based on self consistent quantum impurity models.

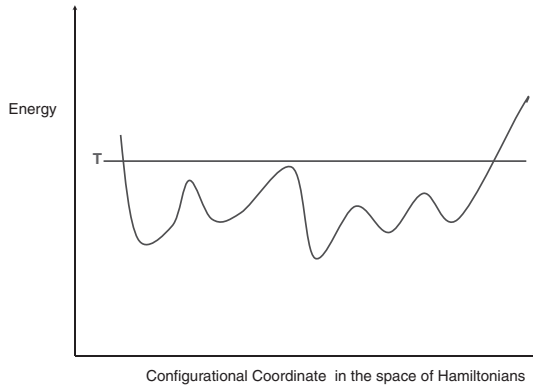


Fig. 2. Schematic view of the DMFT phase diagram of a the energy landscape of a strongly correlated material. The various minima, describe different states (e.g., characterized by different forms of long range order, superconducting, magnetic, stripes), that are captured by different DMFT solutions. This results in great sensitivity to microscopic detail at low temperatures. At high temperatures, the system averages thermally over various minima, and this state can be described in terms of a QIM.

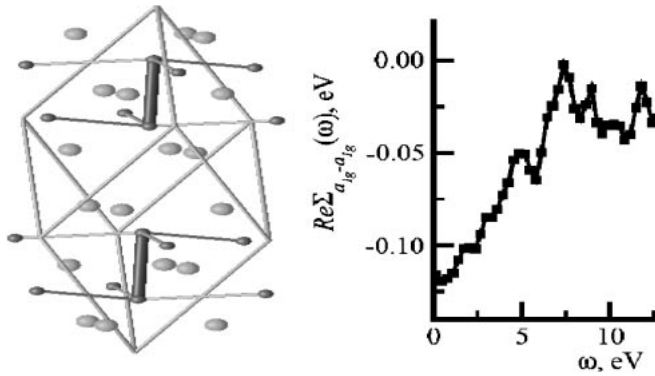


Fig. 3. Structure of Ti_2O_3 (right) highlighting the pair of Titanium atoms as a motif (left), frequency dependence of the self energy connecting the orbitals of the pair that point towards each other from the work of Poteryaev *et al.*⁹⁾ (right).

5. Titanium Sesquioxide, Links as Reference Frame

Titanium sesquioxide, Ti_2O_3 , is isostructural to vanadium sesquioxide, V_2O_3 , the prototypical Mott–Hubbard system. In the corundum structure the pair of titanium atoms form a structural motif which is displayed in Fig. 3. Titanium sesquioxide displays a rapid crossover from a bad metal regime at high temperatures, to an insulating regime at low temperatures. Standard first principles electronic structure methods have failed to account for this crossover.⁹⁾

Single site DMFT cannot account for the observed temperature driven crossover in Ti_2O_3 with a reasonable set of parameters. On the other hand, a cluster CDMFT calculation with a very reasonable set of onsite interactions and an intersite Coulomb repulsion successfully describes the observed crossover.⁹⁾ A surprising result of the cluster calculations,⁹⁾ is the strong frequency dependence of the intersite Titanium self energy displayed in Fig. 3. The real part of this self energy can be interpret as a scale dependent modification of the bare bonding antibonding splitting: $t_{a1g,a1g}^{eff}(\omega) = \text{Re } \Sigma_{a1g,a1g}(\omega) + t_{a1g,a1g}^{bare}$.

The link reference frame provides a simple intuitive picture of the synergistic interplay of the lattice distortion

Peierls–Pauling–Goodenough mechanism²⁷⁾ (which decreases the distance between the Ti atoms) and the Hubbard–Mott mechanism, in correlated materials having dimers in the unit cell. The bare (high frequency) parameters of the problem are such, that a static mean field calculation yields a metal. However as temperature and frequency are lowered, important correlation effects develop. The bandwidth of the $a1g$ and eg bands is reduced by the correlations while the crystal field splitting between the bonding and the antibonding orbital increases in such a way that the low energy renormalized parameters, result in a band insulator.

What is the origin of the strong frequency dependence of the bonding antibonding splitting? One possibility is the Coulomb interactions induced enhancement of the hybridization characteristic of an Anderson impurity model.²⁸⁾ Another possibility is the intersite magnetic interactions and the proximity to a two impurity transition of the kind first discussed by Varma and Jones.²⁹⁾ Both mechanisms require a link as a reference frame for their description, as indicated in Fig. 3. It would be interesting to study other systems, to explore the interplay of electronic and lattice distortions.

6. Kappa Organics and High Temperature Superconductors: The Plaquette as a Reference Frame

The kappa organics is a family of quasi-two dimensional compounds. A crude model for these materials is a Hubbard model with first neighbor hopping and very anisotropic second neighbor hops (see Fig. 4). One member of this family κ -(BEDT-TTF)₂X undergoes a finite temperature Mott transition³⁰⁾.

This experiment motivated a recent theoretical CDMFT study¹⁰⁾ using the plaquette as a reference frame. Far from the Mott transition, the results of the earlier single site DMFT studies are not substantially modified. However, as the transition is approached, new physics emerges: the Mott–Hubbard gap opens in a very anisotropic fashion. The phenomena of momentum space differentiation and partial destruction of the Fermi surface takes place as the Mott transition is approached as illustrated in Fig. 4 from ref. 10. The figure displays the distribution of low energy spectral weight in the Brillouin zone for two values of the on site interaction U . Far from the transition, the contour plots of this quantity follows the non interacting Fermi surface of the material, consistent with the single site DMFT description. However as the interaction strength increases towards the Mott transition, the quasiparticles along the zone diagonals survive as low energy excitations, whereas the quasiparticles along $(0, \pi)$ are gapped.

The mapping onto impurity models, with its limited number of degrees of freedom offer new insights into this phenomena. The main actor responsible for this phenomena is the next nearest neighbor self energy. This quantity grows and develops a large imaginary part, as the Mott transition is approached. Since cluster and lattices self energies are related by:¹³⁾

$$\begin{aligned} \Sigma_{latt}(k) = & \frac{1}{4} \sum_{i=1}^4 \Sigma_{ii} + \frac{1}{2} [(\Sigma_{12} + \Sigma_{34}) \cos(k_x) \\ & + (\Sigma_{24} + \Sigma_{13}) \cos(k_y) \\ & + \Sigma_{14} \cos(k_x + k_y) + \Sigma_{23} \cos(k_x - k_y)] \end{aligned} \quad (10)$$

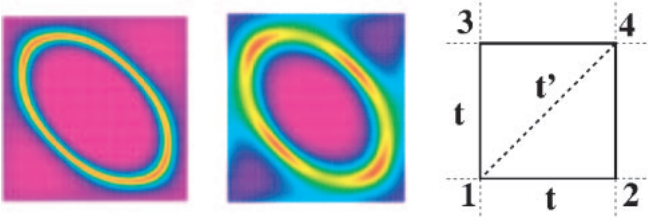


Fig. 4. Left: Distribution of low energy spectral weight in k -space, [$A(k, \omega = 0)$, for $T/D = 1/44$, $U/D = 2.0$ (left panel) and $U/D = 2.25$ (middle panel)], which is close to the Mott transition, indicating the non uniform breakup of the Fermi surface from ref. 10. Red indicates a high intensity, blue indicates a low intensity. Right: hoppings within the unit cell used to model the kappa organics. CDMFT with the above plaquette used to extract the cluster self energies needed to form the lattice self energy.

the effect of Σ_{13} is not visible around the node at $(\pi/2, \pi/2)$ and its maximal in the $(0, \pi)$ region.

The copper oxide materials which exhibit high temperature superconductivity, are a second class of materials for which the plaquette appears as a natural reference frame. Early work using the slave boson method, can now be extended using the modern CDMFT perspective. The application of this technique to the t - J Hamiltonian, successfully predicted the symmetry of the order parameter³²⁾ and the presence of a pseudogap near half filling. This approach substantiates the idea of a connection between the Mott insulating state, and the superconductor.³¹⁾ High temperature superconductivity is an unavoidable consequence of the approach to a Mott insulating state without breaking any additional spatial or spin symmetries since from all the degenerate forms of singlet pairing at half filling, doping selects the d wave superconducting state.³²⁾ Several difficulties of carrying out non perturbative fluctuations around the slave boson mean field hindered the development of this approach. The modern CDMFT offers many conceptual and computational advantages over the slave boson mean field theory method, which now can be viewed as an approximate static limit of CDMFT, eliminating many of its shortcomings.

In CDMFT, we can investigate the normal state underlying the superconducting state by forcing the Weiss field to remain in the normal phase. Then one can proceed to study how the approach to the Mott transition affects this normal state.

Recently, a zero temperature approach to the solution of the CDMFT equations based on exact diagonalization was developed³³⁾ and applied to the study of an isotropic Hubbard model with nearest and next nearest neighbors hopping (t and t') in two dimensions.³³⁾ The distribution of the low energy spectral weight at two different doping levels is illustrated in Fig. 5.

This study provides further evidence that the non uniform breakup of the Fermi surface is an unavoidable consequence of the approach to the Mott insulating state.¹⁰⁾ The location of the low spectral intensity (hot) and high spectral intensity (cold) regions in the Brillouin zone, depends on the details of the Hamiltonian and indeed different values of t'/t , U/t , and doping produce different patterns of low energy spectral intensity³³⁾ as illustrated in Fig. 5.

The investigation of the normal state underlying the superconducting state near the Mott transitions gives valuable physical insights into why the phase diagram of hole doped cuprate materials are so different from their electron doped counterparts. Hole doped cuprates exhibit superconductivity at very small doping values while electron doped cuprates do not. In the hole doped material there is a wide pseudogap region above the superconducting phase. There is a continuous evolution of the gap in physical observables from the pseudogap to the superconducting phase. This behavior is not seen in the electron doped materials.

It is suggestive to relate the left panel of Fig. 5 with the normal state phase the electron doped cuprates and the right hand panel with the hole doped cuprates. We see that the underlying normal state of this materials locates its Fermionic quasiparticles in different locations of the Brillouin zone [at $(0, \pi)$ in the electron doped and at $(\pi/2, \pi, 2)$ in the hole doped materials]. A related observation, for a different values of the parameters of the Hubbard model, was made earlier by S en echal and Tremblay, and

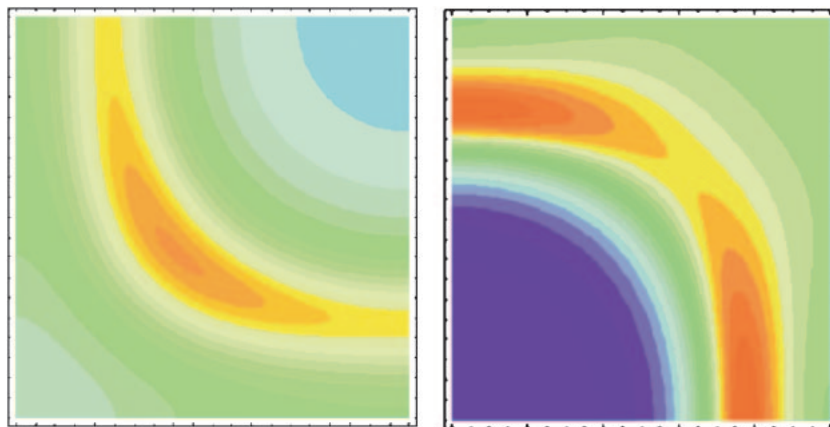


Fig. 5. Distribution of low energy spectral weight in k -space at low temperatures for a Hubbard model with nearest and next nearest neighbor hoppings at density $n = 0.95$ (red denotes high intensity, blue denotes low intensity) for $U = 16$, $t = 1$ and $t' = 0.9$ (right panel) and $t = 1$, $t' = -0.3$ and density 0.95 (left panel).³³⁾ The nonuniform breakup of the Fermi surface as the Mott transition is a general phenomena, but the location of the gapped regions and the surviving quasiparticles strongly depends on model parameters.

their collaborators.³⁴⁾

Hence, in the hole doped case, the quasiparticles of the normal state occur in the same place as the superconducting quasiparticles. This explains the continuous evolution from the anomalous pseudogapped normal state into the superconducting state. In the electron doped case, it is not possible to think about the superconducting state as a continuation of an underlying normal state close to the Mott insulator because the quasiparticles are located in different regions of the Brillouin zone. To reach the superconducting state, in this case requires a large value of doping.

7. Conclusion, Open Questions

Will we be as successful in our attempts to understand and predict the physical properties of correlated materials as we have been for weakly correlated systems using density functional theory and GW methods? As we approach correlated problems from top to bottom starting from high temperatures will CDMFT prove to be rapidly convergent in the relevant temperature regime? Will we succeed in getting the desired momentum resolution using a small number of patches in momentum space chosen in an adaptive manner, corresponding to a small finite size cluster embedded in an optimal medium?

These are very open questions, but there are already several hints pointing to the promise of this strategy. On the quantitative side, recent DMFT predictions for delta Plutonium, a material at the verge of a localization delocalization instability which falls outside the reach of conventional solid state approaches, have been verified experimentally. Comparison of theoretical predictions for the phonon spectrum³⁵⁾ of δ -Pu, and a comparison with subsequent experiments³⁶⁾ are shown in Fig. 6. This material posed a significant challenge to conventional solid state methods. Good agreement over most of the Brillouin zone was achieved using a decoupling scheme to solve the QIM. There is however a noticeable discrepancy around the (111) zone boundary, as shown in Fig. 6. What is the origin of this discrepancy? Is it due to the Kondo Resonance which has been left out of the calculations or due to intrasite effects that require going beyond single site DMFT? Further DMFT studies should be able to clarify this issue. By decomposing the total energy in

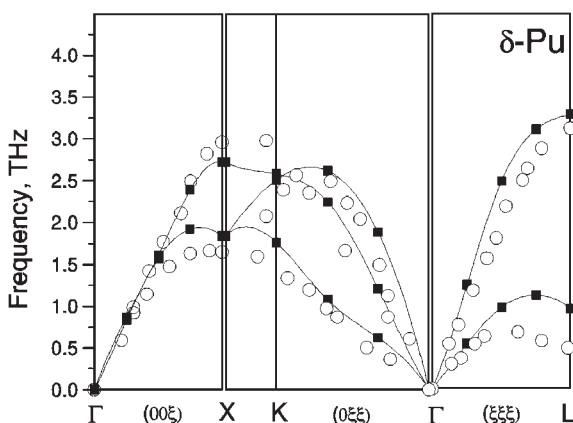


Fig. 6. Comparison of DMFT predictions of the phonon spectrum (solid symbols) in δ -Pu from³⁵⁾ with the results of inelastic X-ray scattering measurements (open symbols) from ref. 36.

contributions from different energy scales and organizing the calculation in a sequence of cluster approximations, we can gain new understanding, into the origin of the bonding in solids.

On the qualitative side, numerous predictions of the evolution of the spectral function, and the transport, in the bad metal and the bad insulator regime, are born out by experiments. These regimes, which could not be accessed with other techniques, is captured using QIM as reference frames. An outstanding task is to simplify the solutions of the DMFT equations, in order to understand these regimes with more analytic methods. Finally, DMFT treats exactly low and high energy degrees of freedom which are local. The combination of this approach with the more traditional renormalization group approaches to incorporate low energy long wavelength modes is an important direction for future research.

These directions are only beginning to be explored, yet it is already clear, that the introduction of the DMFT framework have brought an unexpected and successful use of QIM. Self consistent QIM serve as a reference frames to think and compute the physical properties of complex materials. We are not far from the point where we will be able to focus our intellectual efforts on *deviations* between experimental observations and DMFT results.

Acknowledgements

It is a pleasure to thank G. Biroli, M Capone, M. Civelli, R. Chitra, X. Dai, K. Haule, A. Georges, V. Kancharla, A. Lichtenstein, S. Murthy, C. Marianetti, G. Palsson, O. Parcollet, S. Pankov, A. Poteryaev, S. Savrasov, P. Sun, V. Oudovenko and N. Zein for fruitful collaborations on the subject of clusters and realistic extensions of DMFT. I am very grateful to E. Abrahams, P. Coleman V. Oudovenko and C. Marianetti for thoughtful comments on the content and help with the preparation of this manuscript. We acknowledge the support of the National Science Foundation, the Department of Energy and the Office of Naval Research.

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