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Preface

The article by Fulde, Thalmeier and Zwicknagl traces many of the recent developments in the field of strongly correlated many electron systems. It is very useful both as a reference and a pedagogical exposition since it places these developments into a historical context beginning with early developments in the electron theory of solids. Together with its extensive references and its formal elucidation of important theoretical subjects, the article supplies an excellent entry point into the field which is closely coupled to the classic works on the subject. Many early important ideas, such as Hückel and Heitler–London theory, the Wigner lattice, metal-insulator transitions originated in the thirties and were extensively developed in the sixties when it came to be realized that transition and rare earth metals with their characteristic d and f electrons respectively should be viewed as at least moderately strongly correlated systems requiring more sophisticated theoretical treatments than those supplied by the simplest band theories. The development of the relevant theories are associated with Hubbard and Mott among many others. They introduced model Hamiltonians, which were amenable to easily performed calculation whose results exhibited metal-insulator transitions for appropriate choices of the inter- and intra-atomic physical parameters. The Hubbard Hamiltonian, for example, motivated by lattices containing transition metal constituents has remained, in the authors' words one of the "working horses of many studies of strongly correlated" electron systems. Even though early conventional applications are limited to d electrons, many of the generic effects of strongly correlated electrons are captured by its solutions.

A principal impetus for the development of the field is associated with the discovery of high temperature superconductivity in copper-oxide based perovskites in 1986. Indeed, but for the strong electron correlations in hole-doped superconductors like $La_{2-x}Ba_xCuO_4$ would be metallic instead of insulating antiferromagnetic. It is the richness of the periodic table resulting from the presence of inner shell electrons in the heavier elements and their associated correlations that is responsible for these otherwise unexpected physical effects.

Although superconducting phenomena play an important role in the article, we stress that the principal topic concerns the more general behavior of strongly cor-

related electrons in solids. The article presents a detailed description of Kondo lattice systems and its associated heavy fermions, which preceded the discovery of high temperature superconductivity. It relates the results to a wide variety of experimental observations in real systems wherever possible. Readers having special interests in given heavy fermion materials will thus be well rewarded by browsing its pages and detailed figures of, for example, Fermi surfaces, photoemission results and phase diagrams.

The article begins with a detailed exposition of the physical features that characterize strong electron correlations, and presents a detailed description of the central feature associated with strong correlations leading to the presence of energy scales low compared to the typical metallic Fermi energy possibly resulting in deviations from Fermi-liquid behavior.

This introduction is followed by a detailed description of Kondo lattice systems which deal with magnetic impurities associated with spins embedded in a metal and interacting via exchange scattering. The understanding of Ce-based heavy Fermi systems present particular challenges. The authors describe theoretical techniques for describing such systems that combine *ab initio* approaches with a phenomenologically based Landau theory. A so-called renormalized band scheme is used for calculating realistic quasi-particle bands of materials grown and observed in the laboratory.

Quantum phase transitions in localized and itinerant magnetic systems characterize many systems of direct interest here. Quantum criticality in the Kondo lattice and scaling theory close to quantum critical points are discussed in considerable detail. Charge ordering, which began with the notion of crystallization first introduced in the 30s by Wigner was subsequently observed in 2D electron systems. Originating from a variety of effects, charge ordering can occur in many types of systems. For example, Yb_4As_3, which is discussed in considerable detail from both experimental and theoretical points of view in the present exposition, exhibits charge ordering associated with $4f$ holes. It illustrates the formation of heavy quasiparticles caused by spin chains without involvement of the Kondo effect.

Other subjects discussed here include partial localization found in some actinide-based heavy fermion compounds in which experiments are used to infer the co-existence of delocalized and localized $5f$ electrons, superconductivity mediated by intra-atomic excitations, geometrically frustrated lattices such as metallic spinels, fractional charges resulting from strong correlations, and high energy correlation induced excitations, for example, the appearance of shadow bands and satellites associated with nickel.

Because of its significant reliance on and comparison with experiment, its frequent use of phenomenologically based theory used to calculate quasi-particle band structures and Fermi surfaces, this article is to some extent less focussed on

fundamental microscopic theoretical aspects than on techniques leading to optimal physical insight permitting ready comparison with observations relevant to important materials systems. Clearly both types of expositions are needed.

The second article in this volume, by Bréchet and Hutchinson, concerns pattern formation in metals and alloys. Spontaneous pattern formation is the development of a regularity, either in the spatial distribution of the material in a system or in its development in time, of a lower symmetry than that of its cause. These phenomena have been of considerable interest to the non-linear physics community, in particular in fluid dynamics and in chemical reactions. This article deals with pattern formation in the solid state, which is comparatively less studied. Usually, crystal defects, such as dislocations or interfaces, play an important role and the energetic cost required by their formation requires that the system be prepared or maintained far from equilibrium.

Interface-mediated formation of lamellar microstructures from supersaturated solution is discussed as an example of chemical patterning in a system prepared far from equilibrium. Striking examples are the formation of pearlite and discontinuous precipitation. Grain growth, recovery and recrystallization are discussed as examples of defect pattering in a system prepared far from equilibrium. Grain growth is a rich topological subject, several aspects of which have been presented in earlier articles in this Series, such as that by Weaire and McMurry in vol. 50 and by Thompson in vol. 55.

Systems that are maintained far from equilibrium can be called "driven systems". Martin and Bellon have reviewed the chemical aspects of such systems in their article in vol. 50 of the Series. The present article therefore concentrates more on structural pattering in driven systems, such as the formation of arrays of dislocation loops and voids under irradiation or dislocation patterning in deformation.

Finally, plastic deformation provides an interesting example of pattering in both space and time: the Portevin–Le Chatelier effect, which is a stick-slip effect of plastic waves that move through the sample. The authors show that this can be usefully analyzed as a case of self-organized criticality.

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Strongly Correlated Electrons

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I. Introduction

The field of strongly correlated electron systems has been constantly growing for almost three decades. A milestone in its development was the discovery by Andres, Graebner and Ott[1] of heavy-quasiparticle excitations in $CeAl_3$. Additional verve came from the discovery of superconductivity in the related compounds $CeCu_2Si_2$,[2] UBe_{13}[3] and UPt_3.[4] But a real great push for the field was provided by the discovery of high-temperature superconductivity in the copper-oxide based perovskites.[5] Were it not for strong electron correlations La_2CuO_4, one of the key compounds of that class of materials and the basis of the hole doped superconductors $La_{2-x}Ba_xCuO_4$ and $La_{2-x}Sr_xCuO_4$ would be metallic. Instead it is an antiferromagnet which remains insulating even above the Néel temperature where the unit cell is not doubled anymore. Therefore, electron correlations are apparently so strong that the metallic character of the material is suppressed in favor of an insulating state. That electron correlation may induce a metal to insulator transition had been suggested long before the discovery of heavy quasiparticles and high-T_c cuprates. The names of Mott[6] and Hubbard[7] stand for that phenomenon. At their time the interests in the effects of strong correlations resulted from the transition metal oxides and their various phase transitions. It is

[1] K. Andres, J. E. Graebner, and H. R. Ott, *Phys. Rev. Lett.* **35**, 1779 (1975).
[2] F. Steglich, J. Aarts, C. D. Bredl, W. Liecke, D. Meschede, W. Franz, and H. Schäfer, *Phys. Rev. Lett.* **43**, 1892 (1979).
[3] H. R. Ott, H. Rudigier, Z. Fisk, and J. L. Smith, *Phys. Rev. Lett.* **50**, 1595 (1983).
[4] G. R. Stewart, Z. Fisk, J. O. Willis, and J. L. Smith, *Phys. Rev. Lett.* **52**, 679 (1984).
[5] J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 189 (1986).
[6] N. F. Mott, *Metal–Insulator Transition*, Taylor and Francis, London (1990), 2nd ed.
[7] J. Hubbard, *Proc. R. Soc. London A* **276**, 238 (1963).

worth recalling that the famous Verwey[8] transition in magnetite Fe_3O_4 falls into the same category. One may even go back to Wigner[9] or Heitler and London[10] who dealt with strongly correlated electrons long before corresponding experiments were available. While Wigner pointed out that electrons may form a lattice when their correlations become sufficiently strong, Heitler and London developed a theory for chemical bonding based on strongly correlated electrons. It is the opposite limit of Hückel's theory[11–13] based on molecular orbitals in which electron correlations are completely neglected. This raises the question of how to quantify the strength of electronic correlations. For example, one would like to know how much more strongly electrons are correlated in $LaCu_2O_4$ than, e.g., in iron or nickel or in transition metal oxides.

The differences between systems with strongly and with weakly correlated electrons may be seen by considering the ground state of the simplest possible example, i.e., of a H_2 molecule in the Heitler–London- and in the molecular orbital limit. The Heitler–London form of the ground-state wavefunction is

$$\psi_{\mathrm{HL}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}\big[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2)\big](\alpha_1\beta_2 - \beta_1\alpha_2) \tag{1.1}$$

where the single-electron wavefunctions $\phi_{1,2}(\mathbf{r})$ are centered on atoms 1 and 2 of the molecule and α and β denote spinors for up and down spins. In distinction to Eq. (1.1) the molecular-orbital form of the ground-state wavefunction is

$$\begin{aligned}\psi_{\mathrm{MO}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2^{3/2}}\big[&\phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2) + \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2) \\ &+ \phi_2(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\big](\alpha_1\beta_2 - \beta_1\alpha_2).\end{aligned} \tag{1.2}$$

It is seen that $\psi_{\mathrm{MO}}(\mathbf{r}_1, \mathbf{r}_2)$ but not $\psi_{\mathrm{HL}}(\mathbf{r}_1, \mathbf{r}_2)$ contains ionic configurations $\phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2)$ and $\phi_2(\mathbf{r}_1)\phi_2(\mathbf{r}_2)$. In Eq. (1.2) they have equal weight as the non-ionic configurations. But ionic configurations cost additional Coulomb repulsion energy of the electrons. Therefore they are completely suppressed in the Heitler–London- or strong correlation limit. This demonstrates an important feature of electron correlations, namely a partial suppression of electronic charge fluctuations on an atomic site. The former are called interatomic correlations because charge fluctuations at an atomic site are caused by an overlap of wavefunctions of

[8] E. J. W. Verwey and P. W. Haayman, *Physica* **8**, 979 (1941).
[9] E. Wigner, *Phys. Rev.* **46**, 1002 (1934).
[10] W. Heitler and F. London, *Z. Phys.* **44**, 455 (1927).
[11] E. Hückel, *Z. Phys.* **70**, 204 (1931).
[12] E. Hückel, *Z. Phys.* **72**, 310 (1931).
[13] E. Hückel, *Z. Phys.* **76**, 628 (1932).

different atoms. They are favored by a kinetic energy gain due to electron delocalization. Reducing them compared with uncorrelated electrons keeps the Coulomb repulsions small.

In addition to interatomic correlations we must also consider intra-atomic correlations. Consider an atom of a solid in a configuration with a given number of electrons, for example, a C atom in diamond with, e.g., 4 or 5 valence electrons. Those electrons will optimize their on-site Coulomb repulsions by arranging according to Hund's rules and by in-out correlations. Hund's rules ensure that electrons on an atom are optimally distributed over the angular segments of the atom, so that their repulsions are as small as possible. In-out correlations achieve the same by proper radial distribution of the electrons. Intra-atomic correlations are strongest for $4f$ electrons, i.e., for atoms or ions of the lanthanide series. But also in actinides or transition-metals they play a big role. Large overlaps with atomic wavefunctions of the chemical environment will weaken them. This is understandable: before the electrons can fully establish intra-atomic correlations they leave for the neighboring sites by hopping off the site. Interatomic correlations can be strong even when intra-atomic correlations are moderate or weak. Let us make a gedanken experiment and consider a Si crystal with artificially enlarged lattice parameter. The intra-atomic correlations on a Si site are fairly moderate, but the interatomic correlations are becoming strong when the lattice constant is increased, i.e., when the limit of separate atoms is approached. In that case fluctuations in the electron number at a site reduce to zero.

From the above considerations it follows that a suitable measure of the *interatomic* correlation strength is the reduction of electron number fluctuations on a given atom. An independent-electron or Hartree–Fock description implies too large fluctuations. Let $|\psi_0\rangle$ denote the exact ground state of an electronic system and $|\Phi_{\mathrm{SCF}}\rangle$ the corresponding self-consistent field (SCF) or Hartree–Fock (HF) state. The normalized mean-square deviation of the electron number n_i on atom i is given by

$$\Sigma(i) = \frac{\langle\Phi_{\mathrm{SCF}}|(\Delta n_i)^2|\Phi_{\mathrm{SCF}}\rangle - \langle\psi_0|(\Delta n_i)^2|\psi_0\rangle}{\langle\Phi_{\mathrm{SCF}}|(\Delta n_i)^2|\Phi_{\mathrm{SCF}}\rangle} \tag{1.3}$$

where $\Delta n_i = n_i - \bar{n}_i$ and $\bar{n}_i$ denotes the average value. One notices that $0 \leqslant \Sigma(i) \leqslant 1$. When $\Sigma(i) = 0$ the interatomic correlations vanish, i.e., the Coulomb repulsions between the electrons can be treated in mean-field approximation. In a solid atoms or ions with strongly correlated electrons have $\Sigma(i)$ values near unity. One can also define a correlation strength for different bonds instead of atoms. In that case the denominator is modified when heteropolar bonds are considered. Then we must subtract from $\langle\Phi_{\mathrm{SCF}}|(\Delta n_i)^2|\Phi_{\mathrm{SCF}}\rangle$ a term $(\Delta n)^2_{\mathrm{pc}}$. It takes into account that some number fluctuations are required even when the electrons are perfectly correlated in order to ensure a heteropolar charge distribution within

the bond. Let α_p denote the bond polarity. It is defined by the difference in the average occupation numbers of the two half-bonds 1 and 2 which form the heteropolar bond, i.e., $\bar{n}_{1(2)} = (1 \pm \alpha_p)$. In that case $(\Delta n)^2_{pc} = \alpha_p(1 - \alpha_p)$. Those considerations apply to a solid as well as to a molecule.

For the H_2 molecule one checks immediately that approximating $|\psi_0\rangle$ by $\psi_{MO}(\mathbf{r}_1, \mathbf{r}_2)$ gives $\Sigma = 0$ while a replacement by $\psi_{HL}(\mathbf{r}_1, \mathbf{r}_2)$ yields $\Sigma = 1$ since $\langle\psi_0|(\Delta n)^2|\psi_0\rangle = 0$ in that case. For a C=C or N=N π bond one finds $\Sigma \approx 0.5$ while for a C–C or N–N σ bond $\Sigma = 0.30$ and 0.35, respectively. Let us consider the ground state of La_2CuO_4 and let $P(d^\nu)$ denote the probability of finding ν $3d$ electrons on a given Cu site. Within the independent electron or Hartree–Fock approximation the average d count is found to be $\bar{n}_d \simeq 9.5$ and the probabilities of different configurations are $P(d^{10}) = 0.56$, $P(d^9) = 0.38$ and $P(d^8) = 0.06$. When correlations are included, i.e., the correlated ground state $|\psi_0\rangle$ is used the average d electron number changes to $\bar{n}_d \simeq 9.3$ and $P(d^{10}) = 0.29$, $P(d^9) = 0.70$ while $P(d^8) = 0.0$. One notices that the d^8 configurations are almost completely suppressed in agreement with photoemission experiments. The fluctuations between the d^9 and d^{10} configurations are fixed by the value of $\bar{n}_d$. A similar analysis for the oxygen atoms reveals that there the $2p^4$ configurations are *not* completely suppressed because the Coulomb integrals are not as large as for Cu. Indeed, these configurations are important for superexchange to occur, which determines the antiferromagnetic coupling between Cu ions. In accordance with the above consideration one finds $\Sigma(\text{Cu}) \simeq 0.8$ and $\Sigma(\text{O}) \simeq 0.7$.[14] So indeed, correlations are quite strong in La_2CuO_4. On the other hand, they are still smaller than those of $4f$ electrons in a system like $CeAl_3$.

A measure for the strength of intra-atomic correlations is more difficult to define. One way is by finding out to which extent Hund's rule correlations are building up on a given atomic site i. A possible measure for that is the degree of spin alignment at a given atomic site i

$$S_i^2 = \langle\psi_0|\mathbf{S}^2(i)|\psi_0\rangle \tag{1.4}$$

where $\mathbf{S}(i) = \sum_\nu \mathbf{s}_\nu(i)$ and $\mathbf{s}_\nu(i)$ is the spin operator for orbital ν. The quantity S_i^2 should be compared with the values when the SCF ground-state wavefunction $|\Phi_{SCF}\rangle$ is used and when instead the ground state $|\Phi_{loc}\rangle$ in the limit of complete suppression of interatomic charge fluctuations is taken, i.e., for large atomic distances. Therefore we may define

$$\Delta S_i^2 = \frac{\langle\psi_0|\mathbf{S}^2(i)|\psi_0\rangle - \langle\Phi_{SCF}|\mathbf{S}^2(i)|\Phi_{SCF}\rangle}{\langle\Phi_{loc}|\mathbf{S}^2(i)|\Phi_{loc}\rangle - \langle\Phi_{SCF}|\mathbf{S}^2(i)|\Phi_{SCF}\rangle} \tag{1.5}$$

[14] A. Oleś, J. Zaanen, and P. Fulde, *Physica B* **148**, 260 (1987).

as a possible measure of the strength of intra-atomic correlations. Note that $0 \leqslant \Delta S_i^2 \leqslant 1$. For example, for the transition metals Fe, Co and Ni ΔS_i^2 is approximately 0.5.

Those findings show that the much discussed transition metals are just in the middle between the limits of uncorrelated and strongly correlated electrons. Hund's rule correlations are important in them but relatively large overlaps of atomic wavefunctions on neighboring sites prevent their complete establishment. Starting from the work of Slater[15] and Van Vleck[16] in particular Friedel,[17] Gutzwiller,[18,19] Hubbard[20] and Kanamori[21] have discussed their effects in detail. One of the outcomes of the studies of transition metals is the Hubbard Hamiltonian. It was in fact used independently also by Gutzwiller and in a slightly modified version by Kanamori. This Hamiltonian was extensively treated in various approximations. The multiband Hubbard model has remained until present times the working horse of many studies of strongly correlated electrons.[22,23] The shortcomings of that model are known. For example, it considers d electrons only, i.e., s electrons are neglected. Also it cannot provide for orbital relaxations when electrons hop on or off a site because only one basis function per atomic orbital is used. Nevertheless, it is believed that it covers the most important generic effects of strongly correlated electrons.

The valence electrons which are most strongly correlated are the $4f$ ones because their atomic wavefunction is close to the nucleus and the tendency to delocalize is very small. In fact, in intermetallic rare-earth compounds only f-electrons in Ce or Yb ions show a noticeable degree of itineracy. The consequence are new low-energy scales which may appear in those compounds and as a result heavy-quasiparticle excitations. Not always do quasiparticles show conventional Fermi liquid behavior which governs the low-temperature thermodynamic properties of many metals. In a number of cases one observes what is called non-Fermi liquid behavior, i.e., quantities like the temperature dependence of the specific heat or of the susceptibility deviate from normal metallic behavior. In particular this holds true near a quantum critical point where apparently no characteristic energy scale is prevailing. Fermi liquid behavior requires that at low temperatures all thermodynamic quantities scale with $k_B T^*$, a characteristic energy which in

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