# 1 Electronic Structure Computation Meets Strong Correlation: Guiding Principles

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# 1 Introduction

# 1.1 Read this first!

Before reading the rest of this chapter, please read the following questions, formulate your answers (or at least your approach to answering them) and think about the relation to the topics of this school. After the school check if you think that your understanding has evolved.

- What does the term correlation mean? The general definition in statistics and the definition(s) used in the fields that are the topics of this school.
- What does "strong correlation" mean? "Strong" relative to what? Do we always have to specify the context in order for the term meaningful?
- What are signatures of correlation? What are the types of experimental information from which we may conclude that a material is strongly correlated. What theoretical findings indicate strong correlation?
- What are examples of materials and phenomena that are often called "strongly correlated" in present-day condensed matter physics? What are the reasons for this designation? Why should we care enough for individuals and groups around the world to devote countless hours and resources for decades?
- Van der Waals interactions are due purely to correlated fluctuations between electrons on different atoms or molecules that are weakly coupled. Is this an example of strong correlations?
- What is a "Mott insulator"? What is the Luttinger theorem and to what extent is it an actual theorem?

The purpose of this lecture is to set the tone that interacting, correlated electrons present some of the most difficult challenges in physics. There are no exact solutions except for very few special models; yet there are powerful techniques that are being applied to complex problems. Each method involves approximations and assumptions that may be forgotten or brushed aside when they are applied. This is a perfect example of a field where one should examine critically every aspect of the theory and the methods for calculations.

Modern electronic structure methods successfully determine ground state structures, phonon frequencies, and many other properties to within a few percent for large classes of materials, and they are improving with new ideas, methods, and experience. Yet they may fail miserably to account for some other properties. As calculations become more and more powerful, it is more and more important to formulate the problem clearly and judge what aspects of the results are meaningful. We need fundamental guiding principles to recognize how to use the results to draw well-justified, useful conclusions. In this endeavor, I will give some of my pet principles and examples,<sup>1</sup> and warnings about the care needed to apply them. These are only examples and *you must identify for yourself what is needed in your research*!

<sup>&</sup>lt;sup>1</sup>Many of the ideas and examples in this chapter are taken from [1], with some added comments. Many additional references are given there.

#### **1.2** Strong correlation: What do we mean? What is the evidence?

Since our goal is to develop theories of materials with strong correlation, we should define carefully what is meant by terms like "correlation" and "strong," and what are the experimental signatures. The standard definition of correlation for fermions is anything beyond Hartree-Fock. However, this is not sufficient for present purposes: Correlation is crucial for *all* materials with more than one electron. The correlation energy is a large part of the total energy that determines structures of materials and related properties. Correlation is even more important for excitations: Hartree-Fock leads to band gaps in insulators much greater than experiment and it is completely wrong for the properties of *any* metal because it leads to a singularity at the Fermi energy due to the long-range Coulomb interaction. Any useful theory of excitations must involve a screened interaction which removes the singularity at the Fermi surface. Screening is one aspect of correlation, and it is one of the successes of the RPA and GW approximations considered below. A model with short-range interactions that is proposed to apply to a real material has some assumption, perhaps hidden, of why a short range interaction is appropriate. In short, correlation *must* be included for a reasonable theory in any material, whether it is metallic Na or Ce, insulating NaCl or NiO.

In addition, the definitions depend upon whether one considers *restricted* or *unrestricted* Hartree-Fock. Often there is a broken symmetry solution that lowers the total energy and captures a large part of the correlation energy. In this case, the question is whether or not the broken symmetry is physically reasonable and how to use such a solution even if there is no such broken symmetry. This brings us immediately to issues of broken symmetry, phase transitions, and order parameters.

For many problems correlation is largest at short range, and the approach is to identify some reduced degrees of freedom on each site that already takes into account local on-site correlation. *The key is that there is a degeneracy or near-degeneracy of the local states, e.g., a spin, weakly coupled to the rest of the system. Then the issues have to do with two aspects of correlation, on each site and between the different sites.* This is the type of problem addressed in this chapter and each example involves identifying some set of local degrees of freedom.<sup>2</sup> The typical systems involved are transition elements with localized atomic-like *d* and *f* states illustrated in Fig. 1, which is a rearrangement of the rows of transition elements so that the most localized orbitals are at the upper right and the most extended at the lower left. This provides an intuitive picture of the progression from band-like metallic superconductors colored blue to magnetic systems with localized moments involving 4*f* states colored red. Many of the most interesting elemental solids and compounds contain elements at the boundary where there is the greatest competition between interactions and independent-particle terms.

<sup>&</sup>lt;sup>2</sup>There are other cases such as the fractional quantum Hall effect, where the single-particle kinetic energy is zero and the interaction is the dominant effect.



**Fig. 1:** Rearranged periodic table of the transition elements showing the trend from delocalized orbitals for elements at the lower left indicated by the blue color to the most localized at the upper right colored red. At the boundary are the elements that exhibit anomalous properties. In compounds the occupation of d or f orbitals may vary, for example, the extraordinary properties of the copper oxides where the Cu 3d states are near the boundary. (Similar to figure in [2], originally due to J.L. Smith.)

### **1.3** Experimental signatures

So what is the driving force to identity "strongly correlated" materials and what do we want to determine? A general classification of properties of condensed matter is the division between ground state and excitations, where each can reveal essential aspects of correlation. Of course, the qualitative nature of the excitations is determined by the symmetry of the ground state, for example, a gap in an *s*-wave superconductor, or the magnon dispersion in a magnetic system. This is crucial for understanding but we also want more quantitative information. Consider the example of a high-temperature *d*-wave superconductor which is certainly often called "strongly correlated." However, it was shown by Kohn and Luttinger [3] many years ago that perturbation theory predicts that, due to repulsive electron-electron interactions, the Fermi liquid state of any metal is unstable to a superconducting state with some pair angular momentum if the temperature is low enough, i.e., the ground state is a superconductor. Clearly symmetry is not enough and we must look further if terms like weak or strong are to be useful.

A theme of this lecture is that a ubiquitous signature of "strongly correlated" materials is *strong variations with temperature*. Temperature dependence is often the most important property for actual applications and it is often the property most directly measured in experiments, but it is difficult to calculate the effects directly. Of course, temperature dependence is due to excitations, but measuring spectra for excitations requires specialized experiments which often are difficult to interpret. However, spectra are more directly related to theoretical methods. High energy features in the spectra are direct evidence for large interactions, but it is the low energy

excitations that determine the temperature dependence, the response to perturbations that lead to phase transitions, and other effects. Prime examples of such behavior involve the elements listed in Fig. 1.

It is *not* my purpose to say that we must use theoretical methods that include temperature directly. This may be very difficult and not needed to understand the observed phenomena. This lecture is devoted to sorting out the issues and using various theoretical methods – with judiciously chosen guiding principles.

#### 1.4 Fermi liquids, Mott insulators, .....

Since this is a school on "The Physics of Correlated Insulators, Metals, and Superconductors," certainly terms like "Fermi liquid," "Mott insulator," etc., will arise and we should be clear what is meant in each case. In particular, it is important to be clear about the meaning of the term *insulator*, and realize that there is not a unique definition of "Mott insulator." There is no hope of forcing everyone to adopt a single convention, and probably it is best not to try to make a single term apply to many complex problems. But we can be clear what is meant in specific cases.

A common feature of the different definitions is an insulator that would be a metal if the electrons did not interact. Even this condition already has problems if we want to identify "correlated" systems. If one allows for a broken symmetry, the *unrestricted Hartree-Fock solution* includes some important aspects of correlation and can lead to an insulating state; in fact, it tends to favor an insulator. There may be additional conditions that are used to define the term "Mott insulator." One is that they are only those that can be insulators without a broken symmetry, i.e., the order is not essential. A yet more restrictive definition is only insulators with no broken symmetry at zero temperature, called quantum "spin liquids" (see, e.g., [4] and papers referred to there), which present deep issues concerning the states of matter. These three definitions exemplify the issues addressed in this lecture: the nature of different states of matter; what experimental signatures show that correlations play an essential role; the power of modern computational methods to make quantitative predictions; the difficulty of making robust conclusions even if we have such powerful methods; and some guiding principles to help.

# 2 The four primary methods for quantitative calculations for materials

Quantitative calculations for materials are now an essential part of research, a fact made possible by the development of theoretical approaches together with powerful computational methods. There are four complementary approaches each having a crucial step in its genesis in the 1960's, key advances in the 1980's that made possible effective computational algorithms, and active, ongoing developments. The present discussions follow [1,5] where each approach is described in much more detail.

#### 2.1 Density functional theory (DFT)

It is important to realize that there were two different steps in the development of DFT done in 1964 and 1965.<sup>3</sup> One is the proof by Hohenberg and Kohn [7] that *all* properties of a system of electrons are determined by the ground state density  $n(\mathbf{r})$ , and in principle, each can be expressed as a functional of the functional of  $n(\mathbf{r})$ . This would be only a minor observation were it not for the second step by Kohn and Sham [8] to define an auxiliary system of noninteracting electrons designed to reproduce that exact ground state density and energy. The Kohn-Sham approach uses independent-particle methods, but it is not an independent-particle approximation; instead it is a stroke of genius to reformulate the entire approach to many-body theory to calculate certain properties, in principle exactly, with no guarantee that any other property can be determined by the method. The success of DFT is due to the fact that it is a theory of interacting, correlated electrons and it has proven to be possible to find approximate functionals  $E_{xc}[n]$  for exchange and correlation contributions to the total ground state energy that are remarkably accurate, even for many systems that are called "strongly correlated." Often the local approximation (LDA) is very good, and improved approximations have made DFT an integral part of research in chemistry and other fields. The work of Car and Parrinello in 1985 [9] set the stage for developments of efficient computational approaches that have made DFT into an indispensable method for realistic calculations.

Extensions of the original formulation illustrate the power and the limitations of the approach. The extension to hybrid functionals and methods like "DFT +U" are often important for systems we call strongly correlated, and the role of such methods are discussed in the examples below. Successful functionals have been developed to describe the van der Waals interaction, which is a non-local effect due to correlation (see, e.g., [10]). The ground state of a superconductor is also described in principle by DFT and functionals that include effects of electron-phonon interaction have been developed (see [11] that cites earlier references). Very soon after the Kohn-Sham paper, Mermin [12] showed that the density and free energy at any temperature are given exactly in terms of a temperature dependent functional  $E_{xc}(T)[n]$  for the exchange and correlation energy. However, there has been almost no use of the Mermin functional because it has been so difficult to make useful thermodynamic functionals for exchange and correlation. (Question to the reader: why is this so hard?)

Excitations are not supposed to be given by DFT, even in principle. *It is an independent-particle approximation to use the eigenvalues the Kohn-Sham equations as excitation energies*. This is merely one of many possible independent-particle approximations and it is not justified by any systematic theory. Indeed the results often are badly in error, even for materials as simple as silicon.

 $<sup>^{3}</sup>$ An extensive presentation is in [5] as well as in many good references such as the lecture by Jones in volume 3 of this series in 2013 [6].

#### 2.2 Quantum Monte Carlo

There are various ways quantum Monte Carlo (QMC) simulations can be used to treat interacting quantum systems by sampling the many-body wavefunction. One is variational Monte Carlo, where a wavefunction is optimized to provide the lowest possible energy for that type of function. A different approach is diffusion Monte Carlo that is based upon the analogy of the Schrodinger and the diffusion equations. This approach can provide the *exact* solution for the ground state of an interacting system of particles, and the first such calculation was done in 1965 by McMillan for <sup>4</sup>He [13]. However, the direct application to fermions does not work because the wavefunction must change sign and cannot be treated as a probability distribution. This has led to the fixed-node approximation where the nodal surface (where the wavefunction changes sign in the 3N dimensional space for N particles) is constrained to be the same as that of an optimized many-body variational function. This is the method used in the famous Ceperley-Alder work [14] in 1987 that provided the total energy of the homogeneous electron gas used in the construction of local density approximations to DFT. Other approaches include auxiliary field Monte Carlo and the more recent continuous time [15] methods that are particularly appropriate for embedded systems and are used in DMFT, as discussed below.

#### **2.3** Many-body perturbation theory

A general approach to the theory of excitations in many-electron systems can be developed in terms of a perturbation expansion in the Coulomb interaction. The Green function  $G(\mathbf{k}, \omega)$  is expressed by a Dyson equation in terms of the non-interacting part  $G_0(\mathbf{k}, \omega)$  and a self energy  $\Sigma(\mathbf{k}, \omega)$ , which contains the effects of interaction,

$$G^{-1} = G_0^{-1} - \Sigma.$$
 (1)

The approach used in much current work is the "GW" approximation developed by Hedin [16] in 1965, who applied it to the homogeneous electron gas and gave it the modest name GW to denote that it is lowest-order approximation  $\Sigma = GW$ , where W is the screened interaction. In condensed matter it is essential to screen the long-range Coulomb interaction, so that W itself is an infinite sum of diagrams. In the 1980's it was possible to develop computational methods to apply GW to materials, and it is now widely used to calculate band gaps in systems where the correlation is relatively weak, such as in semiconductors.<sup>4</sup> Extensive description can be found in [1] and reviews such as [17]. A question addressed here is when it can be a reasonable approximation for more strongly correlated systems with d and f states.

#### 2.4 Dynamical mean-field theory (DMFT)

DMFT is a Green function method that treats the correlation in a way that is very different from GW. Instead of a low-order expansion, the approach is to treat the short range correlation more

<sup>&</sup>lt;sup>4</sup>It also can describe the asymptotic  $1/r^6$  form of the van der Waals interaction, which is a pure correlation effect. The difference from the examples of strong correlation considered here is that perturbation theory works because there is a large gap and no low energy electronic excitations.



**Fig. 2:** Single site embedded in a lattice. For the Anderson impurity model (AIM) this depicts a real impurity with interactions embedded in a metal in which the electrons do not interact. It also represents the many-body problem solved in DMFT in the single site approximation: a site with interactions treated explicitly embedded in a medium with a frequency-dependent self-energy, which is equivalent to an AIM solved self-consistently with the requirement that the self-energy for the surrounding lattice is the same as that calculated for the embedded site.

accurately and to treat the longer range correlation more approximately or ignore it altogether. This is designed to treat materials with d and f states and models such as the Hubbard model, and it is the main approach considered in the examples in this chapter. There are precedents, both published in 1965, that capture some of the ideas in DMFT. They are still widely-used for intuitive understanding and are described in Sec. 4.2. Two seminal advances have led to the formulation of DMFT: The first is the work of Metzner and Vollhardt [18] and Müller-Hartmann [19] in 1989, who developed the quantum theory of interacting particles in infinite dimensions. The second advance is the recognition by Georges and Kotliar [20] and, independently, by Jarrell [21] in 1992 that an embedded site can be viewed as an auxiliary system equivalent to an Anderson impurity model (AIM). Thus the analytic and computational methods developed over the years can be used to understand the phenomena caused by interactions. Good resources for the concepts and theoretical methods are the review [22] and many lectures in this series, notably in the volumes devoted to DMFT [23, 24] which also describe ongoing developments and realistic applications.

The essence of DMFT is to calculate a Green function and self-energy by a many-body calculation for a site or cluster of sites embedded in a medium that represents the rest of the crystal.<sup>5</sup> For example, the single-site approximation is to carry out the calculation for a site embedded in the rest of the crystal as illustrated in Fig. 2. This approach can be used for a real impurity on a site, which is the Anderson impurity model (AIM) discussed in Sec. 4.1. However, DMFT is *not* an impurity approximation; the calculation is done self-consistently with the atoms in the rest of the crystal (depicted by the solid gray circles in Fig. 2) required to have the same self-energy as that calculated for the central site. The calculation for the embedded site is used only to determine the self-energy for the states on the site, and the final result is a translation-invariant Green function  $G(\mathbf{k}, \omega)$  given by Eq. (1), where there is no approximation in the independent-particle  $G_0(\mathbf{k}, \omega)$  and the approximation is that the self-energy has only local on-site components, i.e.,  $\Sigma(\omega)$  is independent of momentum  $\mathbf{k}$ .

<sup>&</sup>lt;sup>5</sup>In the literature the term DMFT is often used to denote only the single-site approximation following the traditional definition in statistical mechanics. Here and in [1] DMFT is regarded as a general approach for a site or cluster of sites embedded in a medium. DMFT is designed to give spectra, whereas an alternative approach, Density Matrix Embedding, is designed to give the energies for the ground state [25].

In applications to models with on-site interactions U and hopping matrix elements between sites, DMFT is constructed to be exact in two limits: the non-interacting limit, U = 0, and the limit of infinite dimensions  $d \to \infty$  where there is no correlation between sites and mean-field theory is exact (see especially [24]). In calculations for materials, interactions W and a small basis set are inputs to the method; this introduces approximations and uncertainties, and usually the parameters are calculated using DFT or many-body perturbation methods. Also there are other less correlated bands that are approximated by some other method like DFT or GW. There are various ways to do the many-body calculation for the embedded site or cluster. The natural approach is to use the finite temperature formalism with fixed Fermi energy so that the particle number of the site is not fixed. One on the most powerful approaches uses finite temperature Monte Carlo calculations which samples all possible occupations of the central site. This builds upon the work on the AIM which provided the exact solution by Hirsch and Fye [26] for the case of a single-band with spin 1/2, where there is no sign problem. Those methods have been adapted directly and more recently a continuous time algorithm [15] has been developed just for the embedded site or cluster.

# **3** Guiding principles

All many-body calculations for interacting, correlated electrons – except for a few models that can be solved exactly – involve approximations. How can we justify that the results of such a calculation are meaningful? This is the first question before one addresses the issues of the quantitative accuracy. It is very useful to have some guiding principles that are rooted in deep, fundamental principles like conservation of energy and momentum, symmetry, and topological classification. In addition, there may be guiding principles that are based upon very general arguments that involve theoretical derivations, and one might suspect that the derivations have some loopholes or they break down in some cases. In these cases the guiding principles may be especially fruitful if they are taken seriously: A conclusion that the principle applies is extremely useful and insightful. A demonstration that it is violated may indicate an error or may be truly important; it should not be taken lightly and it may indicate new, here-to-fore unknown possibilities. Let us examine a few guiding principles, and in the following sections illustrate their use.

**T=0 vs.** T > 0: There are crucial differences between T = 0 and T > 0. Much of the theory of electronic structure is formulated specifically for perfect crystals at T = 0. However, we want to consider both T = 0 and T > 0, where there is always disorder and finite entropy, and it is crucial to recognize the differences.

**Metals vs. Insulators**: Strictly the distinction between metal and insulator is well-defined only at zero temperature. At any T > 0 there is some conductivity. However, the difference in conductivity may be very large; the effects of thermal disorder are manifested in the temperature dependence and the characteristic behavior as  $T \rightarrow 0$  is the way metals and insulators are distinguished in practice. We will adopt the terms metal and insulator, with the realization that we must be careful applying arguments valid only at T = 0 to problems at T > 0, and vice versa.

## 3.1 Conservations laws and continuity: Normal metals and Fermi liquid theory

Fermi liquid theory is a fabulously successful theory attributed to Landau. It was initially applied to liquid <sup>3</sup>He, where the interaction is short range, and later extended to include Coulomb interactions by Silin. As told to me by Alexey Abrikosov, Landau arrived at his proposal by asking himself: "What is conserved?" The fact that conservation laws are unchanged by the interaction suggests continuity. Even though <sup>3</sup>He has strong interactions the proposal is that it remains an isotropic liquid with a Fermi surface and low energy excitations that have the same quantum numbers as if it were a system of non-interacting fermions, but with a modified effective mass and susceptibilities. This is not a theory of how to calculate the effective parameters, but rather of relations among them, that are extremely useful and insightful.

The messages that I want to emphasize are the importance of continuity and the separation of the three different aspects of our understanding: the formulation of the theory, explicit mathematical methods to calculate the properties, and proofs (if any) that the results of the calculations are rigorously correct. Some aspects can be argued to be guaranteed if the system evolves continuously from a known state, even if there are no theoretical proofs that the system evolves continuously, and no proofs that the theoretical derivations are foolproof. Systems that are continuously connected to some independent-particle state are termed "normal." The same arguments also apply to insulators where there is a gap. Of course, there are many examples of transitions between states that have different symmetry, and we can ask if each state can be considered to evolve continuously from some known state.<sup>6</sup>

#### 3.2 The Luttinger theorem and Friedel sum rule

The Luttinger theorem states that in a perfect crystal the volume enclosed by the Fermi surface in k-space is the same, independent of interactions. (I will use the term "theorem," but it might be better to call it a sum rule since theorem implies mathematical rigor.) It is sufficient to indicate the sense of the derivation in the original papers by Luttinger and Ward (LW) [27,28], which is summarized in App. J of [1]. The total number of electrons is given by  $d\Omega/d\mu$  where  $\Omega$ is the thermodynamic potential and  $\mu$  is the chemical potential. The derivation by LW involves the particular way of summing diagrams to express  $\Omega$  in terms of the Green function G (which is an infinite sum of diagrams involving the bare  $G_0$ ) summed over Matsubara frequencies, taking the limit of  $T \to 0$  and a partial integration. The derivation uses the fact that the one-particle Green function  $G(\mathbf{k}, \omega)$  evaluated at the Fermi energy  $\omega = E_F$  (where  $E_F = \mu(T = 0)$ ) is real, and the final result is that  $G(\mathbf{k}, E_F)$  changes sign as a function of  $\mathbf{k}$  at the Fermi surface, so that the volume is defined by the region where the Green function is negative. The conclusions apply only at T = 0 where the Fermi surface is precisely defined and the states at the Fermi energy have infinite lifetime, just as for an independent-particle system.

<sup>&</sup>lt;sup>6</sup>There can be further distinctions including classification by the topology of the eigenstates as a function of  $\mathbf{k}$  where topologically trivial and non-trivial states are each connected to an independent-particle state with the same topology.

As far as I know there are no rigorous proofs that the summations are uniformly convergent, and there are no loopholes in the mathematical derivations.<sup>7</sup> However, we can appeal to the principle of continuity, to rephrase the argument: The theorem should be obeyed so long as the system is normal, i.e., can be continuously connected to some independent-particle system. The lack of a rigorous proof applies to any case, such as Na, Al, or Cu, and it is experiment that shows these systems act like normal Fermi liquids with a Fermi surface that obeys the theorem as  $T \rightarrow 0$  for the accessible range of temperatures. We already know one example, superconductivity, which is certainly not normal! Any violation of the theorem would herald a different state of matter; in both theory and experiment we should be doubly careful not to treat violations lightly and to search vigorously for exceptions!

It is instructive to consider also the Friedel sum rule [30] on the sum of phase shifts for an impurity in a metal, which is an example of how much can be learned without heavy mathematical calculations. The sum rule follows from the condition that the sum of phase shifts of the states at the Fermi energy due to the impurity equals the number of electrons added (or subtracted) around the impurity compared to the host. Since charges are perfectly screened in a metal, the number of electrons is balanced exactly by the added charge of the nuclei of the impurity relative to the host. The sum rule was originally derived for independent particles; however, the derivations of LW apply here with the difference that the sum is over the phase shifts that are labelled by the point symmetry of the impurity instead of the momentum **k** that labels the quantum numbers for a translation symmetry of a crystal [31]. But there is a great difference because the impurity cannot induce a phase transition in an extended solid and the system evolves continuously as the interaction is increased. There are no caveats and we can be confident that the Friedel sum rule is valid no matter how strong are the interactions on the impurity.

Knowing only the sum rule we can draw conclusions about the Kondo effect, one of the classic problem of condenser matter physics described in the next section. At zero temperature resistance caused by an impurity in a metal is determined by the phase shifts. A widely-used model for the Kondo effect and the Anderson impurity model is a one-band model where there is only one phase shift. If the band is chosen to be symmetric, the impurity state is half-filled and it follows that the impurity causes the maximum possible resistance no matter how strong is the interaction or how weak is the coupling to the host. It is not many steps to an understanding of the Kondo effect at least qualitatively.

<sup>&</sup>lt;sup>7</sup>However, it is tested in the case where there is an exact solution by Lieb and Wu [29] for the one dimensional Hubbard model. There the Luttinger theorem is rigorously satisfied for any particle filling. The excitation spectrum is different from a Fermi liquid, but nevertheless there is a Fermi surface and it is the same independent of interactions, except at 1/2 filling where there is a gap.

# 4 Instructive models

#### 4.1 The Anderson impurity model and the Kondo effect

The Kondo effect is the observed temperature dependence of the resistivity of solids containing transition metal impurities.<sup>8</sup> The expected behavior is a decrease as T is lowered, since the resistivity due to dynamical effects such as phonons decreases. It should never increase and at low temperature it reaches a plateau determined by the static disorder. However, the Kondo effect is that there is a resistance minimum after which it increases and saturates for  $T \rightarrow 0$ , contrary to all expectations. This set up the problem of a spin embedded in a metal, which is a strong-coupling problem that defied solution until Wilson's invention of the numerical renormalization group [32]. The problem is that a perturbation series *in the coupling of the spin to the metal* diverges due to the low energy excitations in the metal.

If we step back and note that the spin is actually electrons, the problem can be cast as the Anderson impurity model (AIM) with strong interactions on the impurity site [33]. This is depicted in Fig. 2, where the central site is shown with lines that denote the states of the interacting system on the impurity, while the surrounding lattice is considered as a non-interacting metal. As discussed in the previous section, the principle of continuity and the Friedel sum rule leads to the conclusion that the system must evolve, as the interaction increases, keeping the sum of phase shifts unchanged, so that the resistance at T = 0 is constrained. For the simplest problem of a single band there is only one phase shift and the resistance is the maximum possible value at T = 0. There are now exact solutions [34] and useful approximations that fully support the analysis.

Anderson [33] provided an instructive analysis illustrated in Fig. 3. Consider the case of a halffilled band with a symmetric density of states and an added state on one site at the Fermi energy so that it is half-filled. If there are no interactions this leads to a density of states on the impurity site that is broadened due to coupling to the continuum of host states as depicted schematically in the lower panel of Fig. 3. If we add an interaction U only on the impurity site, the problem remains symmetric if the energy to remove an electron is -U/2 below the Fermi energy and to add a second electron on the site is increased by U, i.e., U/2 above the Fermi energy. In this case the impurity state must remain half-filled by symmetry and a restricted Hartree-Fock solution gives exactly the same density of states. However, there can be a broken-symmetry unrestricted solution with one spin mainly occupied and the other mainly empty; for U larger than a critical value this is the lowest energy state as illustrated in the middle panel. As pointed out by Anderson, this is fundamentally incorrect but it heralds the strongly interacting regime where something interesting happens. The exact solution for T = 0 is shown schematically at the top in the large U regime; it has both behaviors: the feature at the Fermi energy that is required by the Friedel sum rule and the high energy features that are at energies similar to that given by the unrestricted Hartree-Fock approximation.

<sup>&</sup>lt;sup>8</sup>Ted Geballe told me that in 1955 he asked John Bardeen to name the most important unsolved problems in condensed matter physics. Bardeen replied, "superconductivity" and, after a characteristic pause, "the resistance minimum" now called the Kondo effect.



**Fig. 3:** Schematic illustration of the spectra for an Anderson impurity in the regime that leads to the Kondo effect. As described in the text, the bottom panel shows the broadened peak for the non-interacting case; the middle illustrates the peaks above and below the Fermi energy for the broken-symmetry unrestricted Hartree-Fock solution in the large U regime; and the top shows the qualitative form of the full spectrum that has a peak at the Fermi energy, which satisfies the Friedel sum rule.

The spectrum in Fig. 3 already shows how we can understand some important aspects of solids illustrated later. The "three-peak" behavior of the spectral density is a characteristic signature of systems that are often called strongly correlated. We can expect high-energy features due to the strong local interactions and low-energy features that lead to strong temperature dependence and large susceptibility; for the impurity there can be no phase transitions but in a crystal with interactions on every site, the large susceptibility can lead to transitions to various kinds of ordered states. Even though the unrestricted Hartree-Fock calculation is unphysical, it indicates the regime of strong interactions. The temperature dependence is not shown in Fig. 3, but it is similar to that shown later in Fig. 5, which shows that the peak at the Fermi energy disappears as T is increased, another signature of strong interactions.

Notice the "strongly interacting" problem with large U is continuously connected to the noninteracting U = 0 state. There is no sharp division between a Mg impurity Na and a Mn impurity in Au. What is the difference? The temperature scale that is denoted by the Kondo temperature!

#### 4.2 The Hubbard and Gutzwiller approximations

Although we have rigorous solutions for the AIM and 1d Hubbard model, we do not yet know whether the conclusions can be used in other problems. Let us try the opposite approach: approximations that are so extreme that they can be solved analytically. The question is what aspects can we use to make confident conclusions about the complicated many-body problem.



**Fig. 4:** Spectral function for a half-filled band with a semicircular density of states shown at the top. The lower four panels show the spectra calculated in the Gutzwiller (dashed lines) and Hubbard (solid lines) approximations as the interaction U increases. The Gutzwiller approximation leads to a narrowed band with a mass (inverse of the band width) that diverges and above a critical  $U_G$  there is no solution, which is a model for a metal-insulator transition. In the Hubbard "alloy" approximation the band widens and above  $U_H$  a gap opens to form an insulating state.

In fact the approximations considered in this section were both proposed in 1965 and they are very enlightening for all the methods and examples in the rest of this chapter!

The approximations described here can be applied to any lattice, but there is a special case that allows an analytic solution, the semicircular form for the independent-particle density of states shown at the top of Fig. 4 where

$$\rho(\omega) = -\frac{1}{\pi} \operatorname{Im} G_0(\omega) = \frac{2}{\pi D^2} \sqrt{D^2 - \omega^2},$$
(2)

which is non-zero only for  $|\omega| < D$  and D is 1/2 the band width. This is the actual density of states for the Bethe lattice in infinite dimensions so that it can be interpreted as an lattice where each atom has an infinite number of neighbors. Since mean-field theory is exact for an infinite number of neighbors where fluctuations average out, DMFT provides the exact solution, as discussed in the following section.

The approach of Gutzwiller [35] was to propose a variational form for the ground state wavefunction that is the same as independent particles (or some other mean-field solution) multiplied by a factor that reduces the probability of double occupation. This is widely used and can be evaluated essentially exactly by Monte Carlo methods. The Gutzwiller approximation is to ignore the correlation of the occupation of electrons on different sites; this leads to equations that can be solved in general numerically and analytically for simple models. Minimization of the energy as a function of U leads to a state with reduced kinetic energy interpreted as a band narrowing or increased mass. For a one-band Hubbard model the result is that the Fermi surface is unchanged but the mass increases as the density approaches half-filling and exactly at half-filling there is a critical  $U_c^G$  where the solution is for infinite mass. This is illustrated for the semicircular density of states at half-filling in Fig. 4. This is widely used as a scenario for a Mott transition as a function of band filling: bands with increasing mass as the density approaches 1/2 until it diverges signalling an insulator.

Hubbard proposed a different approach in terms of the *Green function* [36]. The propagation of an electron in an interacting system is approximated by assuming the rest of the electrons act as a static array of scatterers, called an "alloy approximation." The further approximation that allows analytic solution is the coherent potential approximation which ignores the correlation between occupation on different sites, which was derived independently by Hubbard and others and is now widely used in real alloys. This leads to a Green function given by Eq. (1) with an on-site self-energy  $\Sigma(\omega)$ , like in DMFT, but a static mean-field approximation. The result is that the states near the Fermi energy have a lifetime, which may be reasonable for high temperature but is fundamentally incorrect at T = 0. On the other hand it leads to a gap for large U as illustrated in Fig. 4 with well-defined band edges. This provides a different scenario for a Mott transition as a function of the interaction: a spectrum that broadens until a gap opens above a critical  $U_c^H$ .

Thus we have two widely-used pictures of a Mott transition: one is a band at the Fermi energy that narrows as the interaction increases and the other a broadening of the bands until they are splitting into what are called the upper and lower "Hubbard bands." Each ignores correlation of occupation on different sites and assumes no change of symmetry, and each can be argued to capture a part of the physics.

#### 4.3 Dynamical mean-field theory (DMFT) for the Hubbard model

As discussed in Sec. 2.4, DMFT is an approach to treat interacting electrons in a crystal, but the heart of the many-body calculation is the calculation of the on-site Green function and self-energy for an embedded site that is equivalent to a self-consistent Anderson impurity model (AIM). This section illustrates DMFT by showing a few results for a one-band Hubbard model. It is especially appropriate to consider the semicircular density of states defined in Eq. (2) which allows a direct comparison with the Hubbard and Gutzwiller approximations shown in Fig. 4. Because the single-site DMFT is exact in the limit of infinite dimensions, the result is the exact solution for the Bethe lattice with an infinite number of neighbors. Thus this is an exact solution for a special model and our job is to recognize when the results can help us understand the properties of real complex systems in finite dimensions!<sup>9</sup>

<sup>&</sup>lt;sup>9</sup>In finite dimensions, this is an approximation and an approach to an exact solution requires that the calculations be done for large enough clusters that the correlations between electrons on different sites has converged. For examples like the two-dimensional Hubbard model various size clusters have been treated, which is essential for some important effects [37]. However, this is generally not feasible for calculations for realistic systems with many-bands and all the DMFT calculations in the examples for real materials in the following section are done in the single-site approximation.



**Fig. 5:** Spectral function for a half-filled band with a semicircular density of states calculated using DMFT in the single site approximation. The spectra have features like the Anderson impurity model in Fig. 3 and the approximations for a Bethe lattice in Fig. 4: Gutzwiller (peak at the Fermi level that narrows as the interactions U increases) and Hubbard (spectra that broadens as U increases with weight that decreases at the Fermi level until a gap opens). At the right is shown the effect of temperature: the feature at the Fermi energy at low temperature vanishes at high temperature where the states act like decoupled spins and the spectral weight is transferred to the high energy peaks. Adapted from figures in [22].

The results of DMFT calculations are shown in Figs. 5 and 6. Here we skip all the details of the calculations and give only a few results. As expected, the spectra shown in the left side of Fig. 5 have the characteristics of those for the AIM shown in Fig. 3, a central peak that narrows as the interaction increases and high energy peaks separated by U. The right side of Fig. 5 shows the temperature dependence for a case where the solution has a narrow central peak that disappears as T increases. This is not a broadening but a true many-body effect. For the AIM the analogous result is the Kondo effect where the resistance decreases at T increases. For a lattice, it is the Fermi surface that disappears, which is illustrated later in Fig. 8.

However, unlike the AIM, the self-consistency leads to a very different consequence: As U increases the central peak disappears at some value of  $U_c^1$  and a gap opens at a value  $U_c^2$ . Thus the DMFT result shows both behaviors captured by the Gutzwiller and Hubbard approximations shown in Fig. 4. This provides a scenario for a Mott transition as a function of the interaction that is the exact solution for a model! Whether or not this applies to a real problem in finite dimensions is an issue. Furthermore, if we look more carefully into the solutions for the Hubbard model there is an important issue not considered so far, and a deep issue of physics still to be understood.

The issues are illustrated in Fig. 6. A result of the DMFT calculations is that for some regime of interaction U there are two types of solutions, an insulating solution with a gap for  $U > U_c^1$  and a metallic solution with a central peak for all  $U < U_c^2$ , with  $U_c^1 < U_c^2$ . In the region from  $U_c^1$  to  $U_c^2$  the two solutions indicate two phases with the same symmetry so that there is a first-order phase transition. Furthermore, as a function of temperature the central peak disappears and the gap fills in until there is a critical point and the solutions merge like the water steam transition. This is shown in the left side of Fig. 6 by the dashed line ending in a critical point, which has the features of a Mott transition.



**Fig. 6:** Phase diagram for Bethe-lattice in infinite dimensions which has a semi-circular density of states in the limit of infinite dimensions. Left: Results for a Hamiltonian that has only nearest neighbor hopping t; the dashed line ending in a critical point indicates a transition between the two types of spectra in Fig. 5. However, for this model the actual transition is to an antiferromagnetic insulator (AFI) indicated by the solid line. At the right is the phase diagram if a second-neighbor hopping t' is included; the AFI state is not as favorable (note the expanded vertical scale) and there is a range of temperatures where the first-order metal-insulator transition occurs. (For this t' there is also an antiferromagnetic metal phase that is not shown and is not important for our purposes.) Adapted from figures in [22].

However, there is more that can be learned from the single-site DMFT calculation. The previous calculation is in fact restricted DMFT where it is required that there is no order of the spins or any other order. One possibility is an antiferromagnetic state where each site is allowed to have a net spin and it is surrounded by sites with opposite spin. Such a solution is allowed for any lattice that is "bipartite," i.e., that can be divided into A and B sites, where all A sites have only B neighbors and vice versa. The Bethe lattice has this property and we can expect that such a state is favored just as it is in the multitude of other models and actual materials that order antiferromagnetically. This can still be solved by single-site calculation where the A and B sites are related by time reversal symmetry. Indeed the calculations find an antiferromagnetic phase for temperatures and values of U shown by the solid line in the left side of Fig. 6. The first-order transition is completely eliminated and the only stable phases are a metal with no order and an ordered antiferromagnet.

Nevertheless, there is a way to uncover the first order transition. A second-neighbor hopping (denoted t') couples an A site to the nearest other A site (the same for B sites) which tends to frustrate the antiferromagnetic order and reduce the temperature range where the antiferromagnetic insulator is the stable phase. It turns out that the independent-particle density of states is still semicircular, but with modified width, and the calculations can still be done within the same model. This is shown in the right side of Fig. 6 (note the reduced temperature scale). Now the first-order transition can actually occur for some temperature range about the antiferromagnetic transition. This is the behavior known from the classic example, V<sub>2</sub>O<sub>3</sub>, discussed in Sec. 5.3.

Finally, we arrive at a deep issue that opens the door (or not) to new states and phenomena that are qualitatively different from normal states of matter. If the antiferromagnetic order can be eliminated could the insulating state extend all the way to T = 0? Further discussions are postponed to later.

# 5 A few examples: Data, interpretation, and theory

#### 5.1 Cerium: volume collapse phase transition, heavy fermions, ...

**Experimental facts and interpretations.** Cerium is the first transition element in the lanthanide series. In various compounds it exhibits behavior that is readily identified as due to one electron in the localized, atomic-like 4f shell  $(f^1)$  (for example, in magnetic Ce<sub>2</sub>O<sub>3</sub> where Ce has a formal valence +3) or an empty 4f shell  $(f^0)$  (as in non-magnetic CeO<sub>2</sub>, formal valence +4). As an impurity in metallic La it leads to the Kondo effect expected for a localized  $f^1$ embedded in a metal. Some compounds such as CeIrIn<sub>5</sub> are "heavy fermion" materials [42] with masses (inversely proportional the band widths) orders of magnitude larger than ordinary metallic bands, similarly to the Kondo effect for impurities where the energy scale can vary over orders of magnitude for different impurities and hosts.

For many decades it has been known that elemental Ce has a phase diagram as a function of temperature and pressure with a first-order transition between the high volume  $\gamma$ - and low volume  $\alpha$ -phases, each with the same fcc structure. There is an anomalously large 15% volume change at room temperature and a critical point at higher temperature analogous to the water-steam transition. The  $\gamma$  phase has a temperature-dependent magnetic susceptibly accounted for by weakly coupled  $f^1$  spins, whereas the  $\alpha$  phase appears to be inert magnetically. The first interpretation was the natural one: a transition between magnetic  $f^1$  states and non-magnetic  $f^0$  with an electron transferred to the weakly interacting metallic bands. However, more recent experiments showed that the 4f occupation in the  $\alpha$  phase is also close to  $f^1$ , for example, as indicated by the photoemission and inverse photoemission data shown at the top of Fig. 7, where the sidebands below and above the Fermi energy indicate the strong interactions  $U \approx 7$  eV and f states in both phases, with bands at the Fermi energy in the  $\alpha$  phase like the three peak structure for the Anderson impurity model in Fig. 3.

**Guiding principles for theory.** We are faced with a strongly interacting problem of a lattice of localized f states coupled to delocalized metallic bands. It is certainly very difficult to explain in detail all the properties of cerium and its compounds.<sup>10</sup> The purpose of the present discussion is to examine what we can understand from experiment alone and what we can believe from DFT calculations that are simple to do now-a-days, but which are clearly inadequate in some respects. Furthermore we want the reasoning to apply, a least qualitatively, not just for one material but for many different cases. The same reasoning is also invaluable in judging what can be believed from a heavy many-body calculation, which certainly involves assumptions and approximations.

A great success of DFT calculations using standard functionals like LDA is that for Ce the calculations find an equilibrium volume near that for the  $\alpha$  phase and a 4f occupation of ap-

<sup>&</sup>lt;sup>10</sup>Two mechanisms have been proposed to explain the  $\alpha$ - $\gamma$  transition caused by the large interactions for electrons in the 4f states. In one proposal the primary effect is a "Mott transition" of the f states; the d states do not play an essential role. The other proposal is a "Kondo volume collapse" in which the primary driving force is the coupling of the f states to the band-like d states; this is a simplified version of the results of the DMFT calculations described here.



**Fig. 7:** Electron removal (photoemission) and addition (inverse photoemission) spectra for  $\alpha$  (left) and  $\gamma$  (right) phases of Ce. Top: Measured spectra at room temperature [38] that is mainly the Ce 4f component. Middle: Single-site DMFT calculations for the 4f states with parameters from LDA. For the  $\alpha$  phase (left) theory "b" [39, 40] is broadened by the experimental resolution and includes the 6s–6p–5d states. Theory "a" [41] shows the high-resolution peaks near the Fermi energy including spin-orbit splitting. Note widths are  $\approx 10 \times$  narrower than the LDA peaks in the bottom panel. For the  $\gamma$  phase (right) the calculation finds upper and lower Hubbard bands with no peak at the Fermi energy. Bottom: The density of states for static mean-field calculations: LDA for a non-magnetic solution in the  $\alpha$  phase and unrestricted LDA+U for a magnetically ordered state in the  $\gamma$  phase. The peaks are 4f and the broad spectra are bands formed from 6s–6p–5d states. Each static mean-field calculation describes an aspect of the spectrum, but cannot explain the three-peak spectrum found in the DMFT. Similar to figure in [1] provided by A.K. McMahan except "theory a" modified from figure provided by K. Haule.

proximately one. Such a calculation is *guaranteed* to have partially-filled 4f bands at the Fermi energy, as illustrated in the bottom left panel of Fig. 7, which satisfy the Luttinger theorem including the f states. Quantitatively, the bands are narrow, but yet broad enough that there would be only band-like paramagnetism, consistent with what is observed in the  $\alpha$  phase. However, the LDA calculation cannot explain the peaks well above and below the Fermi energy that indicate a large interaction.

What can we conclude about the results of a heavy many-body calculation even before it is done? So long as the system does not have a transition to an ordered magnetic state and the temperature is much lower than the characteristic energy scales, continuity implies that the Luttinger theorem is obeyed and *any correct many-body calculation* must give bands that are well-defined at the Fermi energy, even though they may be much narrower than the LDA bands and the spectrum is very different as one goes away from the Fermi energy. This is illustrated by the results shown in Fig. 7 for DMFT calculations done in the single-site approximation.

What about the  $\gamma$  phase? Another success of DFT calculations is that if one allows for spin polarization there is another solution with larger volume close to that observed for the  $\gamma$  phase at room temperature. The spectrum is illustrated in the lower right panel of Fig. 7, which shows the result of an "LDA+U" calculation for a magnetically ordered state. The spectrum is qualitatively like the experiment with apparently no 4f bands at the Fermi energy, similar to the unrestricted Hartree-Fock approximation in Fig. 3. Is this inconsistent with the Luttinger theorem? Before we do a many-body calculation, what do we expect to be the different possible results? If the temperature is high compared to some characteristic energy scale (the scale of interactions between spin on different sites), we do not expect there to be bands at the Fermi energy! Indeed, this is the result of the single-site DMFT calculation for the model in Fig. 5, where the central peak vanishes at high temperature, and the same behavior is found in the DMFT calculation for  $\gamma$ -Ce shown in the middle right panel of Fig. 7.

Consider now the heavy fermion material CeIrIn<sub>5</sub> for which DMFT results [43] are shown in Fig. 8. From experiment such as specific heat measurements we know the characteristic energy scale is very low, somewhat above 10 K and there is no magnetic order at 10 K. The figure shows the huge effects of interactions: At room temperature the bands at the Fermi energy are almost like an LDA calculation at T = 0 with the f states artificially removed. This mimics the fact that the f states are essentially decoupled at this temperature and result is a "small fermi surface" that does not include f electrons. At low temperature the bands are like an LDA calculation with the f states included, i.e., a "large Fermi surface," but they are greatly renormalized as shown in the right side of Fig. 8 where the scale is expanded by a factor of 100.

What can we conclude? None of the calculations definitively establishes the mechanisms for the behaviors and there is no theoretical proof that the systems do not order in some way. But if we take from experiment that there is no transition to some ordered phase at the relevant temperatures, then we can have a qualitative picture without doing a heavy many-body calculation. Furthermore, since there is no order, the single-site approximation is reasonable and it appears to be an appropriate starting point for quantitative understanding. The fact that low energy scales emerge implies that susceptibilities are large such that there may be transformations to other states at lower temperature, which is found in many heavy fermion materials [42]. Finally, a lesson from the previous sections is that if we seek the behavior at T = 0, we expect the system to be either a Fermi liquid or have a transition to an ordered state, and we should be very careful about using T = 0 arguments at T > 0 and vice versa.



**Fig. 8:** Momentum resolved spectra at 300 K (left) and 10 K (right) calculated using single-site DMFT. As discussed in the text at 300 K the 4f weight at the Fermi energy is very small, but a very narrow 4f band (note the greatly expanded scale energy in the right figure!) emerges in analogy to the Kondo effect and the model DMFT calculation shown on the right side of Fig. 6. From [43].

#### 5.2 NiO and Mott insulators

NiO is the original "Mott insulator" as identified by de Boer and Verwey [48] and pointed out by Mott and Peierls [49] in 1937. Below the Curie temperature of 525 K, it is an antiferromagnetic insulator with a gap around 4 eV, which can be seen from the spectra shown in the top panel of in Fig. 9. It satisfies the narrower condition for a Mott insulator: If there is no order there should be fractionally filled bands that would indicate a metal, but in fact it acts like an insulator with a gap that does not depend on the magnetic order and remains above the Curie temperature (which is found in experiments not shown in the figure). The structure is fcc and there are no complications about which d states are involved (unlike the other classic case  $V_2O_3$ ).

Guiding principles. This case is simpler than the various problems for Ce compounds since NiO is an insulator with a gap, and it allows us to ask simple direct questions. What about the Luttinger theorem when there is no broken symmetry? Since this is a "Mott insulator" can we trust any results from methods such as the GW approximation, based upon perturbation theory? The theoretical results shown in Fig. 9 suggest that we have a rather good understanding of the basic issues even if there is much yet to be understood. As in many systems, DFT calculations are very successful in predicting the structure. At the bottom is the spectra that shows the result from an LDA calculation for the ordered antiferromagnetic structure; there is a gap, but it is very small and not visible in the figure since the spectra are broadened to compare with the experiment. In addition to the gap being too small, the relative positions of the oxygen p and the Ni d states are wrong. Improved DFT calculations using DFT+U (a generalized gradient functional GGA + U in this case) functionals open the gap but cannot give both the magnitude of the gap and the positions of the p and d in agreement with experiment. The HSE hybrid density and Hartree-Fock functional leads to much improved spectra. An example of GW calculation is shown for "one shot"  $G_0W_0$  starting from the HSE wavefunctions and eigenvalues. Similar results are found using a self-consistent GW method that is independent of the starting point.



**Fig. 9:** Spectra for electron removal and addition in NiO. Top: experimental results for 3d weight from [44] and [45]. The other panels are calculated spectra projected on the O-p (grey) and Ni-3d (red) components. The lower four panels: DFT calculations with different functionals, above these: GW calculation, all for the antiferromagnetic state [46]. The top theoretical results are the spectra for the paramagnetic state calculated using single-site DMFT (called DMFA in the figure) with parameters from DFT calculations [47]. Similar to a figure in [1].

These methods are not chosen to fit NiO; the same approximations give improved results for semiconductors, large classes of oxides, and other systems. The conclusion is that DFT and GW calculations can be very useful and describe systems like NiO *so long as we restrict ourselves to the ordered state at low temperature*.

The gap and insulating behavior of NiO remain for temperatures above the Curie temperature where there is no ordered moment. In this case any T = 0 DFT or GW-type calculation must lead to a metal; this is not shown but must occur by electron counting for partially filled bands that originate from atomic-like d states. Why do these methods not work for NiO above the Curie temperature where there is no order? The simple answer is that temperature has a large effect because the large on-site interactions lead to local moments that persist above the Curie temperature. Approaches that take the disordered moments into account can explain the gap in the high temperature state. A simple approach is a static approximation like the Hubbard alloy approximation that opens a gap like that shown in Fig. 4. A greatly improved approach is the result within the single-site approximation which means that correlations between electrons on a site are included but correlations between different are sites treated only as an average mean-field, which is justified at high enough temperature.

#### 5.3 $V_2O_3$ and the Mott transition

Whereas NiO is described as a Mott insulator,  $V_2O_3$  is the classic example of what has been termed a Mott transition. The famous phase diagram [50] is not shown here but the basic points are illustrated in the phase diagram in the right side of Fig. 6. Experimentally the different parts of the phase diagram are accessed by applying pressure and doping with Cr. Pressure squeezes the atoms together resulting in larger independent-particle hopping terms and a decrease in the relative importance of interactions, which favors the metal. At low temperature and low pressure  $V_2O_3$  is an antiferromagnetic insulator, like the right side of Fig. 6. Applying pressure corresponds to moving to the left in the figure until there is a transition to a paramagnetic metal; these are only two states observed at low temperature. With Cr doping there is also a first-order transition in the paramagnetic phase at higher temperature, like the phase line in Fig. 6 that ends in a critical point. It is this transition that has long been taken as the classic example of a Mott transition with no change of symmetry. Because of the complicated crystal structure and possible ordering of the electronic states, there have been many models proposed to explain the behavior. But for our purposes the only relevant point is that there exists a transition with a change in the spectrum and conductivity from a form expected for an insulator to that for a metal in some range of temperature and pressure. However, the two states are not really distinct since they merge continuously above the critical point.

Does this violate the Luttinger theorem? Just as the analysis for NiO, it does not because the transition is only observed at high temperature. It is important to understand the reasons for insulating-like and metallic-like behavior, but it should be done with the understanding that it is not inconsistent with the theorem unless the transition actually continues all the way to zero temperature, which leads up to the issues in the following section.

# 6 The Mott insulator and topological order

Several times in the previous sections there were references to deep issues in physics that are brought to light by relentlessly pursuing the question of whether or not a Mott insulator with no order can exist at zero temperature. Recall that the difference between a metal and an insulator is precisely defined only at T = 0, and the Fermi surface and Luttinger theorem are precisely defined only at T = 0. An insulating state with fractional occupation and no order T = 0 (termed a quantum spin-liquid; see, e.g., [4] and papers referred to there) would violate the original statement of Luttinger theorem. There is now growing evidence that such a state would have some form of topological order<sup>11</sup> and would be a state of matter with quantum order not described by any classical order parameter [51]. There is a well-known example, superconductivity, and it would be an extraordinary advance to discover other states of matter with quantum order. For states with topological order, there is not a continuous connection to

<sup>&</sup>lt;sup>11</sup>Topological insulators that have been of great interest recently are band insulators with a Hamiltonian  $H(\mathbf{k})$  that has non-trivial topology as a function of  $\mathbf{k}$  in the Brillouin zone. For a Mott insulator there may be related properties, but this has not been worked out to my knowledge.

an independent-particle system, and many works using different approaches find that at a transition to a topologically ordered state the volume enclosed by the Fermi surface can change by a discrete amount. This leads to a possible new formulation of the Luttinger theorem that extends the original derivation to systems with topological order. Perhaps the most direct conclusions related to the Luttinger theorem are due to Sachdev and coworkers who have argued that any state that does not satisfy the original Luttinger theorem must have topological order. (See, e.g., [52].)

# 7 A few final remarks

It is nice to appreciate the prescient work of the 1960's that are the basis of much of the work today and still provide very valuable insights, along with the advances of the 1980's and early 1990's that have provided new ideas and methods that are the basis for actual calculations done today. As the calculations have become more and more powerful we have reached the point where quantitative theory is an essential part of research on actual materials in actual experimental conditions. Despite great successes in many cases, there are failures in others. In addition, present day theories often use different methods for different regimes of correlation, for example, the band-like behavior for the materials at the lower left in Fig. 1 and the extreme localized local-moment behavior for materials in the upper right. It is the materials on the borderline that have interesting, anomalous behavior; they present the greatest challenges because correlation plays an especially important role. At such points we need guiding principles to keep the ship afloat and not be caught on the rocks.

Consider the example presented in Sec. 5.1 of cerium in the  $\alpha$  and  $\gamma$  phases, where temperature is an essential ingredient in the complete picture. It is a luxury to be able to carry out a heavy many-body calculation like DMFT that can span the range of behaviors within one method, but the main point of the discussion in Sec. 5.1 is that we can understand the qualitative behavior using methods like DFT if we use clear guiding principles like the Luttinger theorem together with well-established properties of models such as the spectra of the Anderson impurity model and the temperature dependence in the Kondo effect. The same guiding principles help clarify the limitations of methods like the single-site approximation (or other approximations) in DMFT and help us understand the results.

The guiding principles emphasized here have many tentacles that reach into the very essence of the goal of making robust theories and conclusions that can be trusted. In all the cases described here, whether real materials or models, there is no rigorous proof that the calculations are the final answer. It is very difficult to prove that one has found the global minimum free energy state, i.e., there can be no state with a different type of order that is lower in free energy. Nevertheless, there are many very useful lessons to be learned and interesting results, if they are used judiciously. The combination of experiment, theory, and computational methods, each held to high standards, can provide solid understanding and even open doors to possible new states of matter.

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