A number of methods are discussed which may serve for a treatment of electron correlations in solids. When the electron correlations are relatively weak like in semiconductors or a number of ionic crystals one may start from a self-consistent field calculation and include correlations by quantum chemical methods. An incremental computational scheme enables us to obtain results of high quality for the ground state of those systems. A number of examples demonstrates that explicitly.

Solids with strongly correlated electrons require the use of model Hamiltonians. With their help one can tackle the problem of determining spectral densities for those systems. The projection technique is a useful tool here. In strongly correlated $f$ electron systems electron or holes can crystallize with quite different physical consequences as in the case of a Wigner crystal or Verwey transition. Finally, different routes to heavy-fermion behavior are discussed, another hallmark of strongly correlated electrons.
I. INTRODUCTION

The problem of electron correlations is one of the most fascinating and challenging of condensed matter physics. It is also of great practical importance. An example is the energy gap of a semiconductor which we certainly would like to be able to calculate without any adjustable parameter. Its size depends crucially on electron correlations. Therefore we can hope to calculate it only if we are able to treat correlations without making uncontrolled approximations. Most people are unaware that this goal has not been reached yet. For a detailed understanding and accurate treatment of correlations it is mandatory to calculate the wavefunction of the ground state and the excited states of the electronic system. There are other powerful methods used in electronic theory which base their advantages by avoiding just that, like the density functional theory (DFT) and the local density approximation (LDA) to it [1-4]. The latter has been extremely successful and useful from various points of view. Its conceptual simplicity is particularly noteworthy. However, by construction it excludes detailed insight into the correlation problem which can be gained, e.g., by studying the pair-distribution function $g(r, r')$ of the system. The latter is defined by

$$g(r, r') = \frac{1}{\rho(r)} \frac{1}{\rho(r')} \left\langle \sum_{i \neq j} \delta(r_i - r_j) \delta(r_i - r') \right\rangle \Phi . \quad (1.1)$$

Here $\Phi$ is the ground-state wavefunction of the system, $r_i, r_j$ are the coordinates of the electrons and $\rho(r)$ is their density at point $r_i$. This function yields the probability of finding an electron at point $r_i$ provided there is one at point $r$, relative to the one without that constraint. It is therefore suitable for describing electrons which avoid each other in order to reduce their mutual Coulomb repulsion. This gives rise to a correlation hole which is associated with each electron. An accurate description of this correlation hole, in particular at small distances is the heart of the correlation problem. It is for that reason that the pair-distribution function is intimately connected with the exchange-correlation energy $E_{xc}[\rho]$ in density-functional theory. The relationship is

$$E_{xc}[\rho] = \frac{e^2}{2} \int d^3r d^3r' |\rho(r)|^2 \left( \frac{g(r, r') - 1}{|r - r'|} \right) \rho(r') \quad (1.2)$$

where $\tilde{g}(r, r')$ is related to $g(r, r')$ via

$$\tilde{g}(r, r') = \int_0^1 d\lambda g(r, r', \lambda). \quad (1.3)$$

The parameter $\lambda$ multiplies the interaction constant $e^2$ of the electrons, which enters $g(r, r')$, i.e., $e^2 \rightarrow \lambda e^2$ [5,6] when $g(r, r')$ is calculated. The simplicity of the LDA or comparable approximations to density functional theory results from making a reasonable ansatz for $g(r, r')$ instead of trying to calculate it from first principles.

Given that one aims at calculating the many-electron wavefunction of a periodic solid one is faced with a number of quantum-chemical methods which are designed to do just that for small molecules. Particularly well known are the Configuration-Interaction (CI) method [7], the Coupled Electron Pair Approximation (CEPA) [8-10], and the Coupled Cluster (CC) method [8,9,11,12]. These methods have in common that they start out from a self-consistent field (SCF) Hamiltonian $H_{SCF}$ and its ground-state wavefunction. Correlations are included by admixing SCF excited states to the ground state. For solids it is important to use methods which are size consistent, i.e., which yield a correlation energy proportional to the system size when the systems are large. This excludes the CI method which lacks that property. It is a variational method and therefore has the advantage of giving upper bounds to the energy. The size-consistency problem can be eliminated by expressing the energy in terms of cumulants [13,14]. This ensures that all approximations remain size consistent.

A SCF calculation will be a good starting point for a correlation calculation only when the correlations are not too strong. This will generally be the case for solids which involve $s$ and $p$ electrons only. When $f$ electrons come into play, or in many cases also $d$ electrons, then the electron correlations are usually so strong that a SCF wavefunction is not a good starting point for a computation of the exact wavefunction. In a molecular calculation the problem may be circumvented by starting instead from a multiconfiguration self-consistent field calculation (MC-SCF). By a proper choice of the active space (or of the different Slater determinants which are used) one can include the most important correlations already at that level and treat the remaining weaker ones by a subsequent CI or CEPA calculation. For a solid this is not possible because several configurations per lattice site would be required, i.e., their number would become infinitely large. Possibly, ways can be found in the future to solve this problem. At present, however, we...
depend on treating strongly correlated electrons by simplified model Hamiltonians. Therefore we will subdivide here the discussion of correlations into one of weakly and one of strongly correlated systems.

As regards weakly correlated systems another topic requires attention. When applying methods like CI or CEPA in molecular calculations, the excited states which are admixed with the SCF ground-state wavefunction are usually the SCF ones, which extend generally over the whole molecule. Going over to an infinite solid this would imply the admixture of infinitely many excitations (configurations) to the ground-state wavefunction \( | \Phi_{SCF} > \). On the other hand, it is evident that the correlation hole of an electron is a rather local object, which is confined to the immediate surroundings of it. Therefore, it should be described by local operators acting on \( | \Phi_{SCF} > \) or local excitations. This was first consequently done in Ref. [15]. The same ideas were later applied in slightly modified versions, e.g., in Refs. [16,17]. Working with local operators is also useful in order to limit efficiently the number of configurations one is admixing to \( | \Phi_{SCF} > \). This brings us to the concept of partitioning and projection which has been stressed by Löwdin [18]. Instead of constructing the exact ground state \( | \psi_0 > \) from \( | \Phi_{SCF} > \) by applying operators chosen from the full operator- or Liouville space \( \mathcal{R} \) one limits their choice to a relevant subspace \( \mathcal{R}_0 \). The latter must contain, e.g., all those local operators which are necessary in order to describe the correlation hole of the electrons with a required degree of accuracy. Thus, instead of expanding the ground-state energy in powers of the residual interactions \( H_{res} = H - H_{SCF} \) one partitions \( \mathcal{R} \) into a relevant part \( \mathcal{R}_0 \) and an irrelevant one \( \mathcal{R}_1 \) and projects the wave operators \( \sim \Omega \) defined by

\[
| \psi_0 > = \sim \Omega | \Phi_{SCF} >
\]

onto \( \mathcal{R}_0 \). Within that restricted space the ground-state wavefunction and energy are found by diagonalization of the Hamiltonian.

The concept of projection and partitioning can also be applied to the computation of Green’s functions [19]. This is very useful when we calculate the spectral density of a strongly correlated electron system described by a model Hamiltonian. The ones of Ni metal and of Cu – O planes, the most important structural element of the high \( T_c \) superconducting cuprates serve as examples here.

A particularly interesting phenomenon is that of electron or hole crystallization. The conditions for its occurrence were first determined by Wigner [20], who considered a homogeneous electron gas. A prerequisite for electron crystallization is that the electronic Coulomb repulsion dominates the kinetic energy, a condition fulfilled for a homogeneous electron gas only when the density is very low. In intermetallic rare-earth compounds the 4\( f \) electrons have a small kinetic energy even at large densities because of the small spatial extent of the 4\( f \) orbitals. Therefore, electron or hole crystallization is expected to occur in favourable cases even at high densities. There is clear evidence that \( Yb_4As_3 \) is an example of 4\( f \) hole crystallization at low temperatures [21,22].

One much investigated feature of strongly correlated electron systems is a high density of low-lying excitations. They involve predominantly spin degrees of freedom and lead to heavy-fermion behaviour (for reviews see [23-27]). There is a one to one correspondence between the low-energy excitations of a heavy fermion system and those of a nearly free electron system, provided one renormalizes the effective mass of the latter. The characteristic low-energy scale of a heavy-fermion system can be of different physical origin like the Kondo effect [28], the Zeeman effect [29] or quasi one-dimensional spin chains [30]. The materials \( CeAl_3 \) [31], \( Nd_{2-\delta}Ce_\deltaCuO_4 \) [32] and \( Yb_4As_3 \) [33] are examples for these three different physical cases.

\section{II. WEAKLY CORRELATED SYSTEMS}

We start out describing the formalism used for the calculation of the ground state and some of its properties of a weakly correlated electron system. This is followed up by a presentation of the results for a number of semiconductors and ionic crystals.

\section{II.1. Projection techniques}

In order to ensure size consistency in the sense described above we express all size-extensive quantities in terms of cumulants [13,14].

We divide the Hamiltonian \( H \) into two parts

\[
H = H_0 + H_1
\]

and assume that the ground state \( | \Phi_0 > \) of \( H_0 \) is known while \( H_1 \) must be treated approximately. In the case of weakly-correlated electron systems we shall identify \( H_0 \) with the self-consistent field Hamiltonian \( H_{SCF} \) and \( H_1 \) with

3
the residual interactions, but we prefer keeping the discussion of the projection technique more general. We write for
the ground-state energy

\[ E_0 = (H | \Omega) \]  

(2.2)

where

\[ \Omega = \lim_{z \to 0} \left( 1 + \frac{1}{z - L_0 - H_1} \right). \]  

(2.3)

Here the superoperator or Liouvillean \( L_0 \) refers to \( H_0 \), i.e., it acts on operators \( A \) according to

\[ L_0 A = [H_0, A]. \]  

(2.4)

The brackets in Eq. (2.2) are defined as follows

\[ (A | B) = <\Phi_0 | A^+ B | \Phi_0>. \]  

(2.5)

The upper script \( c \) indicates that the cumulant of that expectation value must be taken. The cumulant of a product
of operators is defined by

\[ <A_1 \ldots A_n>^c = \frac{\partial}{\partial \lambda_1} \ldots \frac{\partial}{\partial \lambda_n} ln <\prod_{i=1}^n e^{\lambda_i A_i}> \bigg|_{\lambda_1=\ldots=\lambda_n=0}. \]  

(2.6)

For two operators this expression reduces to

\[ <A_1 A_2>^c = <A_1 A_2> - <A_1><A_2>. \]  

(2.7)

Using cumulants requires care [34]. For example, we must distinguish between the number 1 and the unit operator \( 1_{\text{op}} \). The difference is

\[ <1 \cdot A>^c = <A> \quad \text{and} \quad <1_{\text{op}} A>^c = 0. \]  

(2.8)

From the properties of cumulants it follows that for any operator \( A \) (but not for \( c \) numbers) the following relation holds

\[ (A|H\Omega) = 0. \]  

(2.9)

The projection or partitioning method approximates \( |\Omega\rangle \) by admitting for its construction only operators from a
reduced relevant subspace \( \mathcal{R}_0 \) of the full operator space \( \mathcal{R} \). The operator \( \Omega \) is thus projected onto \( \mathcal{R}_0 \). The quality of
the approximation can be improved by successively increasing the dimension of \( \mathcal{R}_0 \).

Let \( \mathcal{R}_0 \) be of dimension \( r_0 \) and spanned by a set of operators \( \{A_\nu\} \) with \( \nu = 1, \ldots, r_0 \). We may choose the \( A_\nu \) to be orthonormal, i.e.,

\[ (A_\nu|A_\mu) = \delta_{\mu\nu}. \]  

(2.10)

The wave operator is then given by

\[ |\Omega\rangle = |1 + \sum_\nu \eta_\nu A_\nu). \]  

(2.11)

In case that all \( A_\nu \) couple directly to \( H_1 \), i.e., when

\[ (A_\nu|H_1) \neq 0 \quad \text{for all} \ \nu \]  

(2.12)

one may use Eq. (2.9) to determine the coefficients \( \eta_\nu \), i.e.,

\[ (A_\mu|H\Omega) = (A_\mu|H_1) + \sum_\nu \eta_\nu (A_\mu|HA_\nu) = 0. \]  

(2.13)

The solution of this set of equations can be written in the form
\[ \eta_\nu = - \sum_\mu L^{-1}_{\nu\mu} (A_\mu | H_1) \tag{2.14} \]

where

\[ L_{\rho\tau} = (A_\rho | H A_\tau). \tag{2.15} \]

The shift in the ground-state energy due to \( H_1 \) is given by

\[ \delta E_0(\mathcal{R}_0) = \sum_\nu \eta_\nu (H_1 | A_\nu) \tag{2.16} \]

\[ = \sum_\nu \epsilon(\nu). \]

The energy shift consists of a sum of contributions \( \epsilon(\nu) \) from the operators \( A_\nu \) which span the reduced Liouville space \( \mathcal{R}_0 \). If \( \{A_\nu\} \) contains operators which do not couple directly to \( H_1 \) implying that \( (A_\mu | H_1) = 0 \) for some \( A_\mu \), the latter enter only indirectly the calculations by modifying the coefficients \( \eta_\nu \). In that case they have the form of a generalized continued fraction [13].

In order to give an example, we identify \( H_0 \) with the self-consistent field Hamiltonian \( H_{SCF} \) of \( H \) and \( H_1 \) with the residual interaction part \( H_{res} \). We choose for the set \( \{A_\nu\} \) the single (S) and double (D) excitations out of the SCF ground state \( \Phi_{SCF} \). Single excitations are generated by \( \omega_\mu^i = c_\mu^+ c_\mu \) where the \( c_\mu^+ \), \( c_\mu \) operators destroy and create electrons in the molecular spin orbitals \( \phi_\mu \) and \( \phi_\mu \), respectively. It is common to use Greek indices for orbitals occupied in \( \Phi_{SCF} \) and Latin indices for unoccupied or virtual orbitals. Similarly, \( \omega_{\mu\nu}^{ij} \) describes double excitations. By using compound indices \( K \) and \( \Gamma \) we can write

\[ A_{K}^{\Gamma} = \begin{cases} \omega_{\mu}^i, & i < j \text{ and } \mu < \nu. \end{cases} \tag{2.17} \]

The energy shift (2.16) is here equal to the correlation energy \( E_{corr} \) and the \( \epsilon(\nu) \) are

\[ \epsilon(\Gamma) = \sum_K \eta^K_{\Gamma} (H_{res} | A_{K}^{\Gamma}). \tag{2.18} \]

The above choice of the operator set \( \{A_\nu\} \) and the form (2.18) of the individual contributions to the correlation energy are identical to the coupled-electron-pair-approximation (CEPA – O) in quantum chemistry.

It poses no problem to establish also a link between Eqs. (2.2, 2.9) and the Coupled-Cluster method which was originally developed in nuclear physics [12] but has been successfully applied also to quantum chemistry [8,11]. As has been shown in Refs. [34,35] \( | \Omega \rangle \) can be brought into the form

\[ | \Omega \rangle = | e^S \rangle \tag{2.19} \]

where \( S \) is a prime operator, i.e, one which is treated as an entity when cumulants are calculated. We may decompose \( S \) into

\[ S = \sum_\mu \eta_\mu S_\mu. \tag{2.20} \]

i.e., into a basis \( S_\mu \) of prime operators which have the additional property that \( S_\mu | \Phi_0 \rangle \neq 0 \). Prime operators \( A \) with \( A| \Phi_0 \rangle = 0 \) need no further consideration. The \( \eta_\mu \) are determined from \( (S_\mu | He^{S}) = 0 \). Identifying the \( S_\mu \) with the \( A_{K}^{\Gamma} \) (see Eq. (2.17)) we end up with the Coupled Cluster approach with single and double substitutions (CCSD).

II.2. Incremental method

We can perform correlation calculations of high accuracy for the ground state of semiconductors or insulators applying the method of increments [36-40].

Let us first consider the elemental semiconductors or the III-V and II-VI compounds which all have well defined bonds. We express \( \Phi_{SCF} \) in terms of (localized) Wannier orbitals rather than (delocalized) Bloch states. The Wannier orbitals define the different bonds I. The relevant operators are identified with the operators \( A_I(n) \) and
While that of the other one is the Wannier orbital. After the corresponding correlation energy \( \delta E_0 = \epsilon(I) \) has been determined from Eq.(2.16), one repeats the calculations by releasing electrons in bonds I and J. This yields a new correlation energy \( \delta E(I, J) \) or an increment

\[
\epsilon(I, J) = \delta E_0(I, J) - \epsilon(I) - \epsilon(J),
\]

as compared with the previous case. Thereafter, electrons in bonds \( I, J, K \) are released with the remaining ones kept frozen and so on. After each step a new correlation energy \( \delta E_0(I, J, K) \) etc. is obtained with corresponding increments

\[
\epsilon(I, J, K) = \delta E_0(I, J, K) - \epsilon(I, J) - \epsilon(I, K) - \epsilon(J, K) - \epsilon(I) - \epsilon(J) - \epsilon(K)
\]

and so on. The total correlation energy \( E_{\text{corr}} \) is then written in terms of the energy increments as

\[
E_{\text{corr}} = \sum_I \epsilon(I) + \sum_{<IJ>} \epsilon(I, J) + \sum_{<IKJ>} \epsilon(I, J, K) + ... \tag{2.24}
\]

where \( <IJ> \), \( <IJK> \) denotes pairs and triples of bonds, respectively. The advantage of this expansion is that the series is usually rapidly convergent [36] even when \( H_{\text{res}} \) is not small. It has been demonstrated that there are strong relations between the method of increments and Faddeev’s equations, provided the latter are properly generalized to a hierarchy of cumulant equations [34]. These relations enable us to state the size of the error when the series (2.24) is terminated at some point.

When ionic crystals are considered the increments refer to different ions instead of bonds. For example, the first increment to be calculated for \( MgO \) is the correlation energy attributed to an \( O^{2-} \) ion surrounded by \( Mg^{2+} \) and \( O^{2-} \) ions. An accurate modelling of the surroundings is essential, since an isolated \( O^{2-} \) is not stable. Similarly, the correlation-energy increment \( Mg \rightarrow Mg^{2+} \) has to be determined. The two-body increments involve pairs of \( O-O, O-Mg \) and \( Mg-Mg \) ions and so on.

An important point is the following. The matrix element \( (H_{\text{res}}|A^K_I) \) and \( (A^K_I|HA^K_I) \) which are needed to determine the correlation energy (see Eq. (2.18)) can be computed from clusters. When the cluster is chosen so large that a matrix element does not change any more, we are sure that its value is that for the solid. This enables us to apply quantum chemical program packages like MOLPRO [41] to determine them and hence the different correlation contributions.

### II.3. Results for semiconductors and ionic crystals

Starting point for the computation of the ground-state wavefunction and energy is a SCF calculation. Obtaining accurate SCF energies for solids is still a difficult computational task. Pisani and co-workers have developed the successful program package CRYSTAL [42] which allows for \( SCF - LCAO \) (linear combination of atomic orbital) calculations on periodic solids. It expands the Bloch orbitals in terms of Gaussian-type orbitals (GTO’s) and obtains the canonical SCF solutions. The latter can always be transformed to a localized representation by using a suitable localization procedure [43]. However, convergency problems are encountered when Gaussian functions with small exponents are used. An alternative ab-initio embedded-cluster approach has been developed within the framework of the LCAO method in which the localization procedure is part of the process leading to the SCF solutions [44]. Thereby the solid is modelled as a central cluster embedded in the field created by the remaining part of the infinite solid. Test calculations for \( LiH \) agree with those obtained from the CRYSTAL program, but large scale applications have not been performed yet.

A third possibility for obtaining the SCF ground-state wavefunction of a solid is by means of cluster calculations. A fragment of the lattice is used with dangling bonds saturated by hydrogen atoms. An example is
The calculated localized orbital for the central bond of the cluster can be used to very good approximation for every bond of the solid.

After the SCF ground-state wavefunction has been determined the correlation corrections are incorporated either on a CEPA – O (see Eqs. (2.17-18)) or CCSD (see Eqs. (2.19-20)) level, thereby applying the method of increments. We discuss first the results for the elemental semiconductors and the cubic III-V compounds before we turn our attention to the ionic crystals.

Semiconductors

The SCF calculations for the valence electrons are done with a basis set consisting of GTO’s. Its size is \((4s4p1d)/[3s3p1d]\) in standard notation, i.e., four s-like GTO’s are contracted into three orbitals and similarly for \(p\)-like functions. The inner shells are described by a quasirelativistic pseudopotential [45]. In some cases a polarization potential is added in order to account for the polarization of the inner shells by the valence electrons. For further details concerning the basis set we refer to the original literature [46]. The cohesive energy obtained within the SCF approximation is only between 55-72 % for the elemental semiconductors and between 55 - 67 % for the cubic III-V compounds (see Tables 1,2). Thus, even for these weakly correlated systems the correlation contribution to binding is appreciable. Lattice constants come out much better in SCF approximation, the errors being less than 2% (see Fig. 3). Bulk modulii are generally overestimated by up to 20 % (see, e.g., Table 4). For a treatment of correlations the basis sets have to be enlarged. Instead of using one set of \(d\) functions only, we use two sets of \(d\) functions and one set of \(f\) functions. The basis is therefore of size \((4s4p2d1f)/[3s3p2d1f]\) which is very respectable for diamond and silicon, but less for heavy elements like \(Ge\) or \(Sn\) because of low lying \(d\) states. Results for the cohesive energy of the group IV semiconducting and the cubic III-V compounds are listed in Tables 1 and 2, respectively. One notices that about 90 % of the binding energy are obtained in all cases. The missing percentage is due to basis set limitations. By including a second set of \(f\) functions and one set of \(g\) functions one would further improve the accuracy of the calculated values, in particular for the systems involving heavy atoms.

It is well known that bond lengths or alternatively lattice constants are relatively well reproduced by a SCF calculation. The same holds true for the group IV semiconductors as is seen from Table 3. The inclusion of a core polarization potential is important in order to come much closer to the experimental values. When correlations among valence electrons are included in the way described above the error for the lattice constant is less than 0.7 % in all cases.

The bulk modulus \(B\) is defined by

\[
B = \left( \frac{4}{9a^2} \frac{d^2}{da^2} - \frac{8}{9a^2} \frac{d}{da} \right) E_0(a)
\] (2.25)

where \(E_0(a)\) is the ground-state energy as function of the lattice parameter \(a\). As mentioned before, self-consistent field calculations overestimate generally \(B\). The core-polarization potential as well as the correlation energy lead to a decrease of \(B\) so that the final results are close to the experimental ones (see Table 4). This is easy to understand: when correlations are taken into account they keep electrons apart. Therefore an increase in pressure results in a smaller energy increase than obtained by a SCF treatment, where electrons come too close to each other at the expense of Coulomb repulsion energy.

We are particularly interested in trends concerning the interatomic correlation energy. The latter is obtained when a minimal basis set is used, i.e., one containing one set of \(s\) and \(p\) functions only. Correlations, which require for their description a larger than minimal basis set are termed intra-atomic [14]. Interatomic correlations reduce charge fluctuations between neighboring atoms. The simplest way of obtaining a good estimate of the one-bond and two-bonds increments is by making a bond-orbital approximation (BOA). In this approximation the ground state is written as a product of independent bonds containing two electrons each. In that case the interatomic correlation energy depends on the following quantities: the interaction matrix element \(V_0\) describing the difference of the Coulomb repulsion when two electrons are situated on the same atom and then they are placed on different atoms of the same bond; the electronic hopping matrix element \(t_0\) between atoms of the same bond; the van der Waals interaction, in simplest approximation between neighboring bonds, \(V_1\); the bond polarity \(\alpha\) in case of heteropolar bonds [52].

For the elemental semiconductors the bare hopping matrix element \(t_0\) scales with the tight-binding band width of the system. For diamond the value is \(t_0^C = 10.7 eV\) as obtained from band-structure calculations. We can determine the one for \(Si\), \(Ge\) and \(\alpha\) – \(Sn\) according to Froyen and Harrison [53] from the width of the LCAO bands. Once \(t_0\) is known the parameter \(V_0\) and \(V_1\) follow from the one-bond and two-bonds increments

\[
\epsilon(I) = -\frac{V_0}{4t_0} (1 - \frac{6V^2}{t_0V_0})
\]

\[
\epsilon(I, J) = -\frac{V_1^2}{t_0} (1 - \frac{V_0}{2t_0})
\] (2.26)
and \( \text{NiO} \) here, correlations contribute approximately 1/3 of the cohesive energy. We demonstrate this by studying and bulk modulus were done by applying the program package CRYSTAL. Results are found in Tables 6 and 7.

Before, the increments refer here to ions instead of bonds. SCF calculations for the binding energy, lattice constant

\[ E\text{corr}(\alpha) = (1 - \alpha^2)^\nu E\text{corr}(0) \]

(2.28)

between the interatomic correlation energy in the presence of the polarity \( E\text{corr}(\alpha) \) and the one calculated from \( t_0, V_0, V_1 \) without taking the polarity into account, i.e., \( E\text{corr}(0) \). In fact, the BOA predicts that \( \nu = 5/2 \). But, when one calculates \( E\text{corr}(0) \) from Eqs. (2.28) using the experimental values of \( d \) and compares it with the \( \text{ab initio} \) results using minimal basis sets one finds a value of \( \nu = 4.0 \pm 0.25 \). The difference between the two approaches is the following. In the BOA the excited electrons remain in their original bonds while in the ab initio approach excitations into other bonds are taken into account too. A simple estimate of the \text{intraatomic} correlation energy is more difficult. Using the values of the free atoms is a too rough method. One way is to apply an \text{atoms in molecules} approach originally suggested by Moffitt. It takes into account that the ratio of \( s \) and \( p \) electrons differs from that of a free atom when a solid is formed. Also, the electron number fluctuates when the atom is part of the solid and this is also accounted for in that approach. For more details we refer to the literature [14].

**Ionic crystals**

The calculations for the ground state of semiconductors described above can be extended to ionic crystals. Also here, correlations contribute approximately 1/3 of the cohesive energy. We demonstrate this by studying \( \text{MgO}, \text{CaO} \) and \( \text{NiO} \). Thereby we employ again the method of increments, but in distinction to the semiconductors considered before, the increments refer here to ions instead of bonds. SCF calculations for the binding energy, lattice constant and bulk modulus were done by applying the program package CRYSTAL. Results are found in Tables 6 and 7.

Correlation calculations are performed on clusters of one, two and three ions which are embedded in their proper surroundings. The \( X^{2+} (X = \text{Mg}, \text{Ca}, \text{Ni}) \) ions are described by small-core pseudopotentials and extended basis sets or a large-core pseudopotential together with a small basis set and a core-polarization potential. Test calculations for single ions show that the potentials describe very well the results of CCSD calculations with all-electron basis sets. The latter are in good agreement with the experimental values for the first and second ionization potentials \( X \to X^+, X^+ \to X^{2+}, \) in particular when they are supplemented by a perturbational treatment of the triplet excitations (CCSD(T)). For \( \text{NiO} \) we applied quasi degenerate variational perturbation theory (see Ref. [60]) for technical reasons: the MOLPRO program package does not allow for CCSD calculations of \( \text{NiO} \) with low spin.

The one-body increments are attributed to an \( O^{2-} \) and a \( X^{2+} \) ion. Consider first the \( O^{2-} \) ion. It must be embedded in a proper surroundings, since a free \( O^{2-} \) ion does not exist. Stabilization is achieved describing the six nearest neighbors by means of a pseudopotential. The crystal environment of the resulting seven-atom cluster is represented by 336 ions with point charges \( \pm e \) surrounding this cluster in form of a \( 7 \times 7 \times 7 \) cube. Employing a basis set \( 5 s 4 p 3 d 2 f \) one obtains the increment \( O \to O^{2-} \) shown in Table 8. It is noticed that it is nearly independent of the system considered. This is different for the increment \( X \to X^{2-} \) which increases from \( \text{Mg} \) to \( \text{Ca} \) to \( \text{Ni} \) (see Table 8). This can be understood by realizing that for \( \text{Ca} \) excitations into the low lying \( d \) orbitals are important while for \( \text{Ni} \) the correlation energy is further enhanced by near degeneracies of \( d \) orbitals. A more detailed picture of the one-body increments for \( \text{NiO} \) is shown in Fig. 1. For \( \text{MgO} \) and \( \text{CaO} \) the results are qualitatively similar.

Of particular interest are two-body increments. Hereby we have to distinguish between \( O \to O \), \( X \to O \) and \( X \to X \) increments. When the distance between the two sites becomes large, then in all three cases the increments describe van der Waals interactions of the ions. We show in Fig. 2 the \( O \to O \) increments for \( \text{MgO} \) for different distances. They do not contain their respective weight factors. Table 9 lists the different two-body increments for the three oxides.

Van der Waals interactions can be estimated with the help of London’s formula. It states that the lowering of the energy of two sites \( A \) and \( B \) due to van der Waals interactions is given by [62]

\[ \Delta E \approx -\frac{3}{2}\eta \frac{I_A I_B}{I_A + I_B} \frac{\alpha_A \alpha_B}{R^6}. \]

(2.29)

where \( I_A(B) \) are the ionization energies, \( \alpha_A(B) \) are the polarizability volumes, \( R \) is the distance between sites \( A \) and \( B \) and \( \eta \) is a constant of order unity. It relates a proper atomic mean-excitation energy to the ionization energy. In
Fig. 3 we have plotted the calculated values for the van der Waals interaction between positive and negative ions (circles) and between the negatively charged ions (crosses) when quantum-chemical methods are applied (here CCSD) and when London’s formula is used. The data can be roughly approximated by a straight line of slope 4. This suggests that Eq. (2.29) should be multiplied by a correction factor of order 4.

Three-body increments are very small. For the three oxides the sum of them is of order 0.03 eV (MgO) 0.05 eV (CuO) and 0.11 eV (NiO). In Fig. 4 a summary of the different increments to the cohesive energy of MgO is given. Table 6 summarizes the results for the cohesive energy for all three oxides. Table 7 does the same for the calculated lattice constants. It is found that correlations have two effects on the latter. The van der Waals interactions lead to a reduction of the lattice constant since the corresponding energy gain increases with decreasing distances. On the other hand, the correlation energy of $O^{2-}$ increases with increasing lattice spacing since the excitation energies are lowered in that case. Therefore, an increase of the lattice constant is favoured by that effect. This is opposite to what one would expect from the LDA because the density decreases as the lattice constant increases. We find that the calculated lattice constants deviate by less than 1 % from the experimental values.

Ground-state calculations based on quantum chemical methods are certainly more costly than those based on approximations to density-functional theory. However, they allow for systematic improvements by using larger basis sets. For the systems discussed here the quality of the results is certainly comparable with that of the generalized gradient corrected LDA.

In addition to the ground-state calculations one would like to be able to calculate the energy band for a system like NiO. For work in this direction see, e.g., Refs. [64, 65] and further references cited there.

III. STRONGLY CORRELATED ELECTRON SYSTEMS

In solids with $d$- or $f$- electrons the electron correlations are generally strong. In that case a SCF calculation is not a good starting point. This holds particularly true for $4f$ or $5f$ systems, but also a treatment of the electrons in the $Cu–O$ planes of the high-$T_c$ superconducting cuprates should include from the outset the strong on-site Coulomb interactions of holes in the $Cu 3d$ shell. Calculations of this kind can be presently done only with simplified model Hamiltonians. They all have in common that the basis set is a minimal one, or even less, like in the case of a one-band Hubbard model, which has been proposed for a study of $d$ electrons. From quantum-chemical calculations on small systems it is known, that a minimal basis set gives unsatisfactory results in almost all cases. Nevertheless, the hope has been that an understanding of the model systems will yield generic properties of strongly correlated electron systems which should prevail when eventually a more realistic description should become possible one day. This applies, in particular, to the low-lying excitations in those systems. It should be pointed out that the local-density approximation to the density-functional theory does not have basis set problems. Since the contributions to the energy are calculated from an exchange-correlation expression for a homogeneous electron gas, characteristic features of strongly correlated electrons as obtained, e.g., from a Hubbard Hamiltonian are not present in that approach. This changes partially when a LDA+U scheme is used [66], where an on-site repulsion term $U$ is added by hand to the systems energy. First, we describe the Hamilton operators most commonly used. Afterwards, we use them in order to calculate the spectral density for $Ni$ with special emphasis put on the reproduction of the observed satellite peak in photoelectron spectroscopy [67], and of doped $Cu–O$ planes which are part of the cuprates.

III.1. Model Hamiltonians

The most frequently used model Hamiltonian for strongly correlated electron systems, is the one first suggested independently by Gutzwiller [68], Hubbard [69] and Kanamori[70] and commonly referred to as Hubbard Hamiltonian. It is of the form

$$H = -t \sum_{<ij>} (a_{i\sigma}^+ a_{j\sigma} + h.c.) + U \sum_i n_{i\uparrow} n_{i\downarrow}. \quad (3.1)$$

The first term denotes the kinetic energy with $<ij>$ referring to a pair of nearest-neighbor sites. The second term refers to the on-site Coulomb repulsion with $n_{i\sigma} = a_{i\sigma}^+ a_{i\sigma}$. For strongly correlated systems the ratio $t/U \ll 1$. In that limit the Hamiltonian can be transformed into one acting on a reduced Hilbert space from which all configurations containing doubly occupied sites $i$ are excluded. This effective Hamiltonian is of the form [71]

$$H_{t-J} = -t \sum_{<ij>} (\hat{a}_{i\sigma}^+ \hat{a}_{j\sigma} + h.c.) + J \sum_{<ij>} (\hat{s}_i \cdot \hat{s}_j - \hat{n}_i \hat{n}_j) \quad (3.2)$$
and is called $t - J$ Hamiltonian. The $\hat{a}_{i\sigma}^\dag, \hat{a}_{i\sigma}$ operators act on the reduced Hilbert space only and are given in terms of the $a_{i\sigma}^\dag, a_{i\sigma}$ operators as

$$
\hat{a}_{i\sigma}^\dag = a_{i\sigma}^\dag (1 - n_{i-\sigma}), \quad a_{i\sigma} = a_{i\sigma} (1 - n_{i-\sigma}).
$$

(3.3)

The spin operators are $\hat{S}_i = (1/2) \sum_{\alpha\beta} \hat{a}_{i\alpha}^\dag \hat{S}_{\alpha\beta}^\dag \hat{a}_{i\beta}$ where $\sigma$ refers to the Pauli matrices. Furthermore, $\hat{n}_i = \sum_{\sigma} \hat{a}_{i\sigma}^\dag \hat{a}_{i\sigma}$ and the coupling constant is $J = 4t^2/U$. For transition metals a five-band Hamiltonian describing the rather strongly correlated $d$ electron is often used. It is of the form

$$
H = H_0 + \sum_\ell H_1(\ell)
$$

(3.4)

$$
H_0 = \sum_{\nu\sigma \ell} \epsilon_\nu(\ell) n_{\nu\sigma}(\ell)
$$

$$
H_1(\ell) = \frac{1}{2} \sum_{ijmn\sigma\sigma'} \sum_{\nu} V_{ijmn} \hat{a}_{i\sigma}(\ell) \hat{a}_{m\sigma'}(\ell) a_{n\sigma}(\ell) a_{j\sigma}(\ell)
$$

where $\ell$ is a site index and $i, j, m, n$ label different $d$ orbitals. The $\epsilon_\nu(\ell) (\nu = 1, ..., 5)$ describe the energy dispersions of the canonical $d$ bands. Furthermore, $n_{\nu\sigma}(\ell) = c_{\nu\sigma}^+(\ell) c_{\nu\sigma}(\ell)$. The creation operators $c_{\nu\sigma}^+(\ell)$ of the Bloch eigenstates are expressed in terms of the $a_{i\sigma}^\dag(\ell)$ as

$$
c_{\nu\sigma}(\ell) = \frac{1}{\sqrt{N}} \sum_{\ell} a_{\ell}(\nu, \ell) e^{i\ell R}.
$$

(3.5)

$(N$ is the number of sites). The interaction matrix elements are of the form

$$
V_{ijmn} = U_{im} \delta_{ij} \delta_{mn} + J_{ij} (\delta_{im} \delta_{jn} + \delta_{jm} \delta_{in})
$$

$$
U_{im} = U + 2J - 2J_{im}
$$

(3.6)

where $U$ and $J$ are average Coulomb- and exchange-interaction constants. For a cubic system the matrix $J_{ij}$ can be expressed in terms of the average exchange constant and a single anisotropy parameter $\Delta J$ only. The explicit form of the matrix is found, e.g., in Ref. [72].

For a description of electrons in the $Cu - O$ planes, the crucial structural element of the high-$T_c$ cuprates, a three-band Hubbard model is usually used. It takes into account only the $Cu 3d_{x^2-y^2}$ and the $O 2p_{x(y)}$ orbitals (see Fig. 5). Their orbital energies are $\epsilon_d$ and $\epsilon_p$. Two holes on a $Cu$ or $O$ site interact with an on-site Coulomb matrix element $U_d$ and $U_p$, respectively. The hopping matrix element between a $Cu$ orbital and an $O$ orbital is denoted by $t_{pd}$. Values for the different parameters can be obtained from constrained LDA calculations [73]. There is general consent that the following values are reasonable: $U_d = 10.5 eV, U_p = 4.0 eV, t_{pd} = 1.3 eV, t_{pp} = 0.65 eV, \epsilon_p - \epsilon_d = 3.6 eV$ (in hole representation).

Written in a basis of $O$ orbitals which is diagonal with respect to $O - O$ hopping, the three-band Hubbard Hamiltonian reads

$$
H = \sum_{m k \sigma} \epsilon_m(\ell) p_{m k \sigma}^+ p_{m k \sigma} + U_p \sum_j n_{p\uparrow}(j) n_{p\downarrow}(j) +
$$

$$
+ \epsilon_d \sum_{k\sigma} d_{k\sigma}^+ d_{k\sigma} + U_d \sum_I n_{d\uparrow}(I) n_{d\downarrow}(I) +
$$

$$
+ 2t_{pd} \sum_{m k \sigma} (\phi_{m k\sigma} p_{m k \sigma}^+ d_{k\sigma} + \phi_{m k \sigma}^* d_{k\sigma}^+ p_{m k \sigma}).
$$

(3.7)

Here $I$ and $J$ are indices for the $Cu$ and $O$ sites, respectively. Furthermore, $n_{p\sigma}(J) = p_{J\sigma}^+ p_{J\sigma}$ and $n_{d\sigma}(I) = d_{I\sigma}^+ d_{I\sigma}$. The $\epsilon_m(\ell)$ are given by

$$
\epsilon_m(\ell) = \epsilon_p \pm 2t_{pp} [\cos k(x_1 + x_2) - \cos k(x_1 - x_2)]
$$

$$
(m = 1, 2)
$$

(3.8)

with vectors $x_1, x_2$ pointing from a $Cu$ site to the two $O$ sites of the unit cell. The phase factors $\phi_{m k}$ are
\[ \phi_{m\mathbf{k}} = \frac{-i}{\sqrt{2}} [\sin kr, \pm \sin kr]. \] (3.9)

The model Hamiltonians (3.4) and (3.7) are used in the following in order to calculate the spectral density of \( Ni \) and of the \( Cu - O \) planes, respectively. In both cases the Coulomb repulsion exceeds the hopping-matrix elements and therefore a simple perturbation expansion in terms of the interactions is not sufficient. Instead, the large interactions must be taken into account more accurately. This goal is achieved by applying projection techniques.

### III.2. Spectral densities

Spectral densities can be measured either by photoelectron emission (PES) or inverse photoemission spectroscopy (IPES). They are calculated from the positions and intensities of the poles of the single-particle Green’s function. One way of determining those poles is treating numerically small clusters, e.g., by means of the Lanczos method [74]. Thereby periodic boundary conditions are assumed. Here we shall proceed differently. Using projection and partitioning techniques we are able to do the calculations analytically to a large extent with some numerical work remaining. The latter is by far less than the one in the numerical approaches mentioned before.

We start out describing the projection technique as applied to the calculation of spectral densities. Consider a set of wave-number dependent operators \( A_m(\mathbf{k}) \) in Heisenberg representation, i.e., with a time dependence given by

\[ A_m(\mathbf{k}, t) = e^{it(H-\mu N)} A_m(\mathbf{k}) e^{-it(H-\mu N)}. \] (3.10)

Here \( H \) denotes the Hamiltonian of the system while \( \mu \) is the chemical potential and \( N \) is the operator of the total electron number. Using a grand-canonical ensemble and working with a fixed value of \( \mu \) has the advantage that the calculations can be readily extended to finite temperatures.

We define a matrix of retarded Green’s functions \( G_{mn}(\mathbf{k}, t) \) for the set of operators \( A_m(\mathbf{k}) \) through

\[ G_{mn}(\mathbf{k}, t) = -i \theta(t) < \psi_0 | [A_m^+(\mathbf{k}, t), A_n(\mathbf{k})]_+ | \psi_0 > \] (3.11)

where \( \psi_0 \) is the ground state of the system described by \( H \) while \( \theta(t) \) is the step function which equals 1 for \( t > 0 \) and 0 for \( t \leq 0 \). Introducing the bilinear form

\[ (A|B)_+ = < \psi_0 | [A^+, B]_+ | \psi_0 > \] (3.12)

we can write the Laplace transform of Eq. (3.11) in the form

\[ G_{mn}(\mathbf{k}, z) = (A_m(\mathbf{k}) \frac{1}{z-L} A_n(\mathbf{k}))_+. \] (3.13)

The Liouvillean \( L \) acts on operators \( A \) according to

\[ LA = [H, A]_- \] (3.14)

The spectral functions \( A_{mn}(\mathbf{k}, \omega) \) belonging to the set of operators \( \{ A_m(\mathbf{k}) \} \) are defined according to

\[ A_{mn}(\mathbf{k}, \omega) = -\frac{1}{\pi} \lim \eta \rightarrow 0 \text{Im} \{ G_{mn}(\mathbf{k}, \omega + i\eta) \}. \] (3.15)

Equation (3.13) is in a proper form for applying projection and partitioning techniques. The idea of partitioning was put forward by Löwdin [18] and applied in particular by Pickup and Goswinski [75] and Linderberg and Öhrn [76]. Projection techniques were also introduced by Mori and Zwanzig for the description of dynamical correlation functions. Here we will use an extension of the technique to static quantities in a form which is size consistent [13,14].

We proceed as follows: We add (or remove) an electron in a Bloch state of the system for which we want to compute the spectral density. One of the \( A_m(\mathbf{k}) \) is identified with the corresponding creation (annihilation) operator. The strong correlations are taken into account by a proper choice of local operators to which the added electron (hole) couples strongly. They modify the surroundings of the electron added to the probe (IPES) or of the hole left behind by an ejected electron (PES). We identify the most important of these processes from case to case and, after a Fourier transformation, include the corresponding operators in the set \( \{ A_m(\mathbf{k}) \} \). Examples are given later when the theory is applied to \( Ni \) and the \( Cu - O \) planes. All other microscopic processes are discarded. The operator space \( \Re \) is partitioned this way into a relevant part \( \Re \) spanned by the \( \{ A_m(\mathbf{k}) \} \) and an orthogonal, irrelevant part \( \Re_1 \) which
is neglected. The desired spectral density is then obtained from one of the diagonal elements of the Green’s function matrix \( G_{mn}(\mathbf{k}, \omega + i\eta) \) (see Eq. (3.15)). We rewrite Eq. (3.13) in matrix notation as

\[
G(k, \omega) = \chi(k)\chi(k) - \omega(k)^{-1}\chi(k)
\]  

(3.16)

with the susceptibility and frequency matrix defined by

\[
\chi_{mn}(k) = (A_m(k)|A_n(k))_+ \quad (3.17)
\]

\[
\omega_{mn}(k) = (A_m(k)|LA_n(k))_+ ,
\]

respectively. There is no memory matrix appearing in Eq. (3.15) because we neglect \( R_1 \).

The matrix elements (3.17) can be evaluated in two different ways. One consists in using a general relationship between spectral functions and static expectation values. For the present case it can be written in the form

\[
<\psi_0|A_m^+(k)A_n(k)|\psi_0> = \int_{-\infty}^{+\infty} d\omega A_{mn}(k,\omega)f(\omega).
\]  

(3.18)

Here \( f(\omega) \) is the Fermi function which can be replaced by a step function. With the help of this relation the static expectation values (3.17) can be determined self-consistently. The second way of evaluating them is by applying the projection technique also to these static quantities. Thereby one uses the following relations

\[
<\psi_0|A_m^+(k),A_n(k)|\psi_0> = (\Omega[A_m^+(k),A_n(k)]_+\Omega)
\]

(3.19)

\[
<\psi_0|A_m^+(k),LA_n(k)|\psi_0> = (\Omega[A_m^+(k),(LA_n(k))_+\Omega]
\]

which are derived, e.g., in Ref. [14]. The round brackets and \( \Omega \) are defined by Eqs. (2.5) and (2.3), respectively. The notation \((AB)\) implies treating the product \( AB \) as an entity when the cumulant is calculated. This completes the description of the projection technique as applied to Green’s function calculations. When the theory is applied, a proper choice of the operator set \( \{A_m(k)\} \) and of \( \Omega \) is crucial.

### III.3. Application to 3d transition metals

We apply the above theory in order to calculate the direct and inverse photoemission spectra of 3d transition metals with special reference to \( Ni \). It has been known for a long time that electronic correlations influence considerably the excitation spectra of these materials. A well studied case is that of \( Ni \), where angular-resolved photoemission data reveal a 25 % reduction in bandwidth as compared with LDA bandstructure calculations and also the appearance of a satellite structure 6 eV below the Fermi energy [77]. A number of different investigations have dealt with these experimental findings. Starting with the work of Kanamori [70], different methods have been applied by Penn, Liebsch, Igarashi, Roth, Hertz and Edwards and others [78-82]. We will show that the projection technique is here a valuable tool leading to satisfactory results for \( Ni \) [83].

We start from the Hamiltonian (3.4) for the 3d electron and identify the \( \epsilon_k(L) \) with the canonical \( d \) bands obtained, e.g., from a LDA calculation. The spectral density is obtained from the retarded Green’s functions

\[
G_{\nu\sigma}(k, t) = -i\Theta(t) <\psi_0|c_{\nu\sigma}(k, t),c_{\nu\sigma}^+(k, 0)> .
\]  

(3.20)

We project again onto the relevant part \( \Re_0 \) of the Liouville space spanned by a set of operators \( \{A_m(k)\} \), one of which is \( c_{\nu\sigma}^+(k) \). The associated Green’s function matrix is again of the form of Eq. (3.13) which is rewritten as in Eq. (3.16). The susceptibility and frequency matrix are of the form of Eq. (3.19), i.e.,

\[
\chi_{mn}(k) = (\Omega[A_m^+(k),A_n(k)]_+\Omega) \quad (3.21)
\]

\[
\omega_{mn}(k) = (\Omega[A_m^+(k),(LA_n(k))_+\Omega).
\]

The ground state \( |\Phi_0> \) onto which \( \Omega \) is acting is here the nonmagnetic SCF ground state of \( H \), i.e.,

\[
|\Phi_0> = \prod_{\nu\sigma,|k|<k_F} c_{\nu\sigma}^+(k)|0> .
\]  

(3.22)
The strong correlations are taken into account by including in the set of \( \{ A_m(\mathbf{k}) \} \) the Fourier transforms of a number of local, on-site operators. They are

\[
A_
{ij}^{(1)}(\ell) = \begin{cases} 
2a_i^\dagger(\ell)\delta n_{ij}(\ell), & i = j \\
a_i^\dagger(\ell)\delta n_j(\ell), & i \neq j 
\end{cases} \quad (3.23)
\]

\[
A_
{ij}^{(2)}(\ell) = \frac{1}{2}(a_i^\dagger(\ell)s_j^\dagger(\ell) + a_i^\dagger(\ell)s_j^\dagger(\ell)) 
\]

\[
A_
{ij}^{(3)}(\ell) = \frac{1}{2}a_i^\dagger(\ell)a_j^\dagger(\ell)a_{ij}(\ell). 
\]

The notation \( \delta n_{\sigma \sigma}(\ell) = n_{\sigma \sigma}(\ell) - \langle n_{\sigma \sigma} \rangle \) and \( s(\ell) = (1/2)\Sigma_{\alpha \beta}e_{\alpha \alpha}^\dagger(\ell)\varphi_{\alpha \beta}a_{\beta}(\ell) \) has been used here. The selected \( A_m(\mathbf{k}) \) consist therefore of \( A_0^{(0)}(\mathbf{k}) = c_{\gamma}^\dagger(\mathbf{k}) \) and

\[
A_
{ij}^{(r)}(\mathbf{k}) = \frac{1}{\sqrt{N}}\sum_{\ell}A_
{ij}^{(r)}(\ell)e^{i\mathbf{kR}} 
\]

\[
r = 1, 2, 3. 
\]

For a given value of \( \mathbf{k} \) the total number of relevant operators is 66. This requires the diagonalization of a 66 x 66 matrix for each \( \mathbf{k} \) point. In order to evaluate the matrix elements we must first specify the wave operator \( \Omega \). In accordance with Eq. (2.11) we make the ansatz

\[
|\Omega\rangle = |1 + \sum_{ij\ell}\eta_{ij}\delta O_{ij}(\ell)\rangle 
\]

where the local operators \( \delta O_{ij}(\ell) \) are given by

\[
\delta O_{ij}(\ell) = \begin{cases} 
2\delta n_{ij}(\ell)\delta n_j(\ell), & i = j \\
\delta n_i(\ell)\delta n_j(\ell), & i \neq j 
\end{cases} \quad (3.26)
\]

The operators \( \varphi_{ij}(\ell) \) generate Hund’s rule correlations in the ground state of a transition metal, while the other two types of operators reduce fluctuations of charges from their average values, thus rendering the Coulomb repulsions less effective. More details are found, e.g., in Ref. [14]. The resulting spectrum for \( Ni \) is shown in Fig. 6. All parameter values are in units of the SCF bandwidth \( W \). They are obtained by fitting the measured multiplet structure of transition-metal ions embedded in simple metals [84]. Shown is the SCF density of states and the modifications which are obtained when the correlations are included. In order to bring out more clearly the changes caused by the different interactions we show in Fig. 6 c the special case where the exchange constant \( J \) as well as the anisotropic exchange parameter \( \Delta J \) have been set equal to zero. When \( J = \Delta J = 0 \) one obtains only one quasiparticle and one satellite peak for each \( \mathbf{k} \) point and given band index \( \nu \). The satellite peak in the density of states reflects the \( e_g - t_{2g} \) splitting caused by the ligand field. When \( J \) is included, but \( \Delta J = 0 \) new spectral density appears near -2.1 and -0.7. This reflects the atomic \( d^2 \) (hole) multiplet which splits into a \( 1S \) state, two degenerate singlets \( 1G \) and \( 1D \) and two degenerate triplets \( 3P \) and \( 3F \). The splitting energy between \( 1S \) and \( 1G \) is 5J while the one between \( 1G \) and \( 3F \) is 2J. The spacings between the structures at -2.1, -1.1 and -0.7 are of comparable size. Inclusion of \( \Delta J \neq 0 \) splits the main satellite at -1.1 into smaller peaks. We also show in Fig. 6c the modifications in the spectrum which arise when we set \( \Omega = 1 \), i.e., when we neglect the correlations in \( |\psi_0\rangle \) and replace it by the SCF ground state \( |\Phi_0\rangle \). In conclusion, we may state that the correct position of the satellite peak as well as a band narrowing by 15 % are obtained when experimentally determined parameters for the interactions are used. The band narrowing is less than the observed one which is approximately 25 %.

The spectral density of \( Ni \) can also be calculated by using Faddeev’s equations [85]. The results resemble the ones presented here but they are not identical [86]. Faddeev’s equations also contain three-particle correlations which have not been included here. A serious deficiency of the model is the neglect of the 4s band. This might explain some discrepancies which arise when the present theory is applied to other 3d transition metals. For example, we also obtain multiplet structured satellites in the spectra of \( Co \) and \( Fe \) when we use the Coulomb parameters as determined from optical experiments. However, such structures have not been observed in photoemission experiments. Further details can be found in Ref. [83].

The long-term goal is certainly an extension of the theory to larger basis sets. One would also like to take systematically into account correlations between sites, an extension not yet tried for the 3d transition metals. In principle, the projection technique is a very suitable tool for modern computing.
III.4. Spectral functions of Cu – O planes

The Hamiltonian for the electrons in the Cu – O planes of cuprates has been discussed before (see Eq. (3.7-9)). The main task for obtaining the spectral densities is the proper choice of the set of relevant operators \( \{ A_m(\mathbf{k}) \} \).

The strong electron correlations, which must be accounted for, determine the selection of these operators. They must include, first of all, the hole operators

\[
A_p(m, \mathbf{k}) = p^+_{m\mathbf{k}I}, \quad A_d(\mathbf{k}) = d^+_{\mathbf{k}I}
\]

(3.27)

but also the Fourier transforms of a number of local operators, which generate the correlation hole surrounding the added particle or hole. To those belong the Fourier transforms \( p^+_{m\mathbf{k}I} \), \( d^+_{\mathbf{k}I} \) of the local operators \( p^+_{\mathbf{I}} = p^+_{\mathbf{I}\uparrow} \) and \( d^+_{\mathbf{I}} = d^+_{\mathbf{I}\uparrow} \) (\( J \)), respectively. They ensure reduced weights of configurations with doubly occupied \( Cu \) and \( O \) orbitals, a consequence of the Coulomb repulsions \( U_d \) and \( U_p \). Additional microscopic processes to be included are defined by the operators \([87]\]

\[
A_f(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_I e^{-i\mathbf{R}_I} p^+_{\mathbf{I}\uparrow} S^+_{\mathbf{I}}
\]

\[
A_a(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_I e^{-i\mathbf{R}_I} p^+_{\mathbf{I}\uparrow} n_{\mathbf{d}I}(I)
\]

\[
A_c(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_I e^{-i\mathbf{R}_I} p^+_{\mathbf{I}\uparrow} p^+_{\mathbf{I}\downarrow} d_{\mathbf{I}I}.
\]

(3.28)

The \( N \) different unit cells have been labeled by \( I \) and their lattice vectors by \( \mathbf{R}_I \). The operator \( S^+_{\mathbf{I}} = d^+_{\mathbf{I}\uparrow} d_{\mathbf{I}\downarrow} \) describes a spin flip of a hole in the \( 3d_{x^2-y^2} \) orbital of site \( I \). The operator \( p^+_{\mathbf{I}\uparrow} \) refers to the combination

\[
p^+_{\mathbf{I}} = \frac{1}{2}(p^+_{\mathbf{I}\uparrow} - p^+_{\mathbf{2}\uparrow} - p^+_{\mathbf{3}\uparrow} - p^+_{\mathbf{4}\uparrow})
\]

(3.29)

of the four \( O \) orbitals surrounding \( Cu \) site \( I \). The operator \( A_f(\mathbf{k}) \) ensures inclusion of processes, which result in the formation of a singlet state between a hole on a \( Cu \) site and another one in a nearest-neighbor \( O \) orbital (Zhang-Rice singlet [88]). The operator \( A_a(\mathbf{k}) \) does the same for the triplet state while \( A_c(\mathbf{k}) \) takes charge transfer processes in the vicinity of the added particle (hole) into account. With this choice of a total of nine relevant operators a 9 x 9 matrix \( G_{mn}(\mathbf{k}, \omega) \) must be diagonalized for each \( \mathbf{k} \) point. Thereby the self-consistency condition (3.18) is used throughout. The resulting densities of states for the case of half-filling (corresponding to \( La_2CuO_4 \)) and of hole doping (e.g., \( La_{2-x}Sr_xCuO_4 \)) agree very well with those obtained from numerical diagonalization of a cluster of four units of \( CuO_2 \) [89,90] (see Figs. 7, 8). This proves the usefulness of the method. As seen from those figures the half-filled system is insulating. The structure around 2.5 \( t_{pd} \) results from the singlet state, while the one at 5\( t_{pd} \) represents the upper Hubbard band. When the system is doped (see Fig. 8) spectral density is moved from the upper Hubbard band to the region close to the Fermi energy. The system is then metallic. In electron-doped systems like \( Nd_{2-x}Ce_xCuO_4 \) the Fermi level is in the upper Hubbard band. In that case spectral density is shifted from the singlet states to the upper Hubbard band which can accommodate an increasing number of electrons as the doping increases. When the hole concentration approaches zero, the system has a total spectral weight of 2 as compared with the half-filled case where this weight is 1. For more details we refer to Ref. [87].

IV. ELECTRON CRYSTALLIZATION

In metals the kinetic energy of the electrons is usually more important than their mutual Coulomb repulsion. This is due to Pauli’s principle which results in Fermi energies of the order of a few eV. However, this changes when the electron concentration is very low. Let \( r_0 \) denote the mean radius of the volume an electron has available, i.e., define \( r_o \) via \((4\pi/3)r_o^3 = \rho^{-1} \) where \( \rho \) is the electron density. The average kinetic energy \( \delta\epsilon_{kin} \) of an electron due to the uncertainty relation is \( \delta\epsilon_{kin} = (\Delta p)^2/2m \sim 1/(2mr_0^2) \). But the average Coulomb repulsion is \( \delta\epsilon_{pot} \sim \epsilon^2/r_0 \) and therefore larger than \( \delta\epsilon_{kin} \) in the limit of large \( r_0 \) or low densities. By considering a homogeneous electron gas with the positive charge uniformly spread over the system (jellium model) Wigner [20] discussed the form of the ground state in the low-density limit and concluded that electrons crystallize in form of a lattice in order to keep the Coulomb repulsion as low as possible. The kinetic energy reduces to the zero-point motion of the electrons around
their equilibrium position. The change from a homogeneous to an inhomogeneous electron charge distribution takes place at a value of approximately $r_0/a_B \approx 40 - 100$ where $a_B$ is the Bohr radius. At those densities the electrons are sufficiently far apart that the exchange plays only a minor role because of its exponential decrease with distance. The excitations are given by the vibrations of the electrons around their lattice positions and the low-temperature specific heat $C \sim T^3$ like for a phononic system. Possible realizations of Wigner crystal are found in semiconducting inversion layers \cite{91,92}, or rare-earth pnictides with low carrier concentrations \cite{93}. For a comprehensive review see Ref. \cite{94}. Often is is more appropriate to consider electrons on a lattice. In order to explain the dramatic temperature dependence of the resistivity of magnetite (\textit{Fe}_3\textit{O}_4), Verwey \cite{95} developed a model for charge ordering in that rather complex spinel structure. According to his model the $2 \cdot \text{Fe}^{3+} + 1 \cdot \text{Fe}^{2+}$ ions per formula unit are distributed at low temperatures as follows. One $\text{Fe}^{3+}$ is used to form a stable cubic sublattice. The remaining $\text{Fe}^{2+}$ and the $\text{Fe}^{2+}$ ions form a structure on which they alternate. This is achieved by assuming that the $\text{Fe}^{3+} - \text{Fe}^{3+}$ nearest-neighbor interaction energy is higher than the $\text{Fe}^{2+} - \text{Fe}^{3+}$ one, so that $\text{Fe}^{3+}$ ions prefer $\text{Fe}^{2+}$ ions on nearest neighbor sites. The kinetic energy of the electrons is discarded in Verwey’s theory. According to this model a first-order phase transition of order-disorder type takes place at high temperatures. The ground state suggested by Verwey can be considered as a form of electron crystallization which is quite distinct from the one considered by Wigner. Its explicit form has been questioned though, by neutron-scattering experiments.

A third form of electron crystallization is due to Mott \cite{96,97} and Hubbard \cite{98,69}, and is also based on electrons positioned on a lattice. Here it is the on-site Coulomb repulsion of electrons which may lead to crystallization, provided the system is at half-filling (i.e., with one electron per site), and the Coulomb repulsion is sufficiently large as compared with the hopping matrix element between sites. Mott realized that this is always the case if a chain of $H$ atoms is considered and the latter are pulled sufficiently apart. Hubbard discussed the metal-insulator transition associated with electron-crystallization by suggesting various approximations for the computation of the excitation spectrum of the Hamiltonians (3.1) at half filling.

Recently it has become clear that still another modification of electron crystallization is realized in \textit{Yb}_4\textit{As}_3 \cite{30,22,99,100}. There have been previous observations on charge ordering on \textit{Yb}_4\textit{As}_3 and \textit{Sm}_4\textit{Bi}_3, without interpretations offered \cite{21,101}. Like in the case of the Wigner lattice it is here the long-range Coulomb interaction which results in what is actually a crystallization of holes. But in distinction to the Wigner case crystallization takes place at high densities. This is so since $4f$ holes are involved here which have a very small kinetic energy due to the small hybridization of the well localized $4f$ orbitals.

\textit{Yb}_4\textit{As}_3 is of the anti-$\text{Th}_3\text{P}_4$ structure. The \textit{Yb} ions are positioned on four families of interpenetrating chains which point along the four diagonals of a cube. It is important that the distance of neighboring \textit{Yb} ions within a chain is $3.80 \text{ Å}$ and therefore larger than of \textit{Yb} ions between different chains which is $3.40 \text{ Å}$. The three nearest neighbors of a \textit{Yb} ion therefore belong to the other three families of chains. The structure is shown in Fig. 9.

We write $\text{Yb}_4\text{As}_3$ in order to demonstrate that the system has one $4f$ hole ($\text{Yb}^{3+} \rightarrow \text{Yb}^{13}$) per formula unit. At high temperatures the $4f$ holes are delocalized and the system is metallic. Measurements of the Hall coefficient show that the carrier concentration is indeed approximately $1/4$ per \textit{Yb} ion. At $T_S = 300 \text{ K}$ the system undergoes a weak first-order phase transition below which the $\text{Yb}^{3+}$ ions accumulate on one family of chains, e.g., those along the [111] direction. Since the $\text{Yb}^{3+}$ ions are smaller than the $\text{Yb}^{2+}$ ions, the phase transition is accompanied by a volume conserving trigonal distortion. Thereby chains in the [111] direction are shortened while those in the other three directions parallel to the diagonals of a cube are elongated.

The driving mechanism of the phase transition is the Coulomb repulsion of holes. The energy is minimized when the holes move into one family of chains because of the large distances between ions in a chain. Disregarding first the structural changes associated with the phase transition we are faced with a Hamiltonian for the holes of the form

$$H = -\sum_{ij \sigma} \hat{a}_{i \sigma}^+ \hat{a}_{j \sigma} + \frac{e^2}{2} \sum_{ij} \frac{e^{-\lambda R_{ij}}}{R_{ij}} \hat{n}_i \hat{n}_j + \sum_{<ij>} J_{ij} \hat{S}_i \hat{S}_j. \quad (4.1)$$

The operators $\hat{a}_{i \sigma}^+$, $\hat{a}_{j \sigma}$ are the same as in Eq. (3.3). The first term describes the kinetic energy of the $4f$ holes and the prime indicates that nearest neighbors are considered only. The second term describes the screened Coulomb interaction. We denote with $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$ the distance between lattice sites $i$ and $j$ and $\lambda^{-1}$ is the screening length which depends on the carrier concentration. The last term is due to the exchange and $<ij>$ refers of pairs of ions in the same chain. While exchange plays a minor role in a Wigner crystal due to the large lattice constant it is of importance when crystallization takes place at high densities as it is the case here.

Considering only the Coulomb term without taking screening into account except by using an effective charge, it has been demonstrated that the energy difference between a uniform distribution of holes and one with the holes concentrated in one family of chains is of the order of a few $meV$ per formula unit \cite{102}. A comparison with the effective $f$ bandwidth of order $0.2$ $eV$ makes plausible that hole crystallization will take place. Note that there are also other charge-ordered configurations of low energy. For example, an ordering of charges in the form $\text{Yb}^{3+} - \text{Yb}^{2+} -$
Yb$^{2+} - Yb^{2+} - Yb^{3+} \ldots$ in all four families of chains has also a low Coulomb-repulsion energy. In fact, von Schnering and Grin have found that the Coulomb-repulsion energy is slightly lower than the one with all $Yb^{3+}$ placed into one family of chains. However, that state is fourfold degenerate and therefore can further lower its energy by a Jahn-Teller distortion. This leads back to a state with short and long chains and therefore with holes concentrating in the short chains [30]. However, that order will not be a perfect one for the reason that the 4-fold degenerate state has a slightly lower repulsion energy. Thus, the optimal state must have incomplete order. Experimentally a 10% deviation from perfect order is observed [22]. A different way of looking at imperfect charge order is to realize that the zero-point fluctuations of the holes on chains in the [111] direction necessarily leads to a spreading of holes into the long chains. For a rough estimate of the effect see Ref. [100].

The above physical picture justifies a description of the phase transition in terms of a band Jahn-Teller effect [30].

The corresponding Hamiltonian is

$$H = -t \sum_{\mu=1}^{4} \sum_{<ij>\sigma} (a_{\mu i \sigma}^+ a_{\mu j \sigma} + h.c.) - \epsilon_\Gamma \sum_{\mu=1}^{4} \sum_{i\sigma} \Delta_\mu n_{\mu i \sigma} + c_\Gamma(0) \epsilon_\Gamma^2 N_0.$$  \hspace{1cm} (4.2)

Here $\mu$ is a chain index and $i$ labels a site on chain $\mu$. Furthermore, $\epsilon_\Gamma(\Gamma = \Gamma_5)$ is a volume conserving strain order parameter which couples to the deformation potential $\Delta_\mu = \Delta[|\delta_{\mu1} - (1 - \delta_{\mu1})/3]$ and $c_\Gamma(0)$ is the associated elastic constant. $N_0$ is the number of sites. A Jahn-Teller phase transition takes place if $\Delta^2/(\epsilon_\Gamma(0))^2 > 3$. From LDA calculations one can estimate $4t \approx 0.2eV$. Furthermore, $c_\Gamma(0)/\Omega = 4 \cdot 10^{11}$ erg/cm$^3$ where $\Omega$ is the volume of the unit cell. We choose $\Delta = 5eV$ which gives a Grüneisen parameter of $\Omega_e = \Delta/(4t) \approx 25$ typical for intermediate valence compounds. With this set of parameters a transition temperature $T_S \approx 250K$ is obtained in approximate agreement with the observed value [30]. Note that strong correlations not included in (4.2) may influence considerably the details of the transition [103]. As discussed in Sect. 5.3 the low-temperature specific heat of Yb$_4$As$_3$ is of the form $C = \gamma T$ and therefore quite different from that of a Wigner crystal. This is due to the exchange interactions which are important in the crystalline phase. The charge ordering leads to quasi one-dimensional Heisenberg spin chains and it is known that the latter have a specific heat linear in $T$.

Yb$_4$As$_3$ is most likely not the only material showing electron or hole crystallization. Other candidates are Eu$_4$As$_3$ and Eu$_3$S$_4$ where Mössbauer and other measurements have shown that at low temperatures the Eu$^{3+}$ and Eu$^{2+}$ ions are at fixed lattice sites [130, 131]. More precisely, the valence fluctuation times must be larger than $\tau = 10^{-8}$ sec, a typical testing time in a Mössbauer experiment. It should be mentioned that there has been an attempt to explain the experiments on Eu$_4$As$_3$ and Eu$_3$S$_4$ by a Verwey transition [132 - 134].

V. HEAVY FERMIONS

The investigation of metallic systems with heavy quasiparticle excitations has developed into an own branch of low-temperature physics. In most cases these systems contain Ce, Yb, U or Np ions as one of their constituents, implying that 4$f$ or 5$f$ electrons are essential. Examples are the metals CeAl$_3$, CeCu$_2$Si$_2$, CeRu$_2$Si$_2$, CeCu$_6$, YbCu$_2$Si$_2$, UBe$_{13}$, UPt$_3$, and NpBe$_{13}$. For experimental reviews see Refs. [23,24] and [26,28], respectively. But also the electron-doped cuprate Nd$_{2 - x}$Ce$_x$CuO$_{4}$ shows heavy-fermion behavior [32] in the range $0.1 \leq x \leq 0.2$. Heavy quasiparticles have also been found in semimetals like Yb$_4$As$_3$, Sm$_3$S$_4$ or in some of the monopnictides and even in insulators like YbB$_{12}$ or SmB$_6$ [104].

The following experimental findings define a heavy-fermion system:

(a) A low temperature specific heat $C = \gamma T$ with a $\gamma$ coefficient of order $1 J/mol^{-1} K^{-2}$, rather than $1 mJ/mol^{-1} K^{-2}$ as, e.g., found for sodium metal;

(b) A Pauli spin susceptibility $\chi_S$ which is similarly enhanced as $\gamma$;

(c) A ratio $R = \pi^2 k_B^2 \chi_S/(3\mu_{eff}^2 \gamma)$ (Sommerfeld-Wilson ratio) of order unity.

Both quantities, $\gamma$ and $\chi_S$, are proportional to the quasiparticle density of states $N^*(0)$ per spin direction at the Fermi level. The latter is proportional to $m^*$, the effective mass of the quasiparticles. When $R$ is calculated the density of states $N^*(0)$ drops out. For free electrons $R = 1$, while in the presence of quasiparticle interactions $R = (1 + F_0^a)^{-1}$ where $F_0^a$ is a Landau parameter. When conditions (a)-(c) are met, one may assume a one-to-one correspondence between the low-energy excitations of the (complex) system like CeAl$_3$ and those of a free electron gas, provided a strongly renormalized effective mass $m^*$ is used and, in the case of semimetals or insulators, an effective charge $e^*$, instead of the corresponding bare quantities.
Heavy-fermion behavior requires the presence of a characteristic low-energy scale in the system. The latter is usually characterized by a temperature \( T^* \). As the temperature \( T \) of the system exceeds \( T^* \) the quasiparticles lose their heavy-mass character. The specific heat levels off, and the spin susceptibility changes from Pauli- to Curie-like behavior. With further increase of temperature the rare-earth or actinide ions behave more and more like ions with well-localized \( f \) electrons.

A key problem is to understand the physical origin of the low-energy excitations. For a long time it was believed that the Kondo effect is the sole source of heavy quasiparticles. The physics of the Kondo effect is extensively described in a monograph \cite{28} and a number of reviews \cite{23-27}. However, by now it is known that also other effects may lead to heavy-fermion behavior. In all cases a lattice of \( 4f \) or \( 5f \) ions is involved though. In metallic systems this lattice couples to the conduction electrons. The latter are either weakly correlated like in \( \text{CeAl}_3 \) or strongly correlated like in the cuprates which may become high-\( T \) superconductors. Strong correlations among the conduction electrons may influence substantially the physical properties of the system. Such a situation is encountered in \( \text{Nd}_2-x\text{Ce}_x\text{CuO}_4 \) and as shown below it is here the Zeeman effect which is responsible for the formation of heavy-fermion excitations. In the semimetallic \( \text{Yb}_4\text{As}_3 \) the heavy quasiparticles are intimately related to quasi one-dimensional chains of \( \text{Yb}^{3+} \) ions which interact antiferromagnetically with each other. It is well known that a Heisenberg chain has a linear specific heat associated with the excess specific heat. It is of order \( \gamma T \) at low temperatures and a Pauli like susceptibility. Thus, instead of having a single physical origin, heavy fermions may result from a variety of effects.

Obviously, the low lying excitations, the main feature of heavy-fermion systems involve predominantly spin degrees of freedom. Evidential is the entropy \( S \) associated with the excess specific heat. It is of order \( S \approx k_B \nu_T \) per \( f \) site, where \( \nu_T \) is the degeneracy of the crystal-field ground state of the incomplete atomic \( f \) shell. In the following we discuss the three different routes to heavy-fermion behavior just outlined. It is likely that they will be supplemented by other ones in the future.

\section*{V.1. Kondo lattices}

The essence of the single-site Kondo effect is the formation of a singlet ground state due to a weak hybridization of the incomplete \( 4f \) shell with the conduction electrons. We derive the singlet wavefunction by starting from the Anderson impurity Hamiltonian

\begin{equation}
H = \sum_{km} \epsilon(k) c_{km}^+ c_{km} + \epsilon_f \sum_m n_f^m + \frac{U}{2} \sum_{m \neq m'} n_f^m n_f^{m'} + \sum_{km} V(k) (c_{km}^+ c_{km} + c_{km}^+ f_m) + \hat{H}_0.
\end{equation}

Here \( c_{km}^+ \) denotes the creation operator of an \( f \) electron in state \( m \) of the lowest \( J \) multiplet and \( n_f^m = f_m^+ f_m \). The \( f \)-orbital energy is \( \epsilon_f \) and \( U \) is the \( f-f \) Coulomb repulsion. The \( c_{km}^+ \) create conduction electrons with momentum \( k = k \) and the quantum numbers \( \ell = 3, J \) and \( m \). The hybridization between the \( f \) and conduction electrons is given by the matrix element \( V(k) \). Finally, \( \hat{H}_0 \) contains all those degrees of freedom of the conduction electrons which do not couple to the \( 4f \) shell. The following ansatz for the singlet ground-state wave function is due to Varma and Yafet \cite{105}

\begin{equation}
|\psi_0\rangle = A(1 + \frac{1}{\sqrt{\nu_f}} \sum_{km} a(k) f_m^+ c_{km}) |\phi_0\rangle
\end{equation}

where \( |\phi_0\rangle \) represents the Fermi sea of the conduction electrons. It is closely related to the one suggested by Yoshida \cite{106} for the ground state of the Kondo Hamiltonian. The variational parameters \( A \) and \( a(k) \) are obtained by minimizing the energy \( E_0 = \langle \psi_0 |(H_0 - H) |\psi_0\rangle \). The latter is always lower than the one of the multiplet \( |\psi_m\rangle = f_m^+ |\phi_0\rangle \). The difference \( \epsilon \) is found to be

\begin{equation}
\epsilon = -D \exp[-\epsilon_f / (\nu_f N(0)V^2)]
\end{equation}

and denotes the energy gain due to the formation of the singlet. Here \( D \) is half of the bandwidth of the conduction electrons and \( N(0) \) is their density of states per spin direction. It is customary to associate a temperature \( T_K \), the Kondo temperature with this energy gain. The singlet-triplet excitation energy \( -\epsilon \) is often of the order of a few meV only, and provides a low-energy scale. When a lattice of \( f \) sites is considered instead of a single one, e.g., like in \( \text{CeAl}_3 \) the Anderson-lattice Hamiltonian is replacing Eq. (5.1). The energy scale \( k_BT_K \) is then replaced by a related
one, \(k_B T^*\), which includes modifications due to the interactions between different \(f\) sites. The energy gain due to the formation of singlets competes with the one of magnetic \(f\)-sites interacting via the RKKY interaction [107]. The latter always wins for small enough hybridization \(V\), because it is proportional to \(V^4\) whereas \(k_B T^*\) depends exponentially on \(V\) (see Eq. (5.3)) and therefore is smaller in that limit. This seems to be the case in systems like \(CeAl_2\), \(CePb_3\) and \(NpBe_{13}\), which are antiferromagnets at low temperatures.

In addition to \(T^*\) there does exist another characteristic temperature \(T_{coh} < T^*\) below which the local singlet-triplet excitations lock together and form coherent quasiparticle excitations with large effective mass \(m^*\). The details of this transition are still an open problem, but de Haas-van Alphen measurements have demonstrated convincingly that at low temperatures the \(f\) electrons behave like delocalized electrons [108]. They contribute to the Fermi surface and to large effective mass anisotropies. It is surprising that one can calculate the Fermi surface of some of the heavy-fermion systems and determine the mass anisotropies with one adjustable parameter only. This is achieved by renormalized band-structure calculations (for reviews see [109, 110]). They are based on a description of the effective potential seen by a quasiparticle in terms of energy-dependent phase-shifts \(\eta_k^{\ell}(\epsilon)\) of the different atoms \(A\). The index \(\ell\) refers here to the different angular momentum channels. As an example we discuss in the following the calculation of the Fermi surface of \(CeRu_2Si_2\) [111]. The essential approximation is to use for the phase shifts the ones computed within the LDA, with the exception of the \(\ell = 3\) phase shift of the \(Ce\) ions. Thus, only the \(\eta_k^{\ell=3}(\epsilon)\) phase shift remains undetermined. It contains the strong correlations of the \(4f\) electrons and cannot be properly evaluated within the LDA. This approximation neglects virtual transitions between different crystal-field eigenstates caused by the coupling between conduction and \(4f\) electrons. (The mass enhancement of the conduction electrons in \(Pr\) metal falls into that category [112]).

According to Hund’s rules the ground state multiplet of \(Ce^{3+}\) with a \(4f^1\) configuration is \(j = 5/2\). The multiplet \(j = 7/2\) is sufficiently high in energy that it may be neglected and therefore \(\eta_{j=7/2}(\epsilon_F) = 0\). Of the \(j = 5/2\) multiplet, only the Kramers degenerate crystal-field ground state is taken into account, because it is the only one occupied at low temperatures. Therefore, near the Fermi energy only the phase shift function \(\eta_{\tau=1}^{\ell=3}(\epsilon)\) among the different \(\ell \approx 3\) channels differs from zero. It contains the strong electron correlations and its form is unknown. In the spirit of Landau’s Fermi-liquid theory we expand this function in the vicinity of \(\epsilon_F\) and write

\[
\eta_{\tau}^{\ell=3}(\epsilon) = \eta_{\tau}^{\ell=3}(\epsilon_F) + a(\epsilon - \epsilon_F) + O((\epsilon - \epsilon_F)^2).
\]

(5.4)

The expansion contains the two unknown parameters \(\eta_{\tau}^{\ell=3}(\epsilon_F)\) and \(a\). One of them, i.e., \(\eta_{\tau}^{\ell=3}(\epsilon_F)\) is fixed by the requirement that a \(Ce\) site contains one \(4f\) electron \((n_f = 1)\). According to Friedel’s sum rule this implies \(\eta_{\tau}^{\ell=3}(\epsilon_F) = \frac{\Gamma}{\pi}\). The remaining parameter \(a\) fixes the slope of the phase shift at \(\epsilon_F\). It therefore determines the density of states and with it the effective mass of the quasiparticles. We set \(a = (k_B T^*)^{-1}\) and determine \(T^*\) by the requirement that the specific heat coefficient \(\gamma\) calculated from the resulting quasiparticle dispersion agrees with the experimental one. Calculations of this form have explained and partially predicted [109,111] the Fermi surface and the large mass anisotropies of \(CeRu_2Si_2\) (see Table 10 and also Fig. 10) [113, 114]. For more details on renormalized band theory we refer to the comprehensive reviews [109, 110].

When the temperature exceeds \(T_{coh}\) the excitations lose their coherence properties and we are dealing with approximately independent scatterers. In that regime the specific heat contains large contributions from the incoherent part of the \(f\) electron excitations.

The noncrossing approximation (NCA) is a valuable tool for treating the coupled \(4f\) and conduction electrons in that temperature regime [116-118]. It leads to a system of coupled equations of the form

\[
\Sigma_0(z) = \frac{\Gamma}{\pi} \sum_m \int_{-\infty}^{+\infty} dz' \rho_m(z') K_+(z - z')
\]

(5.5)

\[
\Sigma_m(z) = \frac{\Gamma}{\pi} \int_{-\infty}^{+\infty} dz' \rho_0(z') K_-(z - z').
\]

Here \(\Gamma = \pi N(0) V^2\) and \(K_\pm(z)\) are defined by

\[
K_\pm(z) = \frac{1}{N(0)} \int_{-\infty}^{+\infty} d\epsilon N(\pm\epsilon)f(\epsilon) \frac{z}{z + \epsilon}
\]

(5.6)

where \(f(\epsilon)\) is the Fermi energy and \(N(\epsilon)\) is the energy-dependent conduction-electron density of states. The function \(\Sigma_\alpha(z)\) and \(\rho_\alpha(z)(\alpha = 0, m)\) relate to each other through
\[ \rho_{\alpha}(z) = -\frac{1}{\pi} \text{Im}\{ R_{\alpha}(z) \} \]  
\[ R_{\alpha}(z) = \frac{1}{z - \epsilon_{\alpha} - \Sigma_{\alpha}(z)} \]  

with \( \epsilon_{\alpha=0} = 0, \epsilon_{\alpha=m} = \epsilon_{fm} \). The NCA equations have to be solved numerically [119]. However, one can find simple, approximate analytic solutions which have the advantage that crystal-field splittings can be explicitly included, a goal which has not been achieved yet by numerical methods. Once the \( \rho_{\alpha}(\epsilon) \) are known, one can determine, e.g., the temperature dependence of the \( f \)-electron occupancies \( n_{fm} = < f_{m}^{+}f_{m} > \) through

\[ n_{fm}(T) = \frac{1}{Z_{f}} \int_{-\infty}^{+\infty} d\epsilon \rho_{m}(\epsilon) e^{-\beta(\epsilon - \mu)}, \]  

where \( \mu \) is the chemical potential and

\[ Z_{f} = \int_{C} \frac{dz}{2\pi i} e^{-\beta z} (R_{0}(z) + \sum_{m} R_{m}(z)) \]  

is the partition function of the \( f \) electrons. Knowing the \( n_{fm}(T) \) one can compute quantities like the temperature dependence of the quadrupole moment of the \( f \) sites

\[ Q(T) = \sum_{m} < m | (3J_{x}^{2} - J_{z}^{2}) | m > n_{fm}(T). \]  

The theory has been used to explain the observed \( Q(T) \) behavior of \( Xb \) in \( YbCu_{2}Si_{2} \) [120, 121].

When \( T \gg T^{*} \), the \( f \) electrons can be treated as being localized. Via an exchange coupling they are weakly interacting with the conduction electrons and perturbation theory can be applied in order to study the resulting effects.

A beautiful justification of the above scenario is the observed difference in the Fermi surface of \( CeRu_{2}Si_{2} \) and \( CeRu_{2}Ge_{2} \) which is shown in Fig. 10. When \( Si \) is replaced by \( Ge \) the distance between \( Ce \) and its nearest neighbors is increased. This causes a decrease in the hybridization of the \( 4f \) electrons with the valence electrons of the neighboring sites. While in \( CeRu_{2}Si_{2} \) the characteristic temperature is \( T^{*} \approx 15K \), it is practically zero in \( CeRu_{2}Si_{2} \). De Haas-van Alphen experiments are performed at a temperature \( T \approx 1K \) implying that for \( CeRu_{2}Si_{2} \) it is \( T \ll T^{*} \) while for \( CeRu_{2}Ge_{2} \) one is in the regime \( T \gg T^{*} \). Therefore, the \( 4f \) electron of \( Ce \) contributes to the volume enclosed by the Fermi surface of \( CeRu_{2}Si_{2} \), but not of \( CeRu_{2}Ge_{2} \). Indeed, Fig. 10 shows that the two Fermi surfaces have similar features, but the enclosed volumes differ by one electron. The Fermi surface of \( CeRu_{2}Ge_{2} \) has a decreased electronic part and an increased hole part as compared with the one of \( CeRu_{2}Si_{2} \).

V.2. Zeeman scenario - \( Nd_{2-x}Ce_{x}CuO_{4} \)

Low-temperature measurements of the specific heat and magnetic susceptibility have demonstrated the existence of heavy quasiparticles in the electron doped cuprate \( Nd_{2-x}Ce_{x}CuO_{4} \) [32]. For \( x = 0.2 \) and temperatures \( T \leq 1K \) the linear specific-heat coefficient is \( \gamma = 4J/\text{(mol \cdot K}^{2}) \). The magnetic susceptibility \( \chi_{s} \) is approximately \( T \)-independent in that temperature regime and the Sommerfeld-Wilson ratio is \( R \approx 1.8 \). The experimental findings are shown in Fig. 11. While these features agree with those of other heavy-fermion systems, there are also pronounced differences. In superconducting heavy-fermion systems like \( CeCu_{2}Si_{2} \) or \( UPt_{3} \) the Cooper pairs are formed by the heavy quasiparticles. This is evidenced by the fact that the jump in the specific heat is \( \Delta C \) at the superconducting transition temperature \( T_{c} \) is directly related to the large \( \gamma \) coefficient, i.e., \( \Delta C(T_{c})/(\gamma T_{c}) \approx 2.4 \). The low-energy excitations are therefore strongly reduced below \( T_{c} \) because one must overcome the binding energy of the pair. But in superconducting \( Nd_{1.85}Ce_{0.15}CuO_{4} \) the formation of Cooper pairs has no noticeable effect on the heavy-fermion excitations. They remain unaffected by superconductivity.

A crucial difference between \( Nd_{2-x}Ce_{x}CuO_{4} \) and, e.g., \( CeCu_{2}Si_{2} \) are the strong electron correlations between the conduction electrons present in the former, but not in the latter material. In the two-dimensional \( Cu-O \) planes of \( Nd_{2-x}Ce_{x}CuO_{4} \) with \( x \geq 0.1 \) we have to account for antiferromagnetic fluctuations. There is considerable experimental evidence that these fluctuations are very slow at low temperatures. Consider undoped \( Nd_{2}CuO_{4} \), an antiferromagnet with a Néel temperature of \( T_{N} \approx 270 \) \text{K} \. The exchange interactions between a \( Nd \) ion and its
nearest-neighbor Cu ions cancel because of the antiferromagnetic alignment of the Cu spins. Therefore one is left with the next-nearest neighbor Cu – Nd spin interaction. It is of the form \( \alpha \mathbf{g}_{Cu} \cdot \mathbf{S}_{Nd} \) and larger than the Nd – Nd interaction. The Schottky peak in the specific heat seen in Fig. 11 results from the spin flips of the Nd ions in the staggered effective field \( \alpha < \mathbf{g}_{Cu} \cdot \mathbf{S}_{Nd} \) set up by the Cu spins (Zeeman effect). It is also present in doped systems like \( Nd_{1.8}Ce_{0.2}CuO_4 \) where antiferromagnetic long-range order is destroyed by doping. This can only be understood if the changes in the preferred direction of the Cu spins occur sufficiently slowly, i.e., slower than \( 10^{-10} \) sec in the present case, so that the Nd spins can follow those changes adiabatically. Only then is a similar energy so that in \( Nd_{2}CuO_4 \) required to flip a Nd spin. This physical picture has been confirmed by recent inelastic neutron-scattering and \( \mu SR \) experiments [122, 123]. Spin-glass behaviour can be excluded.

When Nd ions are replaced by Ce ions, the latter contribute approximately 0.5 electrons more to the Cu – O planes than the former. Thus a corresponding number of Cu sites are in a \( 3d^{10} \) configuration. These sites have no spin and consequently they do not interact with the Nd ions. The extra electrons move freely in the Cu – O planes and therefore, the interaction of a Nd ion with the next-nearest Cu site is repeatedly turned off and on. It is this feature which results in heavy-quasiparticles.

Two model descriptions have been advanced in order to explain the low-energy excitations of \( Nd_{2-x}Ce_{x}CuO_4 \). One is based on a Hamiltonian in which the Nd – Cu interaction is treated by a hybridization between the Nd 4f and Cu 3d orbitals. Usually it is much easier to extract heavy quasiparticles from such a Hamiltonian than from one with a spin-spin interaction like the Kondo Hamiltonian. The slow, antiferromagnetic fluctuations of the Cu spins are replaced by a static staggered field acting on them. This symmetry-breaking field also accounts for the (unrestricted Hartree-Fock). The Hamiltonian which results in heavy-quasiparticles.

The second model description of the Nd spins coupled to the Cu spin is based on stochastic forces acting on the latter [124]. They mimic the interaction of a Cu spin with the other Cu spins. In that case we start from the Hamiltonian

\[
H_{int} = \alpha \mathbf{g}_{Cu} \cdot \mathbf{S}_{Cu}, \quad \alpha > 0
\]  

(5.14)

where \( \mathbf{g}_{Cu} \) is the staggered field. The effect of superconductivity on the heavy quasiparticles can be studied by adding an attractive part for the charge carriers in the Cu – O planes to the Hamiltonian. The latter can again be diagonalized. When the density of states is calculated one finds unchanged contributions from the f bands inside the BCS gap. They originate from the Nd spin degrees of freedom and explain why the heavy quasiparticles remain unaffected by superconductivity.

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The excitation spectrum is that of a Heisenberg chain with a coupling constant. The spin susceptibility which follows from reproduces the experiments reasonably well. One shortcoming of the theory in its present form is the low-temperature behavior due to the neglect of Nd–Nd interactions. However, when evaluated for \( T = 0.4 \, K \) one obtains for \( Nd_{1.8}Ce_{0.2}CuO_4 \) a Sommerfeld-Wilson ratio of \( R \approx 1.4 \).

### V.3. Hubbard route: \( Yb_4As_3 \)

The semimetal \( Yb_4As_3 \) is an example of a system in which \( 4f \) holes crystallize at low temperatures. The structure of the material and the transition from a metallic high-temperature phase to a semimetallic low-temperature phase were discussed in Sect. IV. Here we concentrate on the heavy-fermion properties at low temperatures. The following experimental observations are relevant in that respect. Measurements of the Hall constant demonstrate that at low temperatures only one carrier per \( 10^3 \) \( Yb \) ions remains. We interpret this being due to the \( Yb^{3+} \) chains representing almost half-filled Hubbard systems. The resistivity is at low temperatures of the form \( \rho(T) = \rho_0 + AT^2 \) like for a Fermi liquid. A linear specific heat is found at low \( T \) with a \( \gamma \) coefficient of order \( \gamma \approx 200 \, mJ/(mol \cdot K^2) \). The spin susceptibility is Pauli like and similarly enhanced as \( \gamma \), giving rise to a Sommerfeld-Wilson ratio of order unity. No indication of magnetic order is found down to \( T = 0.045 \, K \), but below \( 2K \) the susceptibility starts to increase again indicating the presence of another low energy scale [126]. These findings strongly suggest heavy-fermion behavior which is further confirmed by the observation that the ratio \( A/\gamma^\nu \) with \( \nu = 2 \) is similar to that of other heavy-fermion systems. We reemphasize that the \( \gamma \) coefficient exceeds the one, e.g., of \( Na \) metal by a factor of more than \( 10^2 \) despite a carrier concentration of only 1 per \( 10^3 \) \( Yb \) ions. This shows clearly that the low-energy scale must involve spin degrees of freedom of the \( Yb^{3+} \) ions. Indeed, chains of antiferromagnetically coupled spins have a linear specific heat \( C = \gamma T \). Inelastic neutron scattering experiments by Kohgi and coworkers [22] have demonstrated that the magnetic excitation spectrum is that of a Heisenberg chain with a coupling constant \( J = 25K \). This spectrum leads to a \( \gamma \) value of the observed size. The physical origin of the heavy-fermion excitations is therefore very different here than that in the Kondo-lattice case.

\[
\langle \Omega(0)\Omega(t) \rangle = e^{-2D_r t} \quad (5.15)
\]

where \( D_r \) can be obtained from the nonlinear \( \sigma \) model [125]. Because there is no long-range order \( < \Omega(t) > = 0 \). The motion of the \( Nd \) spin is governed by the equation

\[
\frac{d}{dt} \mathbf{n}(t) = \omega_0 (\Omega(t) \times \mathbf{n}(t)) \quad (5.16)
\]

where \( \mathbf{n}(t) = \mathbf{S}/S \) and \( \omega_0 = \alpha S \). The spectral function

\[
I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t} < \mathbf{n}(0)\mathbf{n}(t) > \quad (5.17)
\]

is evaluated by making use of the corresponding stochastic Liouville equation. We find that \( I(\omega) \) is of the form

\[
I(\omega) = \frac{1}{3\pi} \frac{4D_r}{\omega^2 + (4D_r)^2} + (\text{side peaks at } \omega_0). \quad (5.18)
\]

While \( D_r(T) \) vanishes as \( T \to 0 \) in the presence of long-range order, it remains finite when the latter is destroyed by doping. A linear specific-heat contribution of the \( 4f \) spin is obtained from

\[
C(T)_{\text{imp}} = \frac{d}{dT} < H_{\text{int}} > = \frac{S(S+1)}{T^2} \int_0^\infty d\omega \omega^2 \frac{I(\omega)}{\cosh^2(\omega/2T)} \quad (5.19)
\]

when \( D_r(T = 0) \neq 0 \). The side peaks of \( I(\omega) \) give rise to a Schottky-type contribution. The calculated specific heat reproduces the experiments reasonably well. One shortcoming of the theory in its present form is the low-temperature behavior due to the neglect of \( Nd – Nd \) interactions. However, when evaluated for \( T = 0.4 \, K \) one obtains for \( Nd_{1.8}Ce_{0.2}CuO_4 \) a Sommerfeld-Wilson ratio of \( R \approx 1.4 \).
A theory has been developed which explains consistently the above experimental findings [30]. It is based on interpreting the structural phase transition in terms of a band Jahn-Teller (CBJT) effect. This interpretation is suggested by the physical considerations outlined in Sec. IV in connection with the hole crystallization taking place. In the theory applied here the crystallization is due to a strong deformation-potential coupling which is quite common in mixed-valence systems. This potential has its origin in the Coulomb repulsion of the 4f holes.

The CBJT transition splits the fourfold degenerate quasi-1d density of states into a nondegenerate one corresponding to the short chains and a threefold one due to the long chains. The nondegenerate one is lower in energy and would be half filled if charge ordering were perfect and the holes were uncorrelated fermions. Instead, the holes are strongly correlated. Two holes on a site imply a 4f$^{12}$ configuration for Yb and that has a much too high energy to occur. Therefore, we are dealing with an almost full lower (hole) Hubbard band rather than with an almost half-filled conduction band. Therefore, the system should be close to an insulator. That Yb$_4$As$_3$ is a semimetal and not an insulator is most probably related to the nonvanishing hopping matrix elements between 4f orbitals in the long and short chains. We have discussed in Sec. IV that the zero-point fluctuations of the 4f holes lead to a partial (though small) transfer of holes to the long chains. We speak of self-doping if this transfer causes the gap in the excitation spectrum of (quasi) one-dimensional Hubbard chains to vanish. Accurate conditions for self-doping are not easily worked out, but a first step in this direction was done recently [127].

The phase transition is described by an effective Hamiltonian of the form of Eq. (4.2).

With increasing charge ordering, correlations become more and more important because with the increase in concentration of holes in the short chains their average distance decreases. Therefore, at low temperatures $T$ the $t - J$ Hamiltonian (see Eq. (3.2)) or a Hubbard Hamiltonian (3.1) must be used. Using the former and making use of a slave-boson mean-field approximation we arrive at an effective mass enhancement of the form

$$\frac{m^*}{m_b} = \frac{t}{t\delta + (3/4)\chi J}. \quad (5.21)$$

Here $m_b$ denotes the band mass, $\chi = \chi_{ij} = \langle \sum_{\alpha} f_{i\alpha}^\dagger f_{j\alpha} \rangle$, $\delta$ is the deviation of the short chains denoted by 1 from half filling and $J = 4t^2/U$, where $U$ is the on-site Coulomb repulsion between holes. With $U = 10$eV one finds $J = 1 \cdot 10^{-3}$ eV and using $\chi(T = 0) = (2/\pi)\sin(\pi(1 - \delta)/2)$ with $\delta = 10^{-3}$ one obtains a ratio of $m^*/m_b \simeq 100$. The derivation of the mass enhancement hides somewhat the fact that spin degrees of freedom are responsible for the heavy quasiparticles. They become better visible when one sets $\delta = 0$, which is the case of no charge carriers. Even then one finds fermionic excitations with a large effective mass and corresponding heat coefficient $\gamma$. The theory was recently improved [103] by including in the Hamiltonian (5.21) an on-site Coulomb repulsion $U$ between 4f holes. This one-dimensional Jahn-Teller model can be solved exactly by a Lieb-Wu Bethe type ansatz. Of particular interest is that a self-doped distorted phase is obtained in a sizable regime of parameters. Since spin-wave-like excitations are responsible for the fermionic low-energy excitations associated with the specific heat and susceptibility at low $T$ we are dealing here with charge-neutral heavy fermions in distinction to the charged heavy electrons, which appear, e.g., in CeAl$_3$. Therefore, we speak of an uncharged or neutral heavy Fermi liquid.

The physical interpretation given above allows for an explanation of another experiment. It has been previously found that an applied magnetic field of $H = 4$ Tesla has little influence on the $\gamma$ coefficient above 2 K, but suppresses $\gamma$ considerably below 2 K [128]. This effect is unexpected, since one would have thought that the changes are of order $(\mu_B H/k_B T)^2$ and therefore very small. However, we can explain the experiments by providing for a weak coupling between parallel short chains. When linear spin-wave theory is applied, a ratio of order $10^{-4}$ between interchain and intrachain coupling opens an anisotropy gap which modifies $C(T)$ in accordance with observation [129].

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1. P. Hohenberg and W. Kohn, Phys. Rev. 136, B 864 (1964)
2. W. Kohn and L. J. Sham, Phys. Rev. 140, A 1133 (1965)
3. R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. 61, 689 (1984)
4. R. M. Dreizler and E. K. U. Gross, Density Functional Theory (Springer, Berlin 1990); see also N. H. March, Electron Density Theory of Atoms and Molecules (Academic Press, London 1992)
5. O. Gunnarsson and B. Lundqvist, Phys. Rev. B 7, 1912 (199..)
6. D. C. Langreth and J. P. Perdew, Solid State Comm. 17, 1425 (1975)
7. S. F. Boys, Proc. R. Soc. London A 209, 542 (1950); see also, e.g., C. E. Dykstra, Ab initio Calculations of the Structure and Properties of Molecules (Elsevier, Amsterdam 1988)
8. J. Cizek, Adv. Chem. Phys. 14, 35 (1969)
9. W. Kutzelnigg, in Modern Theoret. Chemistry, Vol. 3, ed. by H. F. Schaefer III (Plenum, New York 1977)
10. R. Ahlrichs, Comput. Phys. Commun. 17, 31 (1979)
11. H. Kümmel, K. H. Lührmann, J. G. Zabolitzky, Phys. Lett. C 36, 1 (1978)
12. F. Coester and H. Kümmel, Nucl. Phys. 17, 477 (1960)
13. K. Becker and P. Fulde, J. Chem. Phys. 91, 4223 (1989)
14. P. Fulde, Electron Correlations in Molecules and Solids, 3 rd. edit. (Springer, Heidelberg 1995)
15. G. Stollhoff and P. Fulde, J. Chem. Phys. **73**, 4548 (1980) and earlier reference cited therein

16. P. Pulay, Chem. Phys. Lett. **100**, 151 (1983); see also C. Hampel and H.-J. Werner, J. Chem. Phys. **104**, 6286 (1996)

17. A. Lizon-Nordström and F. Indurain, solid State Comm. **94**, 335 (1995)

18. P. O. Löwdin, J. Mol. Spectrosc. **10**, 12 (1963) and **13**, 326 (1964); see also Int. J. Quantum Chem. **21**, 69 (1982)

19. K. Becker and W. Brenig, Z. Phys. B **79**, 195 (1990)

20. E. Wigner, Phys. Rev. **46**, 1002 (1934) and Trans. Faraday Soc. **34**, 678 (1938)

21. A. Ochiai, T. Suzuki and T. Kasuya, J. Phys. Soc. Jpn. **59**, 4129 (1990)

22. M. Kohgi, K. Iwasa, A. Ochiai, T. Suzuki, J.-M. Mignon, B. Gollon, A. Gukasov, J. Schweizer, K. Kakurai, M. Nishi, A. Dönni and T. Osakabe (in print)

23. G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984)

24. H. R. Ott, Prog. Low Temp. Phys. **11**, 215 (1987)

25. P. Fulde, J. Keller and G. Zwicknagl in *Solid State Physics*, Vol. 41, ed. by H. Ehrenreich, D. Turnbull (Academic Press, San Diego 1988) p. 1

26. N. Grewe and F. Steglich in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 14, ed. by K. A. Gschneidner, Jr., L. Eyring (North-Holland, Amsterdam 1991)

27. P. Wachter, Handbook on the Physics and Chemistry of Rare Earths, Vol. 19, ed. by K. A. Gschneidner, Jr., L. Eyring, G. H. Lander and G. R. Chappin (Elsevier, Amsterdam 1994) p. 177

28. A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, Cambridge 1993)
29. P. Fulde, V. Zevin and G. Zwicknagl, Z. Phys. B 92, 133 (1993)
30. P. Fulde, B. Schmidt and P. Thalmeier, Europhys. Lett. 31, 323 (1995)
31. K. Andres, J E. Graebner and H. R. Ott, Phys. Rev. Lett. 35, 1779 (1975)
32. T. Brugger, T. Schreiner, G. Roth, P. Adelmann and G. Czjzek, Phys. Rev. Lett. 71, 2481 (1993)
33. T. Suzuki, Phys. Prop. Actinide and Rare Earth Comp. 33 AP, Series 8, 267 (1993)
34. K. Kladko and P. Fulde, (to be published)
35. T. Schork and P. Fulde, J. Chem Phys. 97, 9195 (1992)
36. H. Stoll. Phys. Rev. B 46, 6700 (1992); and Chem. Phys. Lett. 191, 548 (1992)
37. B. Paulus, P. Fulde and H. Stoll, Phys. Rev. B 51, 10512 (1995)
38. K. Doll, M. Dolg, P. Fulde and H. Stoll, Phys. Rev. B 52, 4842 (1995)
39. B. Paulus, P. Fulde and H. Stoll, Phys. Rev. B 54, 2556 (1996)
40. K. Doll, M. Dolg and H. Stoll, Phys. Rev. 54, 13529 (1996)
41. MOLPRPO is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from I. Almlöf, R. D. Amos, M.-J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. Pitzer, A. J. Stone and P. R. Taylor; the CPP program was written by A. Nicklass
42. R. Dovesi, C. Pisani and C. Roetti, Int. J. Quantum Chem. 17, 517 (1980); C. Pisani, R. Dovesi and C. Roethi, Lecture Notes in Chemistry, vol. 48 (Springer, Berlin 1988)
43. J. M. Foster and S. F. Boys, Rev. Mod. Phys. 32, 300 (1960)
44. A. Shukla, M. Dolg, H. Stoll and P. Fulde, Chem. Phys. Lett. 262, 213 (1996)
45. A. Bergner, M. Dolg, W. Küchle, H. Stoll and H. Preuß Mol. Phys. 80, 1431 (1993)
46. G. Igel-Mann, H. Stoll and H. Preuß Mol. Phys. 65, 1321 (1988)
47. W. A. Harrison, Phys. Rev. B 23, 5230 (1981)
48. D. Glötzle, B. Sagall and O. K. Anderson, Solid State Comm. 36, 403 (1980)
49. Y.-M. Juan and E. Kaxiras, Phys. Rev. B 48, 14944 (1993)
50. Y.-M. Juan, E. Kaxiras and R. G. Gordon, Phys. Rev. B 51, 9521 (1995)
51. S. Fahy, X. W. Wang and S. G. Louie, Phys. Rev. B 42, 3503 (1990)
52. W. Borrmann and P. Fulde, Phys. Rev. B 31, 7800 (1985)
53. S. Froyens and W. A. Harrison, Phys. Rev. B 20, 2420 (1979)
54. B. Paulus, PhD Thesis, Universität Regensburg (1995)
55. J. Lievin, J. Breulet, P. Clerq and J. Y. Metz, Theor. Chem. Acta 61, 512 (1982)
56. CRC Handbook of Chemistry and Physics, 75th edition, Editor: David R. Lide (CRC Press, Boca Raton, 1994/95)
57. M. Catti, G. Valerio, R. Dovesi and M. Causa, Phys. Rev. B 49, 14179 (1994)
58. W. C. Mackrodt, N. M. Harrison, V. R. Saunders, N. L. Allan, M. D. Towler, E. Apra and R. Dovesi, Phil. Mag. A 68, 653 (1993)
59. M. D. Towler, N. L. Allan, N. M. Harrison, V. R. Saunders, W. C. Mackrodt and E. Apra, Phys. Rev. B 50, 5041 (1994)
60. R. J. Cave, E. R. Davidson, J. Chem. Phys. 89, 6798 (1988)
61. K. Doll, M. Dolg, P. Fulde and H. Stoll (submitted for publication)
62. P. W. Atkins, Molecular Quantum Mechanics, (Oxford Univ. Press, Oxford 1983)
63. K. Doll (private communication)
64. G. J. M. Janssen and W. C. Nieuwpoort, Phys. Rev. B 38, 3449 (1988); see also C. de Graaf, R. Broer and W. C. Nieuwpoort, Chem. Phys. 208, 35 (1996)
65. M. Takahashi and J. Igarashi, Annalen der Physik. 5, 247 (1996); see also F. Manghi, C. Calandra and S. Ossicini, Phys. Rev. Lett. 73, 3124 (1994)
66. see, e. g., V. I. Anisimov, J. Zaanen, O. K. Andersen, Phys. Rev. B 44, 943 (1991)
67. for a review see S. Hüfner Photoelectron Spectroscopy, Springer Ser. Solid-State Sci., Vol. 82 (Springer Verlag, Berlin, Heidelberg 1995)
68. M. C. Gutzwiller, Phys. Rev. Lett. 10, 159 (1963)
69. H. Hubbard, Proc. R. Soc. London A 276, 238 (1963)
70. J. Kanamori, Prog. Theor. Phys. 30, 275 (1963)
71. A. Brooks Harris and R. V. Lange, Phys. Rev. 151, 295 (1967)
72. A. M. Oleś and G. Stollhoff, Phys. Rev. B 29, 314 (1984)
73. M. S. Hybertsen, M. Schlüter and N. E. Christensen, Phys. Rev. B 39, 9028 (1989)
74. for a review see, e. g., E. Dagotto, Rev. Mod. Phys. 66, 763 (1994)
75. B. T. Pickup and O. Goscinski, Mol. Phys. 26, 1013 (1973)
76. J. Linderberg and Y. Öhrn, Propagators in Quantum Chemistry (Academic Press, London 1973)
77. S. Hüfner and G. K. Wertheim, Phys. Lett. 47A, 349 (1974)
78. D. R. Penn, Phys. Rev. Lett. 42, 921 (1979)
79. A. Liebsch, Phys. Rev. Lett. 43, 1431 (1979) and Phys. Rev. B 23, 5203 (1981)
80. J. Igarashi, J. Phys. Soc. Jpn. 52, 2827 (1983); ibid 54, 260 (1985)
81. L. M. Roth, Phys. Rev. 186, 1, 428 (1969)
82. J. A. Hertz and D. M. Edwards, J. Phys. 3, 2174 (1973); ibid 3, 2191 (1973)
83. P. Unger, J. Igarashi and P. Fulde, Phys. Rev. B. 50, 10485 (1994)
84. D. van der Marel and G. A. Sawatzky, Phys. Rev. B. 37, 10674 (1988)
85. L. D. Faddeev, Zh. Eksp. Teor. Fiz. 39, 1459 (1960) [Engl. transl.: Sov. Phys. - JETP 12, 1014 (1961)]
86. J. Igarashi, P. Unger, K. Hirai and P. Fulde, Phys. Rev. B 49, 16181 (1994)
87. P. Unger and P. Fulde, Phys. Rev. B. 47, 8947 (1993); ibid B 48, 16607 (1993); ibid B 51, 9245 (1995)
88. F. C. Zhang and T. M. Rice, Phys. Rev. B. 37, 3754 (1987)
89. W. Stephan and P. Horsch in Dynamics of Magnetic Fluctuations in High-Temperature Superconductivity, ed. by G. Reiter, P. Horsch, G. Psaltakis (Plenum Press, New York 1990)
90. T. Tohyama and S. Maekawa, Physics C 191, 193 (1992)
91. P. Platzmann, Phys. World p. 22, Dec. 1996
92. J. Durkan, R. J. Elliott and N. H. March, Rev. Mod. Phys. 40, 812 (1968)
93. T. Kasuya, J. Alloys and Compounds, 192, 217 (1993) and earlier work cited there
94. C. M. Care and N. H. March, Adv. Phys. 24, 101 (1975)
95. E. J. W. Verwey and P. W. Haaymann, Physica 8, 979 (1941)
96. N. F. Mott, Phil. Mag. 6, 287 (1961)
97. N. F. Mott, Metal-Insulator Transitions, (Taylor and Trancis, London 1990)
98. J. Hubbard, Proc. Roy. Soc. London, A 281, 401 (1964)
99. M. Rams, K. Krolas, K. Tomala, A. Ochiai and T. Suzuki, Hyperfine Interact. 97/98, 125 (1996); earlier Mossbauer studies by B. Bonville, A. Ochiai, T. Suzuki and E. Vincent, J. Phys. 4, 594 (1994) have shown the existence of nonequivalent Yb sites.
100. P. Fulde, Annalen der Physik (in print)
101. A. Ochiai, T. Suzuki and T. Kasuya, J. Magn. Magn. Mater. 52, 13 (1985)
102. H. G. von Schnering and V. Grin (private commun.)
103. Y. M. Li, N. d’Ambrumenil and P. Fulde, Phys. Rev. Lett. 78, 3386 (1997)
104. see, e. g., Proceedings of the International Conference on Strongly Correlated Electron Systems, Physica B 206 + 207
105. C. M. Varma and Y. Yafet, Phys. Rev. B 13, 2950 (1976)
106. K. Yoshida, Phys. Rev. 147, 223 (1966)
107. S. Doniach, Physica B 91, 231 (1977)

108. H. Aoki, S. Uji, A. Albessand and Y. Onuki, Phys. Rev. Lett. 71, 2120 (1993)

109. G. Zwicknagl, Adv. Phys. 41, 203 (1993)

110. M. N. Norman and D. Koelling, Handbook on the Physics and Chemistry of Rare Earths, Vol. 17, ed. by K. A. Gschneidner Jr., L. Eyring, G. H. Lander and G. R. Choppin (Elsevier, Amsterdam 1993) p. 1

111. G. Zwicknagl, E. Runge and N. E. Christensen, Physica B 163, 97 (1990)

112. P. Fulde and J. Jensen, Phys. Rev. B 27, 4085 (1983); see also R. M. White and P. Fulde, Phys. Rev. Lett. 47, 1540 (1981)

113. H. Aoki, S. Uji, A. Albessand and Y. Onuki, Phys. Rev. Lett. 71, 2120 (1993)

114. G. G. Lonzarich, J. Magn. Magn. Mater. 76 + 77, 1 (1988)

115. C. A. King and G. G. Lonzarich, Physica B 171, 161 (1991)

116. H. Keiter and J. C. Kimball, Int. J. Magnet. 1, 233 (1971)

117. H. Kojima, Y. Kuramoto and M. Tachiki, Z. Phys. B 54, 293 (1984)

118. N. E. Bickers, Rev. Mod. Phys. 59, 845 (1987)

119. N. E. Bickers, D. L. Cox and J. W. Wilkins, Phys. Rev. Lett. 54, 230 (1985)

120. K. Thomala, G. Weschenfelder, G. Czjzek and E. Holland-Moritz, J. Magn. Magn. Mater. 89, 143 (1990)

121. V. Zevin, G. Zwicknagl and P. Fulde, Phys. Rev. Lett. 60, 2331 (1988)

122. M. Loewenhaupt, A. Metz, N. M. Pyka, D. M. McK Paul, J. Martin, V. H. M. Dujin, J. J. M. Trause, H. Mutka and W. Schmidt, Ann. Phys. 5, 197 (1996)

123. J. Litterst (private communication)

124. J. Igarashi, K. Murayama and P. Fulde, Phys. Rev. B. 52, 15966 (1995)

125. S. Chakravarty, B. I. Halperin and D. R. Nelson, Phys. Rev. B. 39, 2344 (1989); S. Chakravarty and R. Orbach, Phys. Rev. Lett. 64, 224 (1990)

126. B. Bonville, A. Ochiai, T. Suzuki and J.-M. Mignon, J. Phys. I. 4, 594 (1994)

127. S. Blawid, Hoang Anh Tuan and P. Fulde, Phys. Rev. B. 54, 7771 (1996)

128. R. Helfrich, F. Steglich and A. Ochiai (private communication)

129. B. Schmidt, P. Thalmeier and P. Fulde, Europhys. Lett. 35, 109 (1996)

130. R. Pott, G. Güntherodt, W. Wichelhaus, M. Ohl and H. Bach, Phys. Rev. B 27, 359 (1983)

131. H. H. Davis, I. Bransky and N. M. Tallan, J. Less Comm. Metals 22, 193 (1970)

132. B. Lorenz, phys. stat. sol. (b) 125, 375 (1984)

133. D. Ihle and B. Lorenz, phys. stat. sol. (b) 116, 539 (1983)

134. J. L. Moran-López and P. Schlottmann, Phys. Rev. B. 22, 1912 (1980)
**Figure Captions**

**Fig. 1:** Detailed presentation of one-body increments for NiO. From Ref. [61].

**Fig. 2:** Two-body oxygen-oxygen increments for MgO. From Ref [38].

**Fig. 3:** Van der Waals interaction in ionic crystals. Calculated values within the CCSD approximation versus values as obtained from London’s equation (2.28). Circles: interactions between positive and negative ions; crosses: between negative ions. From Ref. [63].

**Fig. 4:** Contributions of different increments to the binding energy of MgO. From Ref [63].

**Fig. 5:** Schematic representation of the Cu $3d_{x^2-y^2}$ and O $2p_x(y)$ orbitals which are treated by a 3-band Hubbard Hamiltonian.

**Fig. 6:** Spectral density of Ni as obtained from a 5-band Hubbard Hamiltonian (3.4 - 3.6) with $U = 0.56$, $J = 0.22$, $\Delta J = 0.031$ (in units of the SCF bandwidth) when different approximations are applied:
(a) full spectrum,
(b) SCF approximation,
(c) correlations included but with $J = \Delta J = 0$,
(d) when $\Delta J = 0$,
(e) assuming $\Omega = 1$.
[From Ref [83]].

**Fig. 7:** Spectral density of the Cu – O planes:
(a) at half-filling,
(b) for 25 % of hole doping.
Oxygen and Cu contributions are shown by dashed and solid lines, respectively. Parameter values are $U_d = 8$, $U_p = 3$, $t_{pp} = 0.5$, $\epsilon_p - \epsilon_d = 4$ in units of $t_{pd}$. Note, that with hole doping spectral weight is shifted from the upper Hubbard band to the region close to the Fermi energy (dotted line). (From Ref. [87]).

**Fig. 8:** Spectral density obtained by diagonalization of a cluster of (CuO$_2$)$_4$:
(a) at half-filling,
(b) for 25 % of hole doping.
Parameter values are similar to those in Fig. 7, i.e., $U_d = 8.8$, $U_p = 4.24$, $t_{pp} = 0.41$, $\epsilon_p - \epsilon_d = 3.37$. Note the similarities with Fig. 7. $S$ denotes the Zhang-Rice singlet and $T$ indicates the spin-triplet contribution. Data has been broadened by a linewidth. From Ref. [90].

**Fig. 9:** (a) Structure of Yb$_4$As$_4$, (b) four families of chains on which the Yb ions are located.

**Fig. 10:** Fermi surfaces for CeRu$_2$Si$_2$ and CeRu$_2$Ge$_2$ as derived from de Haas - van Alphen measurements [113 - 115]. The upper part is due to holes and the lower part is due to electrons. In CeRu$_2$Ge$_2$ the $4f$ electron of Ce is well localized while in CeRu$_2$Si$_2$ is participates in the formation of the Fermi surface. The volume enclosed by the Fermi surface differs therefore by one electron resulting in an increase of the hole part and a decrease of the electron part in CeRu$_2$Ge$_2$.

**Fig. 11:** Observation of heavy-fermion excitations in Nd$_{2-x}$Ce$_x$CuO$_4$.
(a) specific heat $C_p(T)$,
(b) $C_p(T)/T$,
(c) Spin susceptibility for an overdoped sample with $x = 0.2$.
From Ref. [32].

**Fig. 12:** Schematic plot of the quasiparticle bands of Nd$_{2-x}$Ce$_x$CuO$_4$ for $x \neq 0$. The Fermi energy is indicated by a dotted line. Solid lines: $f$-like excitations, and dashed lines: $d$-like excitations.
Table Captions

Table 1: Cohesive energy per unit cell (in eV) of the elemental semiconductors in SCF approximation ($E_{coh}^{SCF}$) and with inclusion of correlations ($E_{corr}^{coh}$). Percentages in parenthesis are with reference to the experimental values ($E_{exp}^{coh}$) which include an estimate of the atomic zero-point fluctuations [47]. For comparison results of other methods are shown: local density approximation ($E_{LDA}^{coh}$) [48, 49]; generalized gradient approximation ($E_{GGA}^{coh}$) [50]; quantum Monte Carlo ($E_{QMC}^{coh}$) [51]. From Ref. [37] with corrections included due to atomic spin-orbit splittings.

Table 2: Cohesive energy (in eV) of the III-V semiconducting compounds. The notations are the same as in Table 1. From Ref. [37].

Table 3: Lattice constants for the group IV semiconductors in Angström: in SCF approximation ($a_{SCF}$); including a core polarization potential ($a_{cpp}$); with inclusion of correlations ($a_{corr}$); Percentages in parenthesis are with reference to experimental values ($a_{exp}$). One notices a strong influence of core polarization. From Ref. [37].

Table 4: Bulk modulus of the group IV semiconductors in Mbar in SCF approximation ($B_{SCF}$); including a core polarization potential ($B_{cpp}$); with correlations included ($B_{corr}$); Percentages in parenthesis are with reference to experimental values ($B_{exp}$). From Ref. [37].

Table 5: Parameters in the BOA as obtained by fitting the results for a single and for neighboring bonds to those of the ab initio calculation with a minimal basis set. $\delta E_{inter}^{corr}$ denotes those contributions which come from more distant than nearest-neighbor bonds. From Ref. [54].

Table 6: Cohesive energy (in eV) of three oxides. The notation is the same as in Table 1. $E_{exp}^{coh}$ from Ref. [56], $E_{SCF}^{coh}$ from Ref. [57] (MgO), [58] (CaO) and [59] (NiO). Calculations for $E_{corr}^{coh}$ are on a CCSD(T) level (MgO, CaO) and by applying quasidegenerate variational perturbation theory (QDVPT) [60].

Table 7: Lattice constants (in Å) of three oxides. Same notation as in Table 3. For $a_{SCF}$ see Refs. [57 - 59].

Table 8: One-body increments for MgO, CaO and NiO in eV. From Refs. [38, 40, 61].

Table 9: Sums of different two-body increments in eV. The last line gives the sum of all 2-body increments. From Refs. [38, 40, 61].

Table 10: Measured [114] and calculated [111] mass ratios for CeRu$_2$Si$_2$. Shown are extremal areas of the Fermi surface (in megagauss) and the effective mass ratios $m^*/m_0$. Unlike the LDA, the renormalized band theory (RB) reproduces the large measured mass anisotropies.
|     | C   | Si  | Ge  | α-Sn |
|-----|-----|-----|-----|------|
| $E_{\text{coh}}^{\text{SCF}}$ | 10.74 | 6.18 | 4.25 | 3.65 |
|     | (71%) | (66%) | (53%) | (53%) |
| $E_{\text{coh}}^{\text{corr}}$ | 14.36 | 8.84 | 7.02 | 6.13 |
|     | (95%) | (94%) | (88%) | (90%) |
| $E_{\text{exp}}$ | 15.10 | 9.39 | 8.00 | 6.83 |
| $E_{\text{exp}}^{\text{LDA}}$ | 17.25 | 10.59 | 9.06 | —   |
| $E_{\text{coh}}^{\text{GGA}}$ | —   | 8.79 | 6.83 | —   |
| $E_{\text{coh}}^{\text{QMC}}$ | 14.90 | 9.76 | —   | —   |

Table 1

|     | BN  | BP  | BAs | AlP | AlAs | AlSb |
|-----|-----|-----|-----|-----|------|------|
| $E_{\text{coh}}^{\text{SCF}}$ | 9.09 | 6.26 | 5.50 | 5.39 | 4.71 | 3.97 |
|     | (67%) | (60%) | (64%) | (59%) | (60%) |     |
| $E_{\text{coh}}^{\text{corr}}$ | 12.38 | 9.36 | 8.57 | 7.95 | 7.18 | 6.31 |
|     | (91%) | (90%) | (95%) | (90%) | (90%) | (95%) |
| $E_{\text{exp}}$ | 13.61 | 10.39 | —   | 8.41 | 8.00 | 6.61 |
| GaP | GaAs | GaSb | InP | InAs | InSb |
| $E_{\text{coh}}^{\text{SCF}}$ | 4.00 | 3.54 | 2.97 | 3.86 | 3.51 | 3.18 |
|     | (53%) | (53%) | (49%) | (57%) | (54%) | (55%) |
| $E_{\text{coh}}^{\text{corr}}$ | 6.69 | 6.20 | 5.39 | 6.37 | 5.96 | 5.47 |
|     | (91%) | (93%) | (89%) | (94%) | (92%) | (94%) |
| $E_{\text{exp}}$ | 7.37 | 6.69 | 6.07 | 6.80 | 6.50 | 5.80 |

Table 2

|     | C   | Si  | Ge  | Sn  |
|-----|-----|-----|-----|-----|
| $a_{\text{SCF}}$ | 3.5590 | 5.4993 | 5.7516 | 6.6001 |
|     | (-0.2%) | (+1.2%) | (+1.7%) | (+1.7%) |
| $a_{\text{Ccpp}}$ | —   | 5.4662 | 5.6653 | 6.4549 |
|     | —   | (+0.6%) | (+0.2%) | (-0.5%) |
| $a_{\text{corr}}$ | 3.5833 | 5.4256 | 5.6413 | 6.4443 |
|     | (+0.5%) | (-0.1%) | (-0.3%) | (-0.7%) |
| $a_{\text{exp}}$ | 3.5657 | 5.4317 | 5.6575 | 6.4892 |

Table 3
|        | C     | Si    | Ge    | Sn    |
|--------|-------|-------|-------|-------|
| \(B_{SCF}\) | 4.815 | 1.038 | 0.961 | 0.638 |
| \((+9\%)\) |       | \((+5\%)\) | \((+31\%)\) | \((+20\%)\) |
| \(B_{exp}\) | 4.42  | 0.99  | 0.734 | 0.531 |
| \((+9\%)\) |       | \((+31\%)\) | \((+20\%)\) | \((+20\%)\) |

Table 4

|        | C     | Si    | Ge    | Sn    |
|--------|-------|-------|-------|-------|
| bandwidth \(\text{eV}\) | 46.0  | 17.8  | 17.2  | 13.8  |
| \(t_0\) | 8.34  | 4.14  | 4.01  | 3.20  |
| \(V_0\) | 3.41  | 1.78  | 1.44  | 1.25  |
| \(V_1\) | 0.87  | 0.51  | 0.45  | 0.38  |
| \(E_{\text{corr}}^{\text{BOA}}\) | -2.06 | -1.19 | -0.91 | -0.83 |
| \(\delta E_{\text{corr}}\) | -0.45 | -0.42 | -0.40 | -0.38 |

Table 5

|        | MgO   | CaO   | NiO   |
|--------|-------|-------|-------|
| \(E_{\text{coh}}\) | 5.85  | 5.92  | 4.37  |
| \(E_{\text{corr}}\) | 7.82  | 8.06  | 7.00  |
| \((96\%)\) | (93\%) | (93\%) | |
| \(E_{\text{exp}}\) | 8.14  | 8.65  | 7.49  |

Table 6

|        | MgO   | CaO   | NiO   |
|--------|-------|-------|-------|
| \(a_{SCF}\) | 4.191 | 4.864 | 4.264 |
| \(a_{corr}\) | 4.184 | 4.801 | 4.164 |
| \(a_{exp}\) | 4.207 | 4.803 | 4.170 |

Table 7

|        | MgO   | CaO   | NiO   |
|--------|-------|-------|-------|
| lattice const. | -2.04 | -2.05 | -2.14 |
| \(O \rightarrow O^{2+}\) | -2.04 | -2.05 | -2.14 |
| \(X \rightarrow X^{2+}\) | 0.99  | 1.00  | 1.58  |
| sum of one-body increments | -1.05 | -1.05 | -0.56 |

Table 8
|       | MgO  | CaO  | NiO  |
|-------|------|------|------|
| $O-O$ | -0.36| -0.15| -0.56|
| $X-O$ | -0.41| -0.78| -1.56|
| $X-X$ | -0.002| -0.02| -0.04|
| **sum of two-body increments** | -0.77| -0.96| -2.15|

Table 9
Correlation energy [Hartree]

Ni → Ni$^{2+}$ increment

O → O$^{2-}$ increment

sum of one-body increments
Increment [mH]

Increment [meV]

nearest neighbour
one-body increments

two-body increments

three-body increments

sum

experimental value
$\text{CeRu}_2\text{Si}_2$

$T \ll T^{\text{coh}}$

$\text{CeRu}_2\text{Ge}_2$

$T \gg T^*$
