The behaviour of magnetic impurities in metals has posed problems to challenge the condensed matter theorist over the past thirty years. This book deals with the concepts and techniques which have been developed to meet this challenge, and with their application to the interpretation of experiments.

After an introduction to the basic theoretical models, Kondo's explanation of the resistance minimum is described, which was the first of the major puzzles to be solved. As Kondo's perturbational calculations break down at low temperatures a non-perturbational approach is needed to predict the low temperature behaviour of the models, the so-called Kondo problem. The author surveys in some detail the many-body techniques, scaling, renormalization group, Fermi liquid and Bethe ansatz, which lead to a solution of this problem for most of the theoretical models. The book also deals with special techniques for N-fold degenerate models for rare earth impurities (including mean field and $1/N$ expansions). The theoretical framework having been established, a comparison is made between the theoretical predictions and the experimental results on particular systems in the penultimate chapter.

With the success of the many-body techniques developed to deal with impurity problems the new challenge is the extension of these strong correlation techniques to models with periodicity in order to understand the behaviour of heavy fermion and high T_c superconducting compounds. The work which has provided insights into heavy fermion behaviour is reviewed in the last chapter, together with the questions that need to be answered in future work.

This book will be of interest to condensed matter physicists, particularly those interested in strong correlation problems. The detailed discussions of advanced many-body techniques should make it of interest and useful to theoretical physicists in general.

The Kondo Problem to Heavy Fermions

CAMBRIDGE STUDIES IN MAGNETISM

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The Kondo Problem to Heavy Fermions

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Preface

This book charts the progress in the theory of magnetic impurities since the late 50s, from the early developments leading to the Kondo impurity problem and its solution to the challenging problems posed by the recent work on heavy fermions and the high temperature superconductors. The first eight chapters cover, largely in chronological order, the techniques which have been developed to deal with single impurity problems. Some of these techniques, such as Green's functions, Feynman diagrams and perturbation theory, are covered in standard many-body texts (for example, Fetter and Walecka, 1971: Abrikosov, Gorkov and Dzyaloshinski, 1975: Mahan, 1990). Others may be less familiar so for these techniques I have included general introductory sections in the relevant chapters, and some appendices with further details, in order to make the text as self-contained as possible. The aim has been to make the book readable at two levels. At the higher level I have tried to present the general development of ideas, the emphasis being on the results of the theory and the general physical picture that emerges. The equations at this level are included to make it clear how these results are obtained. I have tried to make it readable also at a second more detailed level by including enough information in the text and appendices so that one can work from one equation to the next. To do so might require quite an effort on the reader's part, and some further hints may be necessary from some of the references cited. If the reader is prepared to make the effort I think he/she will gain more of a working knowledge of the subject. I have in mind second and third year postgraduate students who might wish to extend their range of many-body techniques. What is to be learnt from the Kondo problem is that no one technique has all

the answers. Different formulations and different techniques have clarified different aspects of the problem, a composite picture has emerged which cannot be encompassed by one approach alone.

Chapter 1 deals with the basic models on which most of the work in this field has been based. It also covers some of the early theoretical concepts, such as the idea of a virtual bound state, and includes a derivation of the fundamental theorem of Friedel, known as the Friedel sum rule. Chapter 2 deals with the calculation of the resistivity due to impurities and gives in outline the perturbational calculation of Kondo that led to an understanding of the resistance minimum. Chapter 3 covers the period immediately after Kondo's discovery and the search for an acceptable theory of the low temperature behaviour of the s-d and Anderson models. The ideas of scaling, which provided the framework for the eventual solution of the problem, are described in this chapter and the 'poor man's' method of Anderson is considered in detail. This leads to the renormalization group approach of Wilson, which is introduced in chapter 4. This approach, which gave definitive results for the $S = \frac{1}{2}$ s-d model, is considered in detail based mainly on the seminal 1975 *Reviews of Modern Physics* paper. Insights into the nature of this solution are obtained via Fermi liquid theory, with a remarkably simple derivation of some of the basic results. This is described in chapter 5 where we give a derivation of the phenomenological theory of Nozières, and then outline the steps in the microscopic derivation by Yamada and Yosida. We later found a synthesis of these two approaches which we term 'renormalized perturbation theory', and this is described in appendix L.

The Bethe ansatz approach, which has been used to generate exact solutions for so many of the important magnetic impurity models, is introduced in chapter 6 with a survey of the results for the $S = \frac{1}{2}$ s-d model. The results for the non-degenerate Anderson model in the physically relevant parameter regimes are also described. Techniques for the N-fold degenerate model appropriate for systems with the rare earth impurities Ce and Yb are described in chapters 7 and 8. There is such a variety of techniques that can be applied to this model from the Bethe ansatz, Fermi liquid and various realizations of the large N or $1/N$ expansion methods that I decided to divide the material into two chapters. Chapter 7 gives an introduction to the $1/N$ expansion and the slave boson approaches. Chapter 8 deals with further developments, the self-consistent summation of diagrams (the non-crossing approximation, NCA), the effects of Gaussian fluctuations about the mean field theory, and the extensive calculations of Gunnarsson and Schönhammer on pho-

toemission spectra. This completes the section devoted mainly to the models and theoretical techniques. For those interested mainly in the results there is a brief summary of the main conclusions from chapters 3 to 8 in appendix K.

There is a different emphasis in the remaining chapters which are much less self-contained. Chapter 9 is concerned with the relation between theory and experiment. The theory for magnetic impurities has been successful in accounting for the broad features of the experimental results, the resistance minimum, the power law behaviour at low temperatures, the specific heat peak, and local moment behaviour at higher temperatures. There have been some detailed comparisons between theory and experiment for some specific systems where the agreement is very satisfactory. However, there is scope for more detailed work, particularly for the 3d transition elements. The aim of chapter 9 has been to see what is required for a closer dialogue between theory and experiment. To consider the likely modifications to the results of the simpler models on introducing crystal fields, orbital degeneracy, multiplet splittings, and to identify gaps where the present theory is incomplete. The experiments have been classified on various energy scales, but to keep the chapter within reasonable bounds (it is still rather long) only a selection of experiments has been considered on each energy scale. There are regrettably some obvious omissions such as electron spin resonance (ESR), and the effects of magnetic impurities on superconductors, and some types of experiments have been considered only very briefly.

The final chapter introduces a new generation of problems associated with systems where transition metal or rare earth ions interact with conduction electrons at many sites either in an alloy or a periodic lattice. Lattice models have been formulated to describe these systems in order to explain the behaviour of anomalous rare earth compounds and alloys. These anomalies are the most marked in compounds and alloys known as heavy fermion systems. Similar models have also been proposed to explain the behaviour of the high T_c superconductors. Having spent most of the time on problems which have now been largely solved I thought the balance should be restored by considering the problems which are largely unsolved: to end with more questions than answers. Techniques developed for the single impurity problem have provided some partial answers but much remains to be done. My hope is that the reader might be inspired by the imagination, ingenuity and physical insight of those who took on the challenge of the earlier problems, leading

to our present understanding outlined in chapters 1–8, to take on the challenge of these new problems.

Acknowledgments

I am indebted to present and former colleagues, Dennis Newns, David Edwards, Jawaid Rasul, Nick Read, Ule Desgranges, Lysandros Lysandrou, Theo Costi and Sarah Evans, and many others who over the years have been a source of stimulation and encouragement, and have increased my depth of understanding of this subject. I am also grateful to Natan Andrei, David Edwards and Veljko Zlatić for their encouragement and careful reading of early drafts of the manuscript. I also wish to thank Theo Costi for use of his renormalization group calculations prior to publication which have been used for several of the diagrams, and Nick Read for unpublished notes used in appendix D.

A few words of explanation on references

In covering subjects like the Kondo problem and heavy fermions for which there is such a vast literature the problem of which references to cite is an especially difficult one. I have found no good solution to this problem, but I have adopted a few guiding principles. In the course of describing a particular approach or work I have cited one or two papers (to keep these to a minimum) where the readers can if they wish find further details. The citation of a reference does not indicate priority for a particular work unless this is explicitly stated. The papers have been selected as ones most closely related to the approach I have used, or the ones most familiar to me. The earliest paper of an author on a particular topic is not always the one cited; a later paper may be referenced if I feel that is likely to be more helpful to the reader. Inevitably in trying to keep the number of references to within reasonable bounds much interesting related work will appear to have been overlooked (I apologize to any contributors to the field who feel that this applies to their work). The reader, however, is encouraged to use the references given as 'seed' references for use with the citation index. Used in this way, together with the reference list of the review articles quoted, they should be able to build up a comprehensive reference list to the whole field or any part of it which is of particular interest to them.

Imperial College, April 1992. A.C. Hewson

Preface to paperback edition

I welcome the opportunity that the new edition of this book gives for me to correct a number of minor slips and omissions that escaped my notice in the original text. I am grateful to the help given me by Dr Jan von Delft in compiling this list of corrections.

I have also used this occasion to add a short section in the form of an Addendum to cover some recent developments. The subject of strongly correlated electron systems continues to be a very active field of research so within the short space at my disposal I could only briefly mention some results that are particularly related to the topics covered in the original edition. However, I have also included references to some more recent review articles where a fuller discussion of these topics can be found, as well as references to other related work.

Imperial College, October 1995. A.C. Hewson

Brief History

There have been significant developments in the theory of magnetic impurities in metals in a period extending over more than 30 years. By magnetic impurities we mean those impurities that contribute a Curie–Weiss term to the susceptibility χ,

$$\chi = \frac{C}{T+\theta},$$

where T is the temperature and θ is a constant with a value in the thermal energy range ($0 < \theta < 300$ K). This term is in addition to the largely temperature independent Pauli susceptibility χ_{P} of the host metal. An isolated 'local moment', such as that due to a localized, but otherwise free, spin S, gives a Curie law ($\theta = 0$, $C = 4\mu_{\mathrm{B}}^2 S(S+1)/3k_{\mathrm{B}}$). Impurities which show Curie–Weiss behaviour are from the 3d transition element series or from the 4f rare earth series in the periodic table. Well studied examples are Fe in Cu, and Ce in $LaAl_2$ and LaB_6. The basic questions are: How does such a moment survive in the metallic environment ? How does it affect the conduction electrons of the host metal? Experimentally it is observed that such impurities give anomalous contributions to many metallic properties, particularly to the transport properties such as resistivity and thermopower, but also to the thermodynamic behaviour.

One manifestation of the effect magnetic impurities has been known since the early 30s. This is the observation of a resistance minimum in some metals (in most metals the resistivity monotonically decreases with decrease of temperature because it is dominated by phonon scattering which decreases rapidly at low temperatures). It was only recognized later that this minimum was an impurity effect associated with

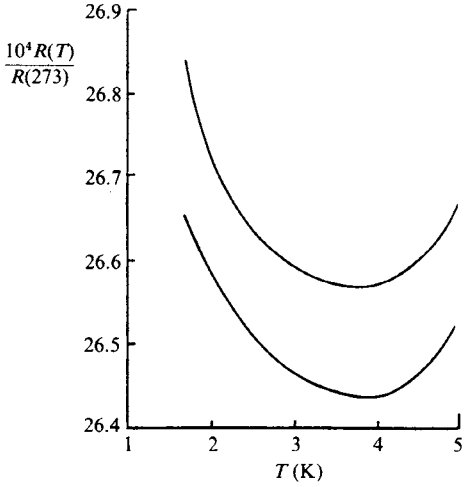

Figure 1 The minimum in the electrical resistivity of *Au* (de Haas, de Boer and van den Berg, 1934).

3d transition metal impurities such as *Fe*, dependent on the impurity concentration.

The resistance minimum as observed in *Au* is shown in figure 1, reproduced from the 1953 edition of *The Theory of Metals* by A.H. Wilson, one of the standard texts of this period. The reason for the minimum was not known at that time and Wilson comments, 'the cause of the minimum is entirely obscure and constitutes a most striking departure from Mathiessens's rule, according to which the ideal and residual resistances are additive — some new physical principle seems to be involved'. A very significant advance in the theory of magnetic impurities was an explanation of this effect by J. Kondo in 1964.

Early theoretical work on impurities in metals in the late 50s by J. Friedel and associates concentrated on explaining the trends in the behaviour as the impurity elements are varied across the transition element series. The most important concept to emerge from this work was that of 'virtual bound states' ; states which are almost localized due to resonant scattering at the impurity site. A different formulation of this idea was put forward by P.W. Anderson (1961), in a version now known as the 'Anderson model'; this model has played a very important role in the later developments of the theory. The model contains, in addition to a narrow resonance associated with the impurity states, a short range interaction U between the localized electrons. This interaction is needed to explain the observation of localized magnetic moments. Kondo's cal-

culation of the resistivity, which was to explain this minimum, was based on a model where it is assumed that there is already a local magnetic moment associated with a spin S which is coupled via an exchange interaction J with the conduction electrons. This is known as the s-d model; it can be deduced from the Anderson model in the appropriate parameter regime. Kondo (1964) showed, using third order perturbation theory in the coupling J, that this interaction leads to singular scattering of the conduction electrons near the Fermi level and a $\ln T$ contribution to the resistivity. The $\ln T$ term increases at low temperatures for an antiferromagnetic coupling and when this term is included with the phonon contribution to the resistivity it is sufficient to explain the observed resistance minimum. Hence the solution of a longstanding puzzle.

There were difficulties with the theory, however, as $\ln T$ terms diverge as $T \to 0$ so that it was clear that Kondo's perturbation calculations could not be valid at low temperatures. A more comprehensive theory was needed to explain the low temperature behaviour of systems giving resistance minima. The search for such a theory became known as the 'Kondo problem' and attracted a lot of theoretical interest in the late 60s and early 70s. Extension of the perturbation approach to the summation of the leading order logarithmically divergent terms, using many-body techniques developed in the 50s and 60s, proved to be inadequate. In the antiferromagnetic case this summation leads to a divergence at a finite temperature T_{K}, known as the Kondo temperature. The perturbation theory provided a good description of the magnetic impurity systems for $T \gg T_{\mathrm{K}}$, but could not be extended to the region $T \ll T_{\mathrm{K}}$. The challenge was, therefore, to find a non-perturbational technique to predict the behaviour for $T < T_{\mathrm{K}}$. The basic models, the s-d model and Anderson model, having only a local two-body interaction, seemed simple enough to hold out the possibility of finding exact solutions. Hence the wide theoretical appeal of the problem.

Experimental work during this period provided some clues for the theory. It was not a straightforward task to determine the behaviour associated with a single impurity, due to interimpurity interactions. These interactions become more of a problem at low temperatures, particularly for transition metals. Careful elimination of these interimpurity effects revealed that the impurity contributions to both thermodynamic and transport properties give power laws in T; the impurity resistivity and the susceptibility, for example, deviating from their $T = 0$ values by T^2 terms.

The theoretical framework for understanding these results was introduced by Anderson in the late 60s. The key idea was that of scaling. Anderson and coworkers showed that if the higher order excitations were eliminated perturbatively to give an effective model valid on a lower energy scale, the effective coupling between the local moment and the conduction electrons increased. Their approach being perturbational broke down when the coupling became large so that it could not be carried out down to the lowest energy scales, those which determine the behaviour in the regime $T \ll T_{\mathrm{K}}$. Nevertheless, close analogies with other systems indicated that this scaling could be continued, and that the coupling would increase indefinitely as the energy scale is reduced. Such a scaling behaviour would imply a ground state with an infinite coupling in which the impurity is bound to a conduction electron in a singlet state. The weak residual interactions, due to virtual excitations to the triplet state, which would come into play on a low energy scale, could then account for the observed power law behaviour. The behaviour at low temperatures would be similar to that of a non-magnetic impurity (the impurity spin having been compensated) but with enhanced coefficients in the power laws.

The important contribution by K.G. Wilson (1974, 1975), which was recognized in the award of a Nobel prize in 1982, was to devise a non-perturbative way, the 'numerical renormalization group', of confirming this hypothesis. Wilson took renormalization group ideas from field theory and scaling ideas from condensed matter, and constructed a powerful tool which he applied initially to problems of phase transitions, particularly to the calculation of critical exponents, and then later to the Kondo problem. Wilson obtained definitive results for the ground state and low temperature behaviour for the spin $S = \frac{1}{2}$ s-d model. One particularly simple result was for the χ/γ ratio of the impurity (γ is the low temperature specific heat coefficient) which he found was enhanced over that for non-interacting electrons by a factor of two. P. Nozières (1974, 1975) gave an interpretation of Wilson's low temperature results in terms of a form of Landau Fermi liquid theory, and also gave an appealingly simple derivation of the χ/γ result, as well as a exact calculation for the T^2 coefficient for the resistivity. A microscopic derivation of this Fermi liquid theory was derived by K. Yamada (1975) based on the Anderson model.

This period marked the end of a phase. The Kondo problem having been solved it appeared that all that was required was a tidying up operation, generalizing Wilson's results to deal with the complexities of more

realistic models for magnetic impurities, to include such terms as the orbital degeneracy of the 3d electrons and the effects of crystal fields. The method was applied to the non-degenerate Anderson model but generalization to models with more degrees of freedom was not an easy task, requiring greatly increased computing resources making it difficult to get satisfactory results. Both theoreticians and experimentalists looked for more exciting tasks.

Two developments in the late 70s and early 80s attracted interest back to the field, one theoretical, the other experimental. The theoretical development was the discovery of exact solutions to the s-d model $S = \frac{1}{2}$ by N. Andrei (1980) and P.B. Wiegmann (1980) using the Bethe ansatz, a hypothesis first used by H.A. Bethe in 1931 to solve the one dimensional Heisenberg model. This approach gave analytic results for the high and low temperature behaviour, and a set of integral equations from which the thermodynamic behaviour of the model could be calculated over the full temperature range. These results confirmed Wilson's calculations. More importantly the method proved to be generalizable to models of greater physical interest.

The experimental development was the study of dilute and concentrated alloys with rare earth elements such as cerium and ytterbium. These systems gave Kondo-like anomalies, similar to single impurity type behaviour, over a wide concentration range. The theoretical developments were timely because a generalization of the Anderson and s-d models appropriate to Ce and Yb systems, the Coqblin–Schrieffer model, could be diagonalized via the Bethe ansatz and exact results generated for comparison with experiment. There is a degeneracy factor N associated with the ground state multiplet of the impurity in the Coqblin–Schrieffer model and exact results revealed qualitatively different behaviour as a function of N, the susceptibility as a function of T, for example, develops a maximum for $N > 3$ (Ce, $N = 6$; Yb, $N = 8$).

For comparison with many of the experimental results, such as photoemission and neutron scattering, dynamic response functions are required. These functions cannot be calculated via the Bethe ansatz. Many approximate techniques, however, were developed in the 80s based on treating $1/N$ as a small parameter. Asymptotically exact results were generated in the limit $N \to \infty$, and good approximations obtained for finite N by a variety of methods; variational, diagram summation, and slave boson mean field calculations with Gaussian corrections. These methods were used to calculate the one electron density of states and the dynamic susceptibility. What they clearly showed was the build up

of a very narrow many-body resonance in the density of states at the Fermi level in the Kondo regime, known as the Kondo resonance. This very sharp resonance accounts for the low temperature anomalies caused by the magnetic impurities. As this resonance is the key insight into understanding the effects of magnetic impurities in metals it has been chosen as the cover illustration of this volume. The many-body calculations, giving exact results for the models or approximate ones within controlled approximations, have extended the range of theoretical predictions and enabled some quantitative comparison between theory and experiment to be made.

The similarities in the behaviour of a class of cerium intermetallic compounds and concentrated alloys to that of impurities and dilute alloys has led to these systems being known loosely as 'Kondo lattices'. Some of these compounds have such dramatically marked low temperature anomalies that they have become known as 'heavy fermions'. This is due to the very large specific heat coefficients which correspond to a large effective mass m^*, of the order 1000 times that of a free electron. Several actinide compounds, mainly of U, show similar behaviour and are included in this class. They show diverse forms of low temperature behaviour; some appear to be unconventional superconductors, some order magnetically, some do both and others seem to remain paramagnetic down to the lowest temperatures measured. There is evidence in certain compounds of a very weak form of antiferromagnetic order with tiny magnetic moments of the order of 10^{-2} Bohr magnetons. De Haas–van Alphen measurements in the paramagnetic phase show that these systems are Fermi liquids. There is as yet no generally accepted explanation for this range of behaviour. Self-consistent band calculations appear to account for the Fermi surface measurements in some cases but not for the very large effective masses observed. Many-body calculations, based on techniques developed for the impurity problem, predict 'renormalized bands' at the Fermi level, similar to the many-body Kondo resonance in the impurity density of states, but composed of coherent states due to the translational invariance of the lattice. These results may explain the enhanced masses; the superconducting and magnetic behaviour are still fully to be understood. It is a very active field in current research.

The anomalies in the magnetic impurity, Kondo lattice, and heavy fermion systems, are basically due to the strong correlations induced by the short range Coulomb interaction U at the transition metal and rare earth sites. There are similarities in the models used to describe these systems and those for the new high temperature superconductors,

such as $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-x}$. The very high T_c materials have CuO_2 planes in common and the effects of the Coulomb interaction U at the copper sites is believed by many to be the key to understanding their anomalous behaviour. They are likely to be technologically very important and are of great interest at the moment. Their behaviour so far is not well understood. Hence, the story of strongly correlated systems is an on-going one, throwing up fresh challenges. There is likely to be as much intellectual excitement in work in this field in the future as there has been over the past three decades.