Strongly-correlated crystal-field approach to 3d oxides - the orbital magnetism in 3d-ion compounds

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dedicated to John H. Van Vleck and to the 75th year anniversary of the crystal-field theory

Abstract

We have developed the crystal-field approach with strong electron correlations, extended to the Quantum Atomistic Solid-State theory (QUASST), as a physically relevant theoretical model for the description of electronic and magnetic properties of 3d-atom compounds. Its applicability has been illustrated for LaCoO$_3$, FeBr$_2$ and Na$_2$V$_3$O$_7$. According to the QUASST theory in compounds containing open $3d$-/4f-/5f-shell atoms the discrete atomic-like low-energy electronic structure survives also when the 3d atom becomes the full part of a solid matter. This low-energy atomic-like electronic structure, being determined by local crystal-field interactions and the intra-atomic spin-orbit coupling, predominantly determines electronic and magnetic properties of the whole compound.

We understand our theoretical research as a continuation of the Van Vleck’s studies on the localized magnetism. We point out, however, the importance of the orbital magnetism and the intra-atomic spin-orbit coupling for the physically adequate description of real 3d-ion compounds and 3d magnetism. Our studies clearly indicate that it is the highest time to “unquench” the orbital moment in solid-state physics in description of 3d-atom containing compounds.

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1 Introduction

An unexpected discovery of high-$T_c$ superconductivity in 3d-ion oxides in 1986 has revealed the shortcomings of our understanding of the 3d magnetism. Today we do not understand the superconductivity but still we do not have a consistent understanding of electronic and magnetic properties of 3d-ion containing compounds. Despite of very different theoretical concepts there is no consensus how to treat electrons in unfilled shells. Many of 3d-ion oxides belong to the class of compounds called the Mott insulators - they exhibit the insulating state despite of the unfilled $d$ shell. The fundamental controversy "how to treat the d electrons" starts already at the beginning - should they be treated as localized or itinerant. Directly related to this problem is the structure of the available states: do they form the continuous energy spectrum like it is in the band picture, schematically shown in Fig. 1, or do they form the discrete energy spectrum typical for the localized states. The standard band picture encounters serious difficulties - it often predicts the metallic state for systems that are in the reality very good insulators, for instance for La$_2$CuO$_4$, CoO and NiO [1, 2, 3, 4]. Characteristic feature of the present literature description of the 3d-ion magnetism is the spin-only description with the neglect of the orbital magnetism. This erroneous, according to us, view is related to the widely-spread conviction about the quenching of the orbital moment in 3d-atom compounds. This observation made in 1932 by Van Vleck is valid, however, only in the first-order approximation and for that time it was a very important theoretical result - it explained high-temperature dependence of the paramagnetic susceptibility with the spin-only effective moment. From year of 1996 we advocate that it is the highest time in the 3d solid-state physics to "unquench" the orbital moment and to take into account the spin-orbit coupling [5] because the spin-orbit coupling is well-known physical effect and its neglect causes unphysical oversimplification of the low-energy electronic structure. With very big surprise we found that the present magnetic community is not much enthusiastic about it, but we are fully convinced that the modern description of the magnetism and the electronic structure have to be made...
in the atomic scale. One of the reason for this lack of enthusiasm, assuming that it is only a scientific sceptism, can be a fact that we unquench the orbital moment with the use of the crystal-field concept that is disdainfully treated by present great solid-state theoreticians (experimentalists are widely using the CEF theory and the atomic-like picture being pragmatic), though there is rapidly growing experimental evidence for its ability to describe exceptionally well many physical properties as it was already shown in numerous papers of Van Vleck beginning from 1929. We are fully aware of the wide overwhelmed critics of the crystal-field approach, started with a paper of Slater in 1953, but we are convinced that this critics is largely improper. However, we have to say that there is many mistakes, misuses and oversimplifications of the crystal field in the present scientific literature, even in the most prestigious physical journals. A reason for these misuses we think is related to lack of the open scientific discussion and, say, a discrimination of the localized approaches in the presently-in-fashion solid-state theories. In fact, there is enormous gap between localized picture discovered everyday by experimentalists and most theoretical descriptions preferring itinerancy of 3d electrons.

In order to illustrate better the physical problems in description of 3d-atom containing compounds let present different electronic structures discussed in recent theoretical approaches to LaCoO$_3$, for instance. This compound has been studied by more than 50 years due to its nonmagnetic ground state and unusual temperature dependence of the paramagnetic susceptibility $\chi(T)$ drastically violating the Curie-Weiss law [6, 7] with a pronounced maximum at about 100 K. Fig. 1 presents result of band-theory calculations for LaCoO$_3$ [8, 9, 10, 11, 12, 13] and FeBr$_2$ [14] - 3d states form continuous energy spectrum wide in the energy by more than 15 eV. Fig. 2 presents oversimplified crystal-field schemes from recent publications [9, 15, 16] - we recognize these schemes as single-electron states with weak correlations. In contrary to band-theory results figure 2 suggests the existence of discrete 3d states but the electronic structure is only very schematic.

The general shape of the bands presented in Fig. 1 can be understood knowing the localized states of Fig. 2. The continuous energy spectrum in the band picture looks like a smooth convolution on the available localized single 3d electron orbitals $t_{2g}$ (occupied) and higher $e_g$ orbitals (empty). The similarity of the band density of states and the energy level scheme of Fig. 2 is related to the single-electron treatment of the 3d electrons in both approaches. In Fig. 3 we present the crystal-field states with strong electron correlations calculated by us - here the discrete energy states are many-electron states of the full Co$^{3+}$ ion [17, 18]. In our approach we treat 3d electrons in the incomplete 3d shell as a forming atomic-like strongly-correlated system. Our strongly-correlated crystal-field approach for the single 3d cation has been extended to the Quantum Atomistic Solid State Theory (QUASST) [19, 20] in order to describe 3d-atom compounds.

The revealed fundamental differences in the presented electronic structures are very important because this low-energy electronic structure determines physical
properties of a real system. We claim that the states calculated by us are becoming to be more and more experimentally observed confirming our approach. The existence of such different electronic structures obviously proves the lack of a consensus in the understanding of 3d-atom compounds. There is general agreement that unusual magnetic and electronic properties of 3d-atom containing compounds and a failure of the standard band calculations are related to the improper treatment of electron correlations, that are apparently strong. Thus, the problem about 3d-atom compounds can be formulated as "how to account for strong correlations". However, the meaning of strong correlations is very unclear. In literature it is not clear if an author means on-site or inter-site electron correlations and which electrons are correlated. In an one gram of a solid there is $10^{22}$ atoms and say, 25 times more electrons. We feel that the strong electron correlations and strongly-correlated electron systems have not well defined physical meaning and are recalled in case of non-conventional magnetic and electronic properties. In fact they are recalled to hide our shortage of the knowledge and the understanding but the explanation sounds scientifically. With time we see, attending the annual Strongly-Correlated Electron Systems (SCES) Conferences and their Proceedings published in Physica B, that practically all compounds with 3d-/4f-/5f- open-shell atoms become at present clas-
Figure 2: Literature schemes of the single-electron discrete energy spectrum of the Co$^{3+}$ ion in LaCoO$_3$ for the low-spin (LS, S=0), intermediate-spin (IS, S=1) and the high-spin state (HS, S=2) realized on the five-fold degenerate atomic 3d orbitals with lower $t_{2g}$ and higher $e_g$ states [8, 15]. According to the current literature these spin states are subsequently realized with the increasing temperature, however, there is no reasonable explanation for so drastic change of $\Delta_{CEF}$ and $J_{ex}$ parameters with temperature. According to the present approach these schemes are wrong.

...classified as strongly-correlated electron systems. Surely all 3d oxides are classified as strongly-correlated electron systems.

Finally, one should note the energy scale on Fig. 3, in particular that of the first excited state at 7 K (=0.6 meV=5 cm$^{-1}$). It is at least 1000 times more detailed calculations than the present band calculations. By present computers we can perform such detailed calculations, but the problem is whether such states and such tiny energy separations are preserved in a solid. Developing the CEF theory and tracing its effects by last 20 years we have been believing in the substantial applicability of the CEF theory to solid compounds. We have evaluated a detailed electronic structure in rare-earth compounds with separations below 0.5 meV (ErNi$_5$ and NdNi$_5$ (both are intermetallics) [21], Nd$_2$CuO$_4$ (ionic) [22]) but application of the CEF theory to rare-earth compounds is more acceptable in the magnetic community. The usefulness of the CEF theory to 3d compounds, even ionic, has been questioned in presently-in-fashion theories but such the detailed energy level scheme, as presented in Fig. 3, has been recently revealed by electron-spin-resonance experiment to exist in LaCoO$_3$ [18, 23] confirming the presented theoretical approach. In doing our research we fully agree with a Max Planck saying, that "Experiments are the only means of knowledge at our disposal. The rest is poetry, imagination."
Figure 3: Calculated lowest part of the fine electronic structure of the Co$^{3+}$ ion in the CoO$_6$ octahedron, related to the $^5$D term, in the presence of the intra-atomic spin-orbit coupling. (a) the cubic $^5$T$_{2g}$ subterm is shown only; $^5$E$^g$ state is at $E=+14 400$ K, i.e. 2.1 eV above. b) the effect of spin-orbit coupling on the subterm $^5$T$_{2g}$. c) the further splitting by the trigonal distortion. According to the presented strongly-correlated CEF approach these spin states are increasingly populated with the increasing temperature. The degeneracy, the magnetic moment and the relative energy of the states are shown. In LaCoO$_3$ 140 K below the structure related to the $^5$D term lies, as shown in (c), a non-magnetic singlet $^1$A$_1$ originating from the $^1$I term. In FeBr$_2$ very similar structure exists for the Fe$^{2+}$ ion for the $^5$D term like shown in (c), but without the $^1$A$_1$ term.
2 The Aim

Very general aim of our long-lasting research is to describe macroscopically-observed physical properties of compounds containing open shell atoms, in particular with the 3d shell. Some our research on rare-earth systems one can found in Ref. [21, 24, 25] where we successfully applied strongly-correlated crystal-field approach both for intermetallic and ionic compounds.

In this chapter we would like to present the strongly-correlated crystal-field approach for the description of electronic and magnetic properties of 3d-atom compounds, with taking into account the relativistic spin-orbit coupling. The strong electron correlations we account for by considering intra-site electron correlations at a given atom to be energetically dominant. These strong correlations assure the atomic-like integrity of the considered 3d atom in the well-defined ionic state even when this paramagnetic atom becomes the full part of a solid. We named this approach Quantum Atomistic Solid-State (QUASST) theory as its starting point for the analysis of a solid containing 3d atoms is the analysis of constituting atoms and their quantum discrete electronic structures in a given solid. Here we confine our discussion to insulating 3d compounds - they are known as Mott insulators. It was Mott who pointed out that 3d oxides are insulators despite of having the open shell, violating in this way the conventional band theory of Wilson and Bloch. The mentioned above LaCoO$_3$ is an example of Mott insulator belonging to the wide class of oxides with the perovskite structure. As an exemplary application of QUASST to real compounds our analysis of FeBr$_2$ and ErNi$_5$ can be advised [17, 18, 19, 21]. The former is an ionic compound whereas the latter is an intermetallic compound.

We do not say that other mechanisms than CEF and the spin-orbit coupling, after dominant coulombic interactions responsible for the cohesion of an ionic compound, are not present in a solid, but we are convinced that analysis of electronic and magnetic properties of 3d-/4f-/5f-atom compounds is necessary to start from the determination of the crystal-field interactions and of the localized CEF-like states.

We understand our theoretical research as a continuation of the Van Vleck’s studies on the localized magnetism. We make use of efforts of many physicists and chemists of the solid state physics in order to construct a consistent understanding of electronic and magnetic properties of 3d-/4f-/5f-atom containing compounds and to correlate the macroscopically-observed properties with the atomic scale electronic structure.
3 General idea of understanding of 3d oxides

3.1 General idea of QUASST - preservation of the atomic-like discrete electronic structure in a solid

A key idea of QUASST is that the paramagnetic ion in a solid largely preserves its atomic-like integrity, and consequently the atomic-like electronic structure, when it becomes the full part of a solid. This atomic-scale low-energy electronic structure predominantly determines the macroscopically observed magnetic and electronic properties of the whole compound. As we are interested in physical properties at room temperature and below we have to have the electronic structure to be determined below 25 meV (≈300 K) with the accuracy better than 1 meV. QUASST is based on physical concepts well-known in solid-state physics, chemistry and material science. In QUASST we incorporate the CEF approach, the group theory, atomic physics, statistical physics, thermodynamics, the consideration of the local symmetry and many others forming a consistent theory for understanding of macroscopically-observed magnetic, electronic and spectroscopic properties of 3d-/4f-/5f-atom compounds in connection to the atomic-scale low-energy electronic structure of the involved atoms/ions. One can recognize in QUASST traces of an ionic model, but we employ the crystal-field approach with strong correlations like shown in Fig. 3. It contrasts single-electron crystal-field schemes, shown in Fig. 2, considered in the current literature. It turns out that most of physics of 3d magnetism lies in details of the low-energy electronic structure. The atomic-like integrity of the 3d electrons is pointed out by the writing of 3d\(^n\) configurations.

3.2 Formation of a solid

During the formation of a solid, say an oxide, there proceeds a charge transfer from the paramagnetic cation to oxygen caused by the large chemical reactivity of oxygen and its large ability to capture two electrons from its surroundings. In case of NiO, for instance, during the formation of the crystal two electrons from outer 4s+3d shells transfer to the oxygen completing its 2p shell. Thus we have the charge distribution written as Ni\(^{2+}\)O\(^{2-}\). An analysis of magnetic and electronic properties of NiO we start from the discussion of properties of the Ni\(^{2+}\) ion in the crystalline solid as the oxygen has the closed 2p shell (2p\(^6\)). We do not expect low-energy states related to the oxygen. Our interest concentrates on the low-energy electronic structure of the Ni\(^{2+}\) ion - in the Ni\(^{2+}\) ion there are 8 electrons which can be in the configuration 3d\(^7\)4s\(^1\), 3d\(^6\)4s\(^2\), 3d\(^8\) or a more complex depending on the invention of a scientist. There is a wide chemical evidence that with completing the atomic shells with electrons 3d shell is filled after the 4s shell whereas during the formation of a compound the 4s electrons are given back the first. So, thinking about the Ni\(^{2+}\) ion in oxides we start with the 3d\(^8\) configuration. The previous two configurations can lead to more metallic states, not realized in NiO.
In LaCoO$_3$, owing to its insulating ground state, we expect the charge ion valences as La$^{3+}$Co$^{3+}$O$_3^{2-}$. In case of an intermetallic compound like ErNi$_5$ or NdNi$_5$ the situation is more complex but they can be analyzed as there localized electrons and itinerant electrons coexist. In case of ErNi$_5$ or NdNi$_5$ it has been proved that magnetic properties are related to the 4f$^{11}$ and 4f$^3$ configurations like in the Er$^{3+}$ and Nd$^{3+}$ ions, respectively. Very good reproduction of the zero-temperature moment, overall temperature dependence of paramagnetic susceptibility $\chi(T)$ and of heat capacity $c(T)$, including the magnetic transition proves the existence of the discrete atomic-like electronic structure with separations below 1 meV [21, 25].

3.3 Atomic physics - the existence of atomic terms as an effect of strong electron correlations

The 3d$^8$ configuration, according to the atomic physics, has \( \binom{10}{2} = 45 \) states grouped in the Russell-Saunders terms (the realization of the so-called LS coupling): term $^3\!F$ with 21-fold degeneracy, $^1\!D$ (5), $^3\!P$ (9), $^1\!G$ (9) and $^1\!S$ (1). The Hund’s rules ground term is $^3\!F$ term, that is described by quantum numbers of the whole 3d$^8$ configuration $S=1$ and $L=3$. These terms in a crystal are split and shifted, sometimes with the energetical reorganization, by the presence of the crystal-field potential but the integrity of the atomic-like 3d$^8$ system is assumed in QUASST to be preserved, at least at the start. In our description of the ion in a solid we start from the knowledge collected in the atomic physics, in particular in respect to the energy of terms and the intra-atomic spin-orbit coupling. Here the data of NIST Atomic Spectra Database are of the great importance [26].

For the 3d$^6$ configuration 210 states are grouped in the atomic terms: $^5\!D$ (25 states), $^3\!H$ (33), $^3\!G$ (27), $^2\!F$ (23), $^3\!D$ (15), $^2\!\!P$ (8), $^1\!I$ (13), $^2\!\!G$ (8) $^1\!F$ (7), $^2\!\!D$ (25) and $^2\!\!S$ (25). The Hund’s rules term is 25-fold degenerate $^5\!D$ term, that is described by quantum numbers of the whole 3d$^6$ configuration $S=2$ and $L=2$. It is realized as the ground term in case of the free Fe$^{2+}$ and Co$^{3+}$ ions.

3.4 Effect of the octahedral crystalline electric field on atomic states

In a solid the states of the free Ni$^{2+}$ ion are split and shifted. In a crystalline solid there is the electrostatic potential due to other charges forming the solid. This electrostatic potential is known as the crystal electric field and its effect on the paramagnetic ion is similar to the Stark effect in atomic physics. However, the crystal field in solids has very multipolar character (quadrupolar, octupolar, ...) due to the regular three dimensional arrangement of charges in a solid. This multipolar character of the CEF potential is hidden in the CEF parameters $B_n^m$. The predominant CEF potential in 3d oxides is the octupolar term - it is related to the octahedral crystal-field parameter denoted as $B_4$.

In our approach we make use of achievements about the crystal field reached in analysis of the electron paramagnetic resonance (EPR) (at present, the name
electron spin resonance (ESR) becomes more popular) on paramagnetic ions put to solids as impurities [27, 28, 29, 30]. The splitting and the shift of the terms of 3d paramagnetic ions under the action of the cubic crystal field interactions have been calculated by Tanabe and Sugano already 50 years ago [31]. Unfortunately this knowledge is not used in presently-in-fashion band-like theories of 3d oxides. The presently-in-fashion theories of 3d oxides generally employ the strong crystal field approach that breaks completely intra-atomic correlations and starts the description of n electrons in the 3d shell as being largely independent. In the one-electron picture electrons are put subsequently on the five octahedral CEF orbitals, with 10 places, on the $t_{2g}$ and $e_g$ single-electron states. This subsequent placing is shown in Fig. 4 drawn with the use of Ref [1] Fig.5.11 on p.150; Ref. [2] p.1049; Refs [15, 16, 32, 33, 34, 35].

In QUASST we apply the weak and intermediate crystal field regime, that does not break intra-atomic correlations, not only to 3d impurities, like is considered for the ESR analysis, but to 3d atoms/ions when they become the full part of a solid.

### 3.5 Why the octahedral crystal field is the starting point for discussion of 3d oxides?

Analysis of the crystallographic structure of many oxides reveals that the 3d cation is often surrounded by 6 oxygens forming almost regular octahedron or rarer by 4 oxygens forming a tetrahedron. The NaCl structure of monoxides NiO or FeO is built up from the face sharing oxygen octahedra. The perovskite structure of LaMnO$_3$ or LaCoO$_3$ is built up from the corner sharing octahedra. The oxygen octahedra, with the Cu cation sitting inside, occur also in La$_2$CuO$_4$, a parent compound of high-temperature superconductivity materials. Thus the customary discussion of crystal-field effects in 3d compounds as related to the octahedral crystal field is largely justified but already here we would like to say that for the fully physically adequate description of 3d-atom compounds lattice distortions are very important and all, required by the local symmetry, terms in the crystal-field potential have to be taken into account.

The effect of the octupolar crystal-field interactions on the energy states of the Hund’s rules ground term is shown in Figs 5b and 6b. The calculated states are states of the $3d^n$ electron configuration in the octahedral crystal field produced by the oxygen octahedron. In case of the tetrahedron the effect of the octupolar crystal field leads to the reversed schemes.

### 3.6 Can CEF parameters be calculated *ab initio*?

Having charge distribution in the elementary cell and consequently in the whole crystal, CEF parameters can be calculated by formulas known from electrostatics as the respective multipolar moments of the surrounding charge distribution. By symmetry of the local surrounding only few multipolar moments are not zero. For
Figure 4: Electronic structures of 3d-ions in high- and low-spin states in the octahedral crystal field. Such the structures are discussed in the present literature [1, 2, 15, 16, 32, 33, 34, 35], but - according to our studies - they are not physically adequate. Each piece denotes one orbital that can be occupied by two electrons with, up and down, spin shown.
Figure 5: The calculated electronic structure of the \( 3d^n \) configurations of the 3d ions, \( 1 \leq n \leq 4 \), in the octahedral crystal field (b) and in the presence of the spin-orbit coupling (c). According to the Quantum Atomistic Solid-State theory the atomic-like electronic structures, shown in (c), are preserved also in a solid. (a) shows the Hund’s rule ground term. Levels in (c) are labeled with degeneracies in the LS space whereas in (b) the degeneracy is shown by the orbital spin degeneracy multiplication. The spin-orbit splittings are drawn not in the energy scale that is relevant to CEF levels shown in figures b. On the lowest localized level the magnetic moment (in \( \mu_B \)) is written. The shown states are many electron states of the whole \( d^n \) configuration. At zero temperature only the lowest state is occupied. The higher states become populated with the increasing temperature.
instance, in case of the ligand (=negative ions) octahedron the only multipolar moment at the center of the octahedron is the octupolar lattice moment, denoted as CEF coefficient $A_0^0$, which in cooperation with the octupolar ion moment provides the CEF parameter $B_0^0$.

### 3.7 Spin-orbit coupling

The relativistic spin-orbit coupling is usually ignored in calculation of the electronic structure of the 3d ions in solids basing on a general consensus that the s-o coupling is for 3d ions relatively weak. We have, however, argued\cite{5} that such a thinking is incorrect - even weak s-o coupling causes dramatic change of the electronic structure by producing the fine electronic structure with a large number of low-energy states with separations even so small as 1 meV ($=11.6 \text{ K } = 8.0 \text{ cm}^{-1}$). One can be surprised, but the influence of the spin-orbit coupling has not been systematically studied despite of a quite simple form of the s-o Hamiltonian $H_{s-o} = \lambda L \cdot S$. We have proved that the spin-orbit coupling has to be taken into account for any meaningful analysis of electronic and magnetic properties of 3d-ion compounds\cite{17,18}. The weaker spin-orbit coupling the more dramatic influence on the physical properties at low temperatures is produced.

The influence of the spin-orbit coupling on the localized states of the strongly-correlated 3d$^n$ electron system produced by crystal-field interactions of the octahedral symmetry is shown in Figs 5c and 6c\cite{5,36}.

### 3.8 Zero temperature properties, the magnetic state and thermodynamics

At zero temperature only the ground state is populated. The magnetic properties of the compound at $T = 0 \text{ K}$ are related to this atomic-like ground state. The states shown in Figs 5c and 6c can be called the crystal-field or in general charged-formed (CF) ground state. In dependence of the magnetic characteristics of the ground state the ion moments can easier or more difficult enter into the game to create a collective magnetically-ordered state. A singlet CF ground state, in particular when there is a large energy separation to the excited states, largely prevents the formation of the magnetic state. It is worth noting that though magnetic state is the collective state its formation can be traced at the single-ion atomic scale as then there appears the breaking of the time-reversal symmetry in the atomic scale. This symmetry breaking the easiest is to be observed in case of the CF Kramers doublet ground state for electronic configurations with an odd number of electrons ($d^1, d^3, d^5, d^7, d^9$ configurations). The Kramers doublet is only split in the magnetic state and in presence of the magnetic field, internal or external. The formation of the magnetic state and a persistent non-magnetic state will be illustrated by two examples FeBr$_2$ and LaCoO$_3$. 
Figure 6: The calculated electronic structure of the $3d^n$ configurations of the 3d ions, $6 \leq n \leq 9$, in the octahedral crystal field in the presence of the spin-orbit coupling. According to QUASST these atomic-like electronic structures are preserved also in a solid.

With increasing temperature excited states become thermally populated. The population of states is described by the Boltzmann statistics. Having the states like those shown in Figs 5c and 6c the Helmholtz free energy $F(T)$ can be calculated by means of statistical physics. It enables calculations of all thermodynamical properties like temperature dependence of the heat capacity $c(T)$, of the paramagnetic susceptibility $\chi(T)$, of the charge quadrupolar ionic moment (measured by the Mossbauer spectroscopy) and many others. Also temperature dependence of the magnetic moment in the magnetically-ordered state can be calculated [17, 21].

QUASST enables calculations of the anisotropy of physical properties. The paramagnetic susceptibility $\chi(T)$, for instance, can be calculated along different crystallographic directions.
4 Hamiltonian, computations and results

4.1 Hamiltonian

In general, the Hamiltonian for the whole compound like NiO or FeBr$_2$ could be written as:

$$H = \sum H_d + \sum H_{d-d}$$

(1)

where $H_d$ should treat intra-atomic whereas $H_{d-d}$ inter-atomic interactions. $H_{d-d}$ comprises, for instance, the energy between Ni$^{2+}$ and O$^{2-}$ ions (called the lattice Madelung energy), that in case of an ionic compound like NiO is dominant, but also much, much smaller energy between magnetic ionic moments leading to the magnetically-ordered state. The separation for intra and inter-atomic interactions is not strict as, for instance, the crystal-field energy, that is considered as the single-ion effect in fact is the coulombic charge multipolar interactions of the 3d cation with the charge multipolar moments of the surroundings.

In consideration of $H_d$ we assume the physical situation for the 3d$^n$ system of a 3d-transition-metal ion to be accounted for by considering the single-ion-like Hamiltonian containing the electron-electron d-d interactions $H_{el-el}$, the crystal-field $H_{CF}$, spin-orbit $H_{s-o}$, and Zeeman $H_Z$ interactions:

$$H_d = H_{el-el} + H_{CF} + H_{s-o} + H_Z$$

(2)

The electron-electron and spin-orbit interactions are intra-atomic interactions, whereas crystal-field and Zeeman-like interactions account for interactions of the unfilled 3d shell with the charge and spin surroundings. These interactions are written in the decreasing strength succession. Important is that we assume that $H_{CF} \ll H_{el-el}$.

It is the essentially important to assume the dominant interactions to be $H_{el-el}$. In fact, here is the clue of our strongly-correlated crystal-field approach based on the atomistic approach. $H_{el-el}$ is responsible for the formation of the atomic terms from $^n\text{P}_{2n+2}$ states. A number of states, allowed by the Pauli exclusion principle, is large and amounts 10 for d$^1$/d$^9$, 45 for d$^2$/d$^8$, 120 for d$^3$/d$^7$, 210 for d$^4$/d$^6$ and 252 for the 3d$^5$ configuration. The given term gather states with the same quantum numbers L and S and they are rather well separated from other terms. The ground term of the free atom/ion is determined by two phenomenological Hund’s rules, i.e. the lowest term of the whole 3d$^n$ system is characterized by 1$^o$) the maximal value of the resultant spin quantum number $S$ and 2$^o$) the maximal value of the resultant orbital quantum number $L$ provided the condition 1$^o$. These rules yield for, for instance, the 3d$^4$ and 3d$^6$ electron configurations, the term $^5D$ with $S = 2$ and $L = 2$ as the ground term. This term is 25-fold degenerated in the spin-orbital space. In a solid other then Hund’s rules ground term can be realized as the ground term, like it occurs in LaCoO$_3$ and is shown in Fig. 3c. Figs 5 and 6 have been calculated for Hund’s rules ground terms.
In QUASST we take into account on-site electron-electron correlations among d electrons by assuming that also for the ion in a solid the term structure is preserved. It does not mean at all that we claim that in a solid the term structure is exactly the same as in the free ion. The term structure in a solid differs from that of the free ion but we say that in calculations of the influence of the crystal-field potential and of magnetic interactions we should follow along well known from atomic physics interactions keeping the atomic-like integrity of the 3d\(^n\) system. The strong intra-atomic correlations allow to work with many-electron quantum numbers \(S\) and \(L\) of the whole 3d\(^n\) configuration instead of single-electron states with \(s_i\) and \(l_i\). In band structure calculations and in the single-electron crystal-field approach it is assumed that the atomic-like d-electron correlations have been broken and then the better starting point is to consider d electrons to be largely independent but experiencing separately the octahedral crystal field \((H_{CF} \gg H_{el-el})\). In the consequence in the single-electron crystal-field approach electrons are put one by one on the five d orbitals determined by the octahedral crystal field (three \(t_{2g}\) states below and two \(e_g\) states higher). In such approach electron correlations are at the beginning absent and then they are introduced into calculations.

At beginning let assume that in a solid the ground term is the one given by phenomenological Hund’s rules. The Hund’s rules ground term of the 3d\(^n\) electron systems are collected in Table 1. The LS ground term is \((2L+1)\cdot(2S+1)\) degenerated. Strong intra-atomic Hund’s-rule correlations allow to work in the \(|LSL_zS_z⟩\) space, though one should remember that the complete QUASST calculations should be performed in the all-terms space with \(^{10}n\) states. In the one-term \(|LSL_zS_z⟩\) space the effect of the crystal-field, of the spin-orbit coupling and of the (internal/external) magnetic field is accounted for by considering the single-ion Hamiltonian of the 3d\(^n\) system of the 3d-transition-metal ion of the form:

\[
H^1_d = \sum \sum B^m_n \hat{O}^m_n(L, L_z) + \lambda L \cdot S + \mu_B(L + g_e S) \cdot B_{ext}
\]  

(3)

where \(^1\) denotes the one-term Hamiltonian left after the dominant action of \(H_{el-el}\). The first term is the CEF Hamiltonian with the Stevens operators \(\hat{O}^m_n\) that depend on the orbital quantum numbers \(L, L_z\). \(B^m_n\) are CEF parameters. The octahedral crystal field takes, for the \(z\) axis along the cube edge, the form

\[
H_{CF} = B_4(\hat{O}^4_0(L, L_z) + 5 \cdot \hat{O}^4_1(L, L_z))
\]

(4)

\(B_4\) is the octahedral CEF parameter that depends on the octupolar charge moment of the 3d shell and the octupolar moment of the lattice surroundings. The octupolar charge moment of the 3d shell is known as the Stevens coefficients \(\beta\) (Table 1, after Ref. [27], p. 873). The second term in Hamiltonian (3) accounts for the spin-orbit interactions. The last term accounts for the influence of the magnetic field, the externally applied in the present case. \(g_e\) value is taken as 2.0023.
4.2 Computations and results

The computations of the many-electron states of the 3d\(^n\) system have been performed by consideration of the Hamiltonian (3) in the \(|LSL_zS_z\rangle\) base. As a result of the exact diagonalization, of the maximal matrix of 28 by 28, we obtain the energies of the \((2L+1)\cdot(2S+1)\) states and the eigenvectors containing information e.g. about the magnetic characteristics. These magnetic characteristics are computationally revealed under the action of the external magnetic field \(B_{\text{ext}}\). The \((2L+1)\cdot(2S+1)\) degeneracy is removed by i) the crystal field (CEF) interactions and ii) by the intraatomic spin-orbit coupling. Despite of the fact that for the 3d ions the spin-orbit coupling is by two-orders of magnitude weaker than the CEF interactions we do not apply the perturbation method, as is usually made in literature, but we treat the CEF and spin-orbit interactions on the same footing. The calculated electronic structure of the 3d ion with the 3d\(^n\) configuration, \(1 \leq n \leq 9\), are collected in Figs 5 and 6 for the octahedral symmetry of the crystal field.

Figs 5 and 6 present the calculated general overview of the octahedral CEF and spin-orbit effect on the Hund’s rule term for the 3d\(^n\) systems. Figures c show the splitting of the ground term by the octahedral cubic CEF interactions in the presence of spin-orbit interactions. The parameters used are collected in Table 1.

The calculations have been performed with the realistic octahedral crystal field parameter \(B_4\). The \(T_{2g}-E_g\) splitting, approximately equal to 120\(B_4\), amounts to 2.1 eV for the 3d\(^1\) system in agreement with the quite frequent experimental observations of the d-d excitations in the optically visible energy range, i.e. 1.7-3.5 eV. The spin-orbit coupling values (\(\lambda = 220-1200\) K) are taken for divalent free ions, see for instance Ref. [27], p. 399. The octahedral crystal field strongly dominates the effect of the spin-orbit coupling. The parameter \(B_4\) alternates with the Stevens coefficient \(\beta\), that is a measure of the angular part of the octupolar charge moment of the 3d cloud for the Hund’s rules ground term, Fig. 7. The shown values of \(B_4\) keep the same lattice contribution, \(A_4\), i.e. the same octupolar charge moment of the surroundings, because we take always the octahedral oxygen surroundings into account. In the simplest form for the point-charge model the CEF parameter \(B_4\) for the given term is expressed as:

\[
B_4 = \beta \cdot <r^4_d> \cdot A_4
\]

(5)

For the octahedral symmetry the CEF coefficient \(A_4\) is expressed as [27], p. 669:

\[
A_4 = -\frac{7}{16} \frac{Ze^2}{d^5},
\]

(6)

where \(Z\) is the charge of oxygen (-2) and \(d\) is the cation-oxygen distance (192.5 pm in LaCoO\(_3\)). It yields a value of \(A_4\) of +432 Ka\(_B\)^{-4}, \(a_B\) is the Bohr radius. Taking for the Co\(^{3+}\) ion \(\beta = +2/63\) and \(<r^4_d> = 2.342 a_B^4\) [37] we get \(B_4 = +32\) K. This value is eight times smaller than the recent evaluation of \(B_4\) of 260 K [18], but the
| n  | S   | L   | free ion | octahedral crystal-field | with the spin-orbit coupling |
|----|-----|-----|----------|--------------------------|------------------------------|
|    |     |     |          | ground term | degen. | CEF state | degen. | β      | B₄ (K) | λ (K) | ξ (K) | degen. |
| d¹ | ¹/₂ | 2   | ²D       | ²T₂g        | 6      | +⁵/₆₃  | +200   | +220   | +220   | 4     |
| d² | 1   | 3   | ³F       | ³T₁g        | 9      | -²/₃₁₅ | -40    | +150   | +300   | 2     |
| d³ | ³/₂ | 3   | ⁴F       | ⁴A₂g        | 4      | +²/₃₁₅ | +40    | +125   | +375   | 4     |
| d⁴ | 2   | 2   | ⁵D       | ⁵E₉         | 10     | ²/₆₃   | -200   | +120   | +480   | 1     |
| d⁵ | ⁵/₂ | 0   | ⁶S       | -           | 6      | 0      | -      | -      | -      | 6     |
| d⁶ | 2   | 2   | ⁵D       | ⁵T₂g        | 15     | +²/₆₃  | +200   | -140   | +560   | 3     |
| d⁷ | ³/₂ | 3   | ⁴F       | ⁴T₁g        | 12     | -²/₃₁₅ | -40    | -260   | +780   | 2     |
| d⁸ | 1   | 3   | ³F       | ³A₂g        | 3      | +²/₃₁₅ | +40    | -480   | +960   | 3     |
| d⁹ | ¹/₂ | 2   | ²D       | ²E₉         | 4      | ²/₆₃   | -200   | -1200  | +1200  | 4     |
| d¹⁰| 0   | 0   | ¹S       | 1           | -      | 1      | -      | -      | -      | 1     |

Table 1: Spin S and orbital L quantum numbers of the two Hund’s rules ground term for the strongly-correlated 3dⁿ electron systems with the total degeneracy in the spin-orbital space. The ground octahedral subterm and the degeneracy in the octahedral cubic CEF field with the respective values of the octupolar CEF parameter B₄, that alternates with the Stevens coefficient β. The spin-orbit coupling parameter: many-electron λ and single-electron ξ; λ = ±ξ/2S. The last column - the degeneracy resultant from the spin-orbit coupling in the presence of the octahedral cubic CEF interactions. These values of B₄ and λ have been used for calculations of Figs 5 and 6.
most important is that 1) this \textit{ab initio} calculations give the proper sign of the $B_4$ parameter as it determines the ground state in the oxygen octahedron and 2) the experimentally derived strength of crystal-field interactions turns out to be much weaker than it was thought in literature for justification of the strong crystal-field approach. We are not going to discuss the discrepancy in $B_4$ - surely it is necessary to take into account all charges. Next neighbors, the cube of La$^{3+}$ ions adds to the nearest-neighbors oxygen contribution. This adding, despite of different sign of charges of the La and oxygen ions, is of great importance as there is a hope that by taking into account all charges the parameter $B_4$ will increase becoming closer to the experimental value. For Figs 5 and 6 we assume $B_4 = +200$ K. In a pragmatic approach in the start we take $B_4$, and other CEF parameters, as parameters to be evaluated from the analysis of properties of a real compound in frame of the CEF approach with the given symmetry.

Figures 5 and 6 are full of information. One can see the similarities, but also the differences, between the CEF effect and s-o interactions on, for instance, the $2D$ and $5D$ terms for the $d^1$ ($\lambda > 0$) and $d^6$ ($\lambda < 0$) configurations. The particle-hole symmetry can be studied for the $d^n/d^{10-n}$ configurations. We mention here only a few most important points.

1. For 3d ions there are only D and F terms as L can be only 2 and 3. The spin degeneracy depends on the number of electrons involved. The total degeneracy of low-energy states as large as 15 is realized.

2. The pairs $d^1/d^6$, $d^2/d^7$, $d^3/d^8$ and $d^4/d^9$ have the same orbital ground state. The spin-orbit effect is, however, entirely different due to different values of S, the reversal of the s-o constant $\lambda$ and the transformation of non-Kramers ions into Kramers ions (even $vs$ odd number of d electrons).

3. The adoption (affinity) or the loss of the one electron draws the full reconstruction of the fine electronic structure.

4. The spin-orbit coupling removes largely the degeneracy in all cases apart of the spin-only $d^5$ system. In case of the $d^4$ configuration the s-o coupling yields a singlet ground state, but there are 10 closely lying levels.

5. The s-o coupling produces a fine electronic structure with allowed excitations even much below 5 meV. These low-energy excitations can be detected by heat capacity and spectroscopic methods like Electron Spin Resonance.

6. There is a tiny splitting of the $5E_g$ cubic subterm realized for the Mn$^{3+}$ ion in LaMnO$_3$, recently a very popular compound.

7. There is also the extra second-order s-o splitting of the $T_{2g}$ originated states in comparison to the perturbation method and to the so-called T-P term equivalence used in Ref. \cite{29}.
Figure 7: Octupolar moment of the 3d\textsuperscript{n} shell in the Hund’s rules ground term. 
a) $\beta$ is the Stevens coefficient that describes the angular part of the quadrupolar 
moment. b) $< r^4 >$ is the mean values of the radius in power of 4, in atomic units, 
for 3d cations in different valence states calculated by Freeman and Watson \cite{37}; 
here taken from Ref. \cite{27}, p. 399.

8. The ground-state magnetic moment substantially differs from the spin-only 
value, i.e. from the integer value of $2n \mu_B$. A very small moment has been 
revealed for the d\textsuperscript{1}, d\textsuperscript{2} and d\textsuperscript{4} configurations.

9. The states shown are many-electron states of the whole 3d\textsuperscript{n} system. At 0 K only the lowest state is occupied. Higher excited states become 
populated with increasing temperature.

10. The population of higher states manifests in e.g. temperature variation of 
electronic and magnetic properties like the heat capacity $c(T)$ and the magnetic 
susceptibility $\chi(T)$. Detailed calculations of $\chi(T)$ will be presented for 
the d\textsuperscript{6} system in FeBr\textsubscript{2} for the Fe\textsuperscript{2+} ion.
For the physical understanding the most important are the points 9, 8 and 3. They illustrate the fundamental difference with the very often recalled one-electron picture with subsequent occupation of the \(t_{2g}\) and \(e_g\) states, as is shown in Fig. 4, without the reconstruction of the electronic structure in contrast to the present result of 3. In the many-electron picture at 0 K only the lowest state is occupied, i.e. the lowest-state energy is the energy of all \(n\) electrons as the whole \(d^n\) configuration.

The evaluation of the fine electronic structure, with the given energy and magnetic characteristics, allows for the calculation of temperature dependence of many physical properties like heat capacity or the paramagnetic susceptibility similarly to the description successfully used for the rare-earth compounds [19, 21, 22, 25].

4.3 Example I: Magnetic Mott insulator: FeBr\(_2\) (antiferromagnet)

4.3.1 Properties and Hamiltonian

FeBr\(_2\) exhibits insulating ground state with the charge distribution Fe\(^{2+}\)Br\(^{-}\). It is antiferromagnetic with \(T_N\) of 14 K (for references to experimental data see to Ref. [17]). After the metamagnetic transition at 3 T, it exhibits magnetic moment of 4.3 \(\mu_B\) per formula unit, for what we charge the Fe\(^{2+}\) ion. The electronic structure of the Fe\(^{2+}\) ion in the \(5\)\(D\) term is shown in Fig. 8e. It is very similar to that shown in Fig. 3 for the Co\(^{3+}\) ion (Fe\(^{2+}\) and Co\(^{3+}\) ions are isoelectronic 3d\(^6\) systems) but the lowest splitting is opposite, i.e. the doublet is lower than singlet, see also Fig. 9a.

For the description of the magnetic state we use a Hamiltonian for the Hund’s rules ground term (\(S=2, L=2\)) completed with a spin-dependent magnetic term [17]:

\[
H_d^1 = -\frac{2}{3} B_4 (\hat{O}_4^0 - 20\sqrt{20}\hat{O}_4^3) + \lambda L \cdot S + n \left( -\hat{m} < \hat{m} > + \frac{1}{2} \hat{m} >^2 \right) + B_2^0 \hat{O}_2^0
\]  

(7)

where \(\hat{m} = (\hat{L} + 2\hat{S})\) \(\mu_B\) is the magnetic-moment operator of the \(d\)-atom and \(n\) is the molecular-field coefficient. The first term is the octahedral CEF Hamiltonian written for the \(z\) axis taken along the cube diagonal (then a coefficient \(-2/3\) to \(B_4\) appears), because FeBr\(_2\) exhibits trigonal distortion. The third term accounts for spin-dependent interactions. The last term accounts for the slight off-octahedral trigonal distortion of the local Br\(^{-}\) octahedron. The magnetically-ordered state is calculated self-consistently. The optimal parameters found for FeBr\(_2\) are: the octahedral CEF parameter \(B_4 = +200\) K, the spin-orbit coupling \(\lambda = -161\) K, \(n = -0.8\) K/\(\mu_B^2\) and the trigonal off-cubic distortion \(B_2^0 = -30\) K. The magnetic ordering temperature occurs for:

\[
n = \chi^{-1}(T_N) \tag{8}
\]

4.3.2 Thermodynamics - Counting of atoms

The calculated temperature dependence of the ordered magnetic moment and of the heat capacity are shown in Fig. 9 together with the temperature dependence of the
Figure 8: Fine electronic structure of the strongly-correlated $3d^6$ electronic system.

a) The 25-fold degenerated Hund’s rules $^5D$ ground term. b) the effect of the oxygen octahedral crystal field, c) the effect in combination with the spin-orbit coupling; d) and e) further splittings due to trigonal distortions - the case e) is realized in FeBr$_2$.

energy of the three lowest localized states shown in Fig. 8. Everybody admits that the attained agreement in description of properties of FeBr$_2$, both zero-temperature magnetic moment of 4.3 $\mu_B$ and thermodynamics, is remarkably good. The full reproduction of temperature dependence of the heat capacity, of the paramagnetic susceptibility and of the macroscopic magnetization proves that all Fe atoms equally contribute to these properties. It means that all atoms are in the Fe$^{2+}$ ion state with the same electronic structure. In fact, by the reproduction of values of the macroscopically-observed properties actually we count magnetic atoms. For comparison of the calculated microscopic atomic-scale values and macroscopic molar values simply the Avogadro number is used only.

So good description is thanks the crystallographic structure (and the good theory, of course). Thanks the hexagonal structure all Br octahedra are aligned with the main diagonal along the hexagonal c axis. Then the trigonal distortion of the local octahedron can proceed coherently on all Fe sites without breaking of the hexagonal symmetry of the elementary cell.
Figure 9: Magnetic phase transition in FeBr$_2$. a) The calculated temperature dependence of the lowest part (3 lowest states) of the electronic structure of the 3d$^5$ configuration in the octahedral crystal field ($B_4=+200$ K), in the presence of the spin-orbit coupling ($\lambda = -150$ K), trigonal distortion $B_0^2 = -30$ K and the molecular-field coefficient $n = -0.8$ K/$\mu_B^2$. b) Temperature dependence of the atomic magnetic moment of the Fe$^{2+}$ ion; c) Calculated temperature variation of the contribution of the d subsystem to the heat capacity of FeBr$_2$. Points denote literature experimental data.
Figure 10: Calculated temperature dependence of the paramagnetic susceptibility $\chi(T)$ of FeBr$_2$ for magnetic fields applied along and perpendicular hexagonal c axis. Calculations have been performed for $B_4=+200$ K, $\lambda_{s-o}=-150$ K and the trigonal parameter $B_0= -30$K. Points are experimental values. A shadow area shows the antiferromagnetic state below $T_N$ of 14.2 K. Curve marked as $S=2$ shows $\chi(T)$ expected from Curie law with $S=2$ [17].

4.3.3 Orbital and spin moments

Very important superiority of QUASST among the present solid-state theories lies in the possibility of the calculations of the orbital magnetic moment. The orbital moment comes out from the intra-atomic spin-orbit coupling. In FeBr$_2$ we have found that the Fe$^{2+}$ ion moment is composed from the orbital moment $m_O=+0.80 \mu_B$ and the spin-moment $m_S=+3.52 \mu_B$ [17]. In NiO with the 3d$^8$ configuration of the Ni$^{2+}$ ion we have calculated the orbital moment $m_O$ of $+0.54 \mu_B$ and the spin moment $m_S$ of $+1.99 \mu_B$ [38]. The existence of a quite large orbital moment in NiO and CoO has been revealed recently by X-ray synchrotron radiation [39, 40], we take this fact as confirmation of the QUASST theory. Consistent description, keeping the same lattice octupolar moment, of properties of NiO and CoO has been presented in Ref. [41]. The same lattice octupolar moment is desirable owing to the same crystallographic structures. The attained good description indicates on the dominant single-ion mechanism.
4.4 Example II: Nonmagnetic Mott insulator: LaCoO$_3$

LaCoO$_3$ attracts a large scientific interest by more than 50 years due to its intriguing non-magnetic ground state and anomalous temperature dependence of the paramagnetic susceptibility $\chi(T)$ with a pronounced maximum at about 100 K. This nonmagnetic state is at the atomic scale. It is widely believed that with increasing temperature the Co$^{3+}$ ion changes its state from the low-spin (LS) to high-spin (HS) state via an intermediate (IS) state [9], as is schematically shown in Fig. 2. Our studies provide much more exact description of states, see Fig. 3 [18], and exclude the existence of the IS state. Within a HS configuration, described in QUASST by the $^5D$ term with $S=2$, the Co$^{3+}$ ion can have non-magnetic singlet ground state as an effect of a lattice off-octahedral distortion in the presence of the spin-orbit coupling, but in LaCoO$_3$ the singlet ground state is a non-magnetic $^1A_1$ subterm that originates from the $^1I$ term. Recently it has been unambiguously proved by very sophisticated electron-spin-resonance experiments on single crystal [42] in external magnetic field up to 30 T and the frequency up to 1390 GHz ($\hbar\omega = 66.7$ K = 5.75 meV) that such the singlet-doublet structure, as shown in Fig. 3, with a splitting of 0.6 meV only is realized in LaCoO$_3$ indeed, Fig. 11 [18, 42], but there is about 12 meV lower another singlet as the ground state. This singlet ground state is a $^1A_1$ subterm and originates from the $^1I$ term. The $^1I$ term in the free Co$^{3+}$ ion lies 4.43 eV above the $^5D$ term [21], but in LaCoO$_3$ in the presence of the octahedral crystal field interactions the $^1I$ term is split into six subterms and a subterm $^1A_1$ ($^1I$) lowers so much its energy due to the very large orbital moment of the $^1I$ term ($L=6$) and substantial octahedral crystal-field interactions, Fig. 12.

The octahedral CEF turns out to be about 25% stronger than we originally thought [43, 44, 45] (instead of $B_4$ of 200 K it turns out to be of 260 K) [18], but these octahedral CEF interactions are still not so strong to break intra-atomic correlations among electrons within 3d shell (the preservation of dominant intra-atomic correlations among electrons within 3d shell, leading to the 3d$^6$ configuration, is our meaning of “atomistic”).

In Fig. 11 we present our calculations of the behavior of the three lowest Co$^{3+}$ states of the fine electronic structure shown in Fig. 3 under the action of the external field up to 70 T. The calculated results for the energy separations perfectly reproduce the experimental data measured up to 30 T for the field applied along the cube diagonal as well as for other two main crystallographic directions. A remarkably good description of the experimentally derived quasi-triplet states with its behavior in magnetic fields up to 30 T applied along different main crystallographic directions [18] proves the high physical adequacy of the used by us intermediate CEF approach to 3d-ion compounds in contrary to the generally used strong CEF approach. Despite of a non-Hund’s rule ground state of the Co$^{3+}$ ion in LaCoO$_3$ the QUASST theory is still valid for LaCoO$_3$ as the $^1A_1$ subterm is the term expected from the atomic physics. In fact, we never expected that in a 3d solid electronic states will be so thin, in the energy scale below 1 meV, and so well characterized by
Figure 11: Calculated field dependence of the lowest part of the electronic structure of the Co$^{3+}$ ion in LaCoO$_3$ for external magnetic fields applied along the diagonal of the cube of the perovskite structure of LaCoO$_3$ of the quasi triplet originating from the 25-fold degenerate $^5D$ term for the octahedral crystal field $B_4 = +200$ K and the spin-orbit coupling $\lambda = -185$ K and the distortion trigonal parameter $B_2^0 = +7.2$ K. The ESR transitions $f_1$ ($=17.2$ T) and $f_2$ ($=25$ T) for the frequency of 1000 GHz ($=48$ K) are shown - they are in perfect agreement with recent experimental observation of Ref. [42]. The zero energy is at the level of the unsplit $^5D$ term. The ground term is subterm $^1A_1$ originating from the $^1I$ term that is shifted down by 4.43 eV by octahedral crystal-field interactions.

the atomic physics. The recent ESR results on LaCoO$_3$, its theoretical anticipation and the perfect description provide strong, if not unambiguous, evidence for the existence of the discrete atomic-like fine electronic structure in the 3d-atom containing compound confirming the basic concept of QUASST.

The QUASST predicts next ESR absorptions at the field of 40-42 T for the 1000 GHz frequency, Fig. 11, provided non-zero matrix elements. There is also expected at a field of 60 T a level crossing and the transition to the magnetic state. It will be the field induced magnetic state.

The QUASST description proves that in LaCoO$_3$ there is no IS state as comes out from band-structure calculations [9]. Moreover, the nature of the HS state is completely different from that shown in Fig. 2c. According to Fig. 2c the HS state, characterized by $S=2$, is a spin-polarized state, caused by $J_{ex}$, what is wrong owing
Figure 12: Influence of the strength of the octahedral crystal field interactions on the atomic terms of the 3d⁶ configuration occurring in Co³⁺ and Fe²⁺ ions. After Tanabe and Sugano [31]. The zero energy is at the level of the unsplit 5D term. At strong crystal field subterm ¹A₁, originating from the ¹I term, is shifted down by 4.43 eV by octahedral crystal-field interactions becoming the ground term instead of Hund's rules ⁵D ground term. In LaCoO₃ Dq/B, Dq=12B₄ and B is Raccah parameter B=1065 cm⁻¹ for the Co³⁺ ion, amounts to 2.05 and the ¹A₁ term is only 140 K below the ⁵D. The value Dq/B=2.05 in LaCoO₃ corresponds to B₄=+260 K. For the Fe²⁺ ion in FeBr₂ Dq/B≈1.4.
to the fact that in LaCoO$_3$, being not magnetically-ordered, there is no internal magnetic field and no spin polarization. Our HS state, also with $S=2$, is not-spin-polarized state in accordance with the experimentally-observed paramagnetic state.

Figure 13: Calculated temperature dependence of the paramagnetic susceptibility $\chi(T)$ of LaCoO$_3$. Calculations have been performed for the fine electronic structure as shown in Fig. 3, but taking only into account one third of Co atoms and a diamagnetic contribution of $-1.5 \times 10^{-3} \mu_B/T (= -0.83 \times 10^{-3} \text{emu/mol})$. Low-temperature upturn is due to impurities, about 1% of the Co$^{3+}$ ions in the $^5D$ term ground state. Points denotes recent experimental values, rough data of Ref. [46].

There is a problem left whether the electronic triplet structure derived from ESR is representative for all Co ions in LaCoO$_3$ or may be the observed ESR signals originate from some impurity atoms. Impurity atoms can be also Co ions on the surface and others not being full part of the crystallographic structure. In Fig. 13 the temperature dependence of $\chi_d(T)$ calculated for the electronic structure shown in Fig. 3 is presented - the calculations reproduce the overall shape of the temperature dependence in the whole temperature range but the agreement with the experimental maximal value at 100 K has been reached by multiplying by $N_A/3$ only - it could mean that only one third of Co ions contribute to the observed susceptibility. In calculations we took into account a diamagnetic contribution of $-1.5 \times 10^{-3} \mu_B/T (= -0.83 \times 10^{-3} \text{emu/mol})$ according to formula

$$\chi_{exp} = \chi_d + \chi_{dia}$$

showing that the expected experimental value should be lower than the calculated
value $\chi_d$. In literature the opposite treatment of the diamagnetic contribution is made for LaCoO$_3$, see Ref. [46], for instance, but we think that our treatment is correct.

For the explanation of this discrepancy, too large calculated susceptibility, we would recall many reasons like the covalency (but somebody has to prove it clearly defining its effect on physical properties, in particular on the susceptibility), the hybridization (the same as above), the reality is more complicated than the single-ion approach and so on. We are looking for for more physical and better-defined explanations, that we require, and we think that the smaller observed susceptibility can be caused by a zig-zag arrangement of the oxygen octahedra in the distorted perovskite structure (Co-O-Co angle in LaCoO$_3$ is not 180° but amounts to 163° only [16]) but we would suggest that indeed only 1/3 of Co ions contribute to the susceptibility observed at 100 K. It would require that local distortions distinguish Co sites in a proportion 1 to 2 and that in the second sites the octahedral crystal field is larger yielding $\Delta_{s-t}$, say, of 1000 K. It would cause that their contribution to $\chi(T)$ would be experimentally invisible. For such the increase of $B_4$ the tiny closer oxygen-cobalt distance, less than 1 percent, is needed and surely cannot be excluded from the experimental point of view.

The calculated results, taking into account one third of Co ions, well describe the recent experimental result for $\chi(T)$ [46] as is seen in Fig. 13. For detailed comparison one should remember that $\Delta_{s-t}$ in LaCoO$_3$ is very small and that there are going very subtle effects with temperature. With temperature due to conventional thermal expansion the strength of octahedral CEF interactions slightly decreases. This thermal expansion effect is small but in case of LaCoO$_3$ it is enough to reverse the ground state. Taking into account the thermal expansion result of Ref. [47] we have calculated that $\Delta_{s-t}$ becomes zero at T about 500-600 K - we think that this level crossing is responsible for the anomaly in the $\chi(T)$ dependence [7, 46] in this temperature region. The effect opposite to the thermal expansion, i.e. the decrease of the Co-O distance and the increase of the $B_4$ parameter can be produced by external pressure. Then, with the applied pressure the maximum temperature of $\chi(T)$ is shifted to higher temperatures indicating the increase of $\Delta_{s-t}$ [48, 49] consistently with the increase of $B_4$.

All of these facts show that LaCoO$_3$ is very unique system, indeed. Thanks physical coincidences the ground state is close to the level crossing of states related to different terms. It enables exact evaluation of the strength of CEF interactions and to study the Stark effect on different terms.

4.5 Example III: Nonmagnetic Mott insulator: Na$_2$V$_3$O$_7$

In 2002 Gavilano et al. [50] have discovered a drastic violation of the Curie law in Na$_2$V$_3$O$_7$ in the experimentally measured temperature dependence of the magnetic susceptibility. Analysis of the $\chi(T)$ dependence in terms of the Curie law shows that the effective moment of the V$^{4+}$ ion is reduced by the one order of magnitude
upon reducing the temperature from 100 to 10 K. Gavilano et al. have provided an explanation that "The reduction of the effective magnetic moment is most likely due to a gradual process of moment compensation via the formation of singlet spin configurations with most but not all of the ions taking part in this process. This may be the result of antiferromagnetic interactions and geometrical frustration." Using some crystallographic-arrangement arguments they further conjectured "the compensation of eight out of the nine V spins ..." in order to reproduce the observed reduction of the effective moment by one order of magnitude. There is no sign of the magnetic order down to 1.9 K [50]. So we have to accept that Na$_2$V$_3$O$_7$ is in the paramagnetic state down to this temperature.

We could reproduce very well the observed temperature dependence of the paramagnetic susceptibility by considering the electronic structure associated with the V$^{4+}$ ion (3d$^1$ configuration) under the action of the crystal field taking into account the spin-orbit coupling. Despite of the Kramers doublet ground state, a ground-state with quite small magnetic moment is obtained as an effect of the spin-orbit coupling. It turns out that even weak s-o coupling unquenches a quite large orbital moment. In our explanation we have been oriented by our earlier calculations for the V$^{4+}$ ion presented in Refs [51].

The one 3d electron in the V$^{4+}$ ion is described by quantum numbers $L=2$ and $S=1/2$. The ground term $^2D$ is 10-fold degenerated. Its degeneracy is removed by the intra-atomic spin-orbit interactions and in a solid by crystal-field interactions. This situation can be exactly traced by the consideration of a single-ion-like Hamiltonian [51, 52]

$$H_d = H_{CF}^{\text{oct}} + H_{S-o} + H_{CF}^{\text{tr}} + H_Z = B_3(O_4^0 + 5O_4^1) + \lambda L \cdot S + B_2^0 O_2^0 + \mu_B (L + g_e S) \cdot B$$  \hspace{1cm} (10)

in the 10-fold degenerated spin-orbital space. We approximate, for simplicity, the CEF interactions at the V site by considering dominant octahedral interactions with a trigonal distortion. For the octahedral crystal field we take $B_3 = +200$ K. The sign "+" comes up from ab initio calculations for the ligand octahedron. The spin-orbit coupling parameter $\lambda_{S-o}$ we take as +360 K, as in the free V$^{4+}$ ion [27], p. 399.

The resulting electronic structure of the 3d$^1$ ion contains 5 Kramers doublets separated in case of the dominant octahedral CEF interactions into 3 lower doublets, the $T_{2g}$ cubic subterm, and 2 doublets, the $E_g$ subterm, about 2 eV above (Fig. 14). The $T_{2g}$ subterm in the presence of the spin-orbit coupling is further split into a lower quartet and an excited doublet (Fig. 14(2)). Positive values of the trigonal distortion parameter $B_0^2$ yields the ground state that has a small magnetic moment (Fig. 14(3)). For $B_2^0 = +9$ K the ground state moment amounts to $\pm 0.21 \mu_B$. It is composed from the spin moment of $\pm 0.48 \mu_B$ and the orbital moment of $\mp 0.27 \mu_B$ (antiparallel). The sign $\pm$ corresponds to 2 Kramers conjugate states. The excited Kramers doublet lies at 58 K (5 meV) and is almost non-magnetic - its moment amounts to $\pm 0.03 \mu_B$ only ($= \pm 1.03 \mu_B + 2 \cdot (\mp 0.50 \mu_B)$) due to the cancelation of
Figure 14: Fine electronic structure of the strongly-correlated 3d\(^1\) electronic system related to the 10-fold degenerated Hund’s rules \(^2\)D ground term. 1) the effect of the oxygen octahedral crystal field, 2) the effect in combination with the spin-orbit coupling; 3) further splittings due to trigonal distortions. The calculated resulting susceptibility is shown in Fig. 15 and it well reproduces experimental results for Na\(_2\)V\(_3\)O\(_7\).
the spin moment by the orbital moment. So small and so different moments for the subsequent energy levels is an effect of the spin-orbit coupling and distortions.

Figure 15: Temperature dependence of the paramagnetic susceptibility $\chi(T)$ of Na$_2$V$_3$O$_7$ (curve 3) calculated for $B_4=+200$ K, $\lambda_{s-o} = +360$ K and the trigonal parameter $B_0^2 = +9$ K. Curve 1 - results for the octahedral crystal field without the spin-orbit coupling. Curve 2 - the octahedral crystal field with the spin-orbit coupling [52]. Curve marked as $S=1/2$ shows $\chi(T)$ expected from Curie law with $S=1/2$. Crosses are rough experimental values of Ref. [50].

The resulting susceptibility is shown in Fig. 15. It is clear that we could describe overall temperature dependence of $\chi(T)$ [52]. For comparison of the calculated susceptibility value with experimental data we follow Eqn. 9 taking into account a diamagnetic contribution of $-0.7 \cdot 10^{-3} \mu_B/T$ V-ion (= $-0.4 \cdot 10^{-3}$ emu/mol V).

We are fully convinced that the observed violation of the Curie-Weiss law in Na$_2$V$_3$O$_7$ is the effect of the spin-orbit coupling and CEF interactions. From almost perfect reproduction of the absolute value we can say that all V ions are in the tetravalent state and that all V$^{4+}$ ions contribute equally to the susceptibility.

QUASST predicts Na$_2$V$_3$O$_7$ to exhibit a Schottky-like peak at 25 K and below 1 K a large low-temperature specific heat, resembling heavy-fermion phenomena, as the Kramers degeneracy of the ground state has to be removed before reaching the absolute zero temperature. Obviously the study of Na$_2$V$_3$O$_7$ at low temperatures is of large scientific interest - a magnetic ordering at ultra-low temperatures is discussed recently in terms of the quantum critical point.
5 Further remarks about QUASST in a solid

5.1 Single ion vs a three dimensional solid

The crystal-field approach itself is usually considered as the single-ion approach and then arguments are given against its usefulness in the discussion of a real three dimensional (3D) solid. We disagree with such a thinking and in order to point out the physical relevance of the CEF concept to a solid the more general name, Quantum Atomistic Solid State Theory (QUASST), has been given. At first, it is important to notice that we consider in QUASST not a single 3d cation but the cation in the octahedral surroundings, i.e. the complex $\text{MO}_6$. In the crystal there is the translational symmetry and the whole 3D crystal of, say NiO with the NaCl structure, is built up from the face-sharing octahedra along three main crystallographic directions.

The CEF parameters reflect interactions of the charge multipolar moment of the 3d cation with the charge multipolar moments of the surroundings of the whole crystal, not only of the local octahedron.

5.2 Jahn-Teller effect - fundamental importance of the spin-orbital space

The Jahn-Teller (J-T) effect can be easily illustrated in the electronic structures presented in Figs 5c and 6c. According to the Jahn-Teller theorem there is always a spontaneous distortion of the local lattice surroundings going on in order to remove the degeneracy of the ground state. Inspecting Figs 5c and 6c we can say that lattice off-cubic distortions will proceed for all 3d cations in order to remove the ground state degeneracy. The subsequent manifestation of the J-T effect is to increase the energy separations among the lifted-degeneracy levels. The quartet degeneracy of the lowest state in case of the $d^1$ configurations can be lifted only to two doublets owing to the Kramers theorem as is calculated in Fig. 14. Similarly in case of the $d^3$ and $d^9$ configurations. The splitting of the triplet in case of the 3d$^6$ configuration into (lower)singlet and excited doublet has been analyzed already in case of LaCoO$_3$ despite the fact that this triplet is the excited state. It reveals more subtle Jahn-Teller effect on the excited states. In FeBr$_2$ the triplet degeneracy is removed, see Fig. 8, yielding the lower doublet and higher singlet structure. Such the structure is somehow in disagreement with the subtle Jahn-Teller effect - Nature reaches, however, the singlet ground state in FeBr$_2$ by the formation of the magnetic state, Fig. 9a. This discussion can be concluded that all 3d ions are practically Jahn-Teller ions, i.e. that in all compounds we should expect the local off-octahedral distortions to occur.

One should note that the present discussion of the Jahn-Teller theorem in the spin-orbital space differs completely from the removal of the degeneracy in the orbital-space only as is customarily discussed in the present literature related
to iron group compounds. It is obvious that the definition of the physical space is crucial for the proper analysis of the Jahn-Teller theorem. We claim that the spin-orbital space is the physically proper space for 3d-ion compounds [53]. For rare-earth systems the Jahn-Teller effect is discussed using the total angular momentum quantum number J as the good quantum number. Such the J space of the three Hund’s rules ground multiplet is equivalent to the spin-orbital space, because J becomes the good quantum number as a result of the strong spin-orbit coupling, in fact infinitively strong. It means, that thanks taking into account the spin-orbit coupling in description of 3d ions we make the unification in description of the electronic structures of 3d and 4f ions and compounds.

5.3 Symmetry breaking with lowering temperature as a general QUASST rule

In the QUASST we point out that with decreasing temperature there appears more and more breaking symmetry mechanisms in order to remove the ground-state degeneracy and to increase the energy separation to the excited states. Here we can mention a lowering of the local symmetry, the site differentiation and the formation of magnetic state. The magnetic state related to the time reversal symmetry breaking often appears with the lowering temperature. In case of the site differentiation instead of the single energy level scheme for the crystal (what means, the same energy scheme at each 3d site) we can have many energy schemes superimposed on each other originating from different sites. It could resemble a band. Of course, the nature of this band is completely different from the band in the band theories. This band-like closely lying CEF states are due to the site differentiation and a structural disorder. One should note that for the band formation the perfect translational symmetry is needed. Our atomistic approach can be used for a low-symmetry, non-stoichiometric systems and even for amorphous systems.

LaCoO$_3$ undergoes the rhombohedral distortion at 1610 K [54]. A low-temperature upturn below 30 K in $\chi$(T), see Fig. 13, is supposed to be due to about 1 percent impurities or Co atoms/ions on the surface, i.e. atoms with largely reduced dimensionality and very low symmetry.

5.4 Zeeman effect and evaluation of the internal molecular field

An effect of the internal or external magnetic field on the electronic states, known as Zeeman effect, can be nicely analyzed on states shown in Figs 5c and 6c with the use of Hamiltonian (3). In the magnetically-ordered state in a solid there appears the internal magnetic field. Its effect on the lowest triplet of the Fe$^{2+}$ ion in FeBr$_2$ is shown in Fig. 9a. We have calculated that in FeBr$_2$ at 0 K the Fe$^{2+}$-ion moment experiences the molecular field $B_M(0)$ of 5.15 T [17]. This field diminishes with temperature becoming zero at $T_N = 14.2$ K. In LaMnO$_3$, an antiferromagnet with $T_N$ of 140 K, $B_M(0) = 108$ T [55]. In CoO, an antiferromagnet with $T_N$ of 290 K,
$B_M(0) = 169 \text{T} \ [41]$. In NiO, an antiferromagnet with $T_N$ of 525 K, $B_M(0) = 500 \text{T} \ [38]$. In general, the higher $T_c(T_N)$ the larger molecular field is.

5.5 Clear distinction between magnetically-ordered and paramagnetic state

In QUASST there is clear distinction between the magnetically-ordered and the paramagnetic state. In the magnetic state the time reversal symmetry (TRS) is broken. This TRS breaking is possible to trace in the atomic scale as then appears the magnetic spin-like polarization of the eigenfunctions and states. The Kramers doublets become split and then there appears a spin-like gap of a few meV size, depending on values of $T_c(T_N)$. In the magnetic state the mean value of the operator $\langle \hat{J}_z \rangle$ in case of rare-earth ions and the mean values of $\langle \hat{S}_z \rangle$ and $\langle \hat{L}_z \rangle$ operators defining the total magnetic moment by $(\hat{L}_z + g_e \hat{S}_z)$, in case of iron-group ions, becomes different from zero. These values of the ground state do not have any direct connection to the effective moment derived from the paramagnetic susceptibility, that is a measure of $\hat{J}^2$ and $\hat{S}^2$ operators. In the paramagnetic state the time-reversal symmetry is preserved despite that the local moment is still described by quantum numbers $S \neq 0$ and $L \neq 0$.

In QUASST the paramagnetic-magnetic transition is nicely describes in the temperature dependence of the heat capacity $c(T)$, as it was shown in Fig. 9c for FeBr$_2$. It is worth noting that in QUASST the overall $c(T)$ dependence is reproduced both in the absolute value and the $\lambda$-type peak at $T_c(T_N)$. It is a surprise that already so simple mean-field Hamiltonian, the third term in Eqn (7), provides so good reproduction of the $\lambda$-type peak.

5.6 Single-ion magnetism vs collective nature of the magnetic state

One can think that the presented approach is too simple. Surely it is, but the most important is that it is confirmed by experiment. So, the physics of solids could be complex, but it turns out that Nature is not so complicated as could be. God is gracious to us! However, the evaluation of CEF interactions, effects of the lowering symmetry with decreasing temperature, the site-to-site change of the quantum local z-axis (so-called zig-zag alignment of octahedra in real perovskite compounds) and a possible site differentiation with respect to the charge and local surroundings in cooperation with the spin-orbit coupling and magnetic interactions make the problem far from being easy to tackle for real compounds. It is the reason that though the concept of the crystal field is known already by 75 years there is a quite limited number of compounds in which CEF interactions and magnetic interactions have been unambiguously evaluated. In particular, for 3d-atom containing compounds.

In pointing out, in our presentation of QUASST, of the importance of the atomistic description we would like to remind an obvious fact that it is atoms and ions that are the source of magnetism of solids.
5.7 Many-electron vs single-electron states

In QUASST we deal with many electron states and consequently with many-electron wavefunctions in contrary to single-electron states and single-electron wavefunctions considered in the band theories. In general, the wavefunction and the energy of the whole atomic-like $3d^n$ many-electron system of a given cation can be constructed from single-electron wavefunctions. In QUASST it is in fact assumed that this many-electron construction from single-electron wavefunctions will lead to the atomic-like wavefunctions. Other words, we think that the ambitious \textit{ab initio} theories starting the description of a solid from a (gaseous) jellium of independent electrons have to put such conditions and introduce such mutual electron interactions into their theories in order to get atoms or given ions. In QUASST we take the existence of atoms or ions as the physical fact that is not necessary to prove. Their existence in the reality confirms the validity of our assumption. We treat the problem of description of atoms or ions as the subject of atomic physics.

5.8 The nature of the states

The states discussed in QUASST are physical states - they can be experimentally observed by energy spectroscopic methods, like the inelastic neutron scattering, the light absorption, or the Electron Spin Resonance. The existence of these states give physical effects like an extra heat capacity, quite pronounced for low-energy states giving a non-trivial Schottky-like heat contribution at low temperatures, or a violation of the Curie-Weiss law at low temperatures. We point out the physical nature of the discussed states as in presently-in-fashion theories often virtual states and energy transitions of 2-5 eV are considered to give substantial physical effects below the room temperature.

In QUASST the number of involved states is counted by the configurational entropy. This configurational entropy is experimentally measured by the integration of the heat capacity, after the subtraction of the lattice heat. The presence of a large number of electronic states in energies below 25 meV is made use in the practice for magnetocaloric materials. The related entropy is freed at the magnetic ordering temperature. Inspecting Figs 5 and 6 we expect large magnetocaloric effect to occur for $3d$ ions in the octahedral voids for the Mn$^{3+}$ ions - there entropy related to 10 lowest states can be freed.

5.9 Insulating ground state

Within the QUASST the insulating ground states of oxides is easily understood. After the charge transfer during the formation of a compound later electrons are bound to atoms. They are staying localized in case of the perfect stoichiometry and the perfect crystallographic structure. In oxides the conductivity appears as an effect of an imperfection of the crystal structure, off-stoichiometry, the appearance
of vacancies and, in general, as disorder effects. There can appear the conductivity in perfect crystals in case of, for instance, the existence of few sites with ions with different valences. This latter case occurs in Fe$_3$O$_4$, in which Fe$^{2+}$ and Fe$^{3+}$ ions coexist at different crystal sites. Thus, the conductivity in oxides is in general of the hopping mechanism and has the activation character.

In LaCoO$_3$ the resistivity dramatically grows up with decreasing temperature reaching at 60 K already $10^7$ Ωcm confirming that LaCoO$_3$ is the Mott insulator despite of the existence of the incomplete 3d shell. With increasing temperature the resistivity smoothly drops reaching at about 700 K a value of $10^{-3}$ Ωcm which is a Mott border-resistivity value for beginning of the metallic. Some people discuss this 10 order of magnitude reduction of the resistivity as an insulator-metal transition, though there only smooth crossover occurs with temperature.

In intermetallic compounds there are itinerant electrons, apart of bound localized electrons, as it was discussed for ErNi$_5$ and NdNi$_5$ [21, 25].

5.10 Pauli exclusion principle and Boltzmann statistics

For description of thermodynamical properties in CEF and QUASST theories the Boltzmann distribution function is used. The Pauli exclusion principle is made use in the description of particular atoms, i.e. in the description of electrons in shells, that appears in the allowed terms. The Boltzmann distribution function is used for the calculation of thermodynamical properties because it describes the thermal equilibrium of the collection of atoms having available different energy states.

5.11 Unification of description of 3d and 4f paramagnetic ions

Rare-earth ions (4f) are customarily described using J as the good quantum number [21, 24, 25]. This the one-multiplet approximation gives physically adequate result because the spin-orbit coupling is large. Due to the strong s-o coupling the ground multiplet is well separated from the exited multiplets. Thus, the description within the ground multiplet, resulting from three Hund’s rules, is a justified approximation of calculations within the $|LSL_zS_z\rangle$ space. In contrast, 3d paramagnetic ions are customarily described, if not a one-electron approach is used, in the separate L and S spaces. It means, that the magnetic moment is the spin-only moment, whereas the electronic structure is built up from orbital states only. In our approach we describe both 4f and 3d paramagnetic ions within the same spin-orbital space $|LSL_zS_z\rangle$. Thus, QUASST provides the unified description of 3d and 4f paramagnetic ions.
6 Theoretical background of the crystal field and QUASST

6.1 Old arguments against the crystal-field approach

As mentioned already, after very successful achievements of Van Vleck and his associates in years of 1929-1953 \[56, 57, 58, 59\] Slater in 1953 \[60\] came out with, according to Stevens in a paper written in 1979 \[61\], p. 4, a strong attack on the crystal field theory. The attack must have been really very strong as many researchers even very successful in the application of the CEF theory to real systems drop the crystal-field ideas retaining, as Stevens wrote \[62\], the spin-Hamiltonian as an effective description only. The main objection of Slater was that the crystal-field theory violates the physical principle of the indistinguishability of electrons. Presenting Slater’s argument Stevens wrote in Ref. \[61\], p. 5, that by fact that in the CEF theory we treat a single magnetic ion in a crystal lattice, say the Nd\(^{3+}\) ion for example, the electrons become distinguished by ascribing electrons 1, 2 and 3 to the 4f shell and regarding all the others as simply constituting part of the electrostatic field. According to us this argument is not appropriate - in the CEF theory they are states but not electrons that become distinguished. Other argument of Slater, also related to the electron indistinguishability principle, was that electrons are distinguished by ascribing them to the respective sites. Again the Slater’s understanding of the electron indistinguishability principle is erroneous in case of solids - this ascribing of electrons is to the atoms and the electrons are localized being bound to its original atom. One could say, remembering a term of slave bozons popular in modern solid-state theory, that electrons in CEF and in QUASST are slaves of atoms.

Later questioning of CEF in seventies of XX century was by Freeman \[63\], pp 321-327, for the inability to calculate exactly CEF parameters. There was no doubt that author of Ref. \[63\] favors the band theory. We think that the inability argument should be taken as critics of a detail of the CEF theory, like point-charge approximation, rather than the CEF theory itself. According to Freeman other environmental effects, overlap and covalency should have much bigger effect on the crystal-field splitting than the electrostatic field description. We could only very partly agree with this point but simultaneously we would like to point out that a Freeman’s 30-year-old hope that the band theory \textit{ab initio} soon solve the description of magnetic and electronic properties still awaits for the realization. As far as exact calculations of CEF parameters are discussed we would like to say that all CEF interactions, in particular for rare-earth compounds that have been of the Freeman interest, are of very small energies, say of 10 meV. It is at least 2-3 orders of magnitude weaker than potentials discussed in the band theory. Thus, we prefer to reverse this scientific problem - the evaluation of the low-energy electronic structure and its parametrization by means of CEF parameters can be used for the evaluation of the charge distribution in the elementary cell. In such
the methodology we use, in fact, 3d/4f/5f cations as a microscopic probe for the existence of the crystal-field multipolar potentials in a solid. Such the evaluation is only possible provided the full energy level scheme is perfectly established. The full scheme, not only the ground state, is needed for the meaningful evaluation of different multipolar contributions. Moreover, we would like to point out that the CEF theory and QUASST reveal the need of 0.5 meV accuracy in the evaluation of the electronic structure. It is 1000 times more exact than the presently attained accuracy of band-structure calculations.

The questioning of the crystal-field theory has caused that today, despite of the fact, that there is continuously growing number of compounds described in terms of the CEF Hamiltonian the crystal-field theory itself, often identified with the shortage of the point-charge model, is often regarded as “naive”. We fully disagree with a statement of Freeman [63], p. 322, that "The success of this naive (and from the theoretical point of view inadequate) model is thought to lie in the fact that \( V_c \) gives the Hamiltonian the correct symmetry and a sufficient number of empirical parameters which somehow absorb all the various environmental effects not included in the simple description given by Eqn (6.49)”, i.e. by a CEF potential expanded in terms of spherical functions.

Other aspect of the problem of a disdainful treatment of the crystal field is related to the education - students of physics are not taught, or only very little, of the crystal field and of the group theory.

6.2 Theoretical basis for the crystal-field and QUASST

A basic message of the QUASST is that the low-energy discrete electronic structure of the atomic-like 3d\(^n\) configuration, determined by crystal-field and spin-orbit interactions, is largely preserved in a solid 3d-atom containing compound. According to us the theoretical basis for the crystal-field theory is the atomistic construction of matter and we are very surprised that it was not recognized earlier. The atomistic construction of matter is the basic well-established principle of Nature - one could say that this knowledge is already known from 2500 years, thinking about loosely ideas of Democritos, another one, that from 100 years, when atoms have been accepted in physics to exist in the reality (1913 - Bohr’s model for the hydrogen). Thus we are fully convinced that the crystal field and QUASST theory are based on well-known and well-established physical concepts, like the local symmetry, the group theory, atomic physics with Stark and Zeeman effects, statistical physics and many others. The crystal field and QUASST theory discuss the discrete states, the existence of which is a characteristic feature of the quantum mechanics.

In such the formulation QUASST can be experimentally verified and, as Carl Popper says in the scientific methodology, it can be falsified. The falsification possibility is the basic requirement, according to Popper, demanded for a scientific theory. We are ready for the open scientific discussion about the physically adequate description of the electronic structure and the magnetism of 3d-/4f-/5f-atom
containing compounds.

We are convinced that the CEF theory not only provides a conceptually simple framework for the interpretation of numerous experimental results, as many people are ready to accept the crystal field approach, but the CEF theory must be a basic ingredient of each modern solid state theory dealing with electronic and magnetic properties of transition-metal compounds.

QUASST reconciles the CEF theory with localized moments with the lattice periodicity, a problem, that according to Stevens [62], p. 7, has divided magneticians for many years.

In QUASST d electrons take part both in the bonding and in the magnetism. The primary bonding proceeds via electrostatic interactions. The magnetic interactions, in fact spin-dependent interactions, responsible for the formation of the magnetically-ordered state are much weaker than coulombic interactions and are of order of $T_c(T_N)/k_B$, i.e. of, say, 30 meV.

In QUASST the magnetic moment is associated with the open-shell atoms. QUASST enables calculations of both the spin and orbital moments [20]. There is rapidly growing experimental evidence for the existence of the orbital moment, thanks X-ray synchrotron experiments, and QUASST enables its calculation using well-established physical concepts. The used home-made computer program BIREC for 3d is available on our web-side: [http://www.css-physics.edu.pl](http://www.css-physics.edu.pl)

QUASST nicely illustrates that the whole magnetism is the macroscopic quantum effect.

QUASST offers a solution of the Mott-insulator problem - an 3d oxide is the insulator having bound electrons in the incomplete 3d shell, that govern magnetic, electronic and spectroscopic properties.

QUASST bridges the atomic physics and the solid-state physics.

In frame of QUASST low-energy excitations are neutral spin-like excitations between CEF-like d states. According to QUASST these neutral low-energy spin-like excitations, between two Kramers conjugate states cause anomalous behavior of some Ce, Yb and U compounds at low temperatures known as heavy-fermion phenomena.

Our approach is in agreement with a general idea of Mott that it is strong electron correlations in 3d oxides that make electrons in the incomplete 3d shell to stay rather localized than itinerant. We are convinced that there is no other nowadays theory of a solid containing transition-metal atoms that can describe properties in so detailed and in so consistent way, both zero-temperature properties and thermodynamics with the physically clear distinction of the magnetically-ordered and paramagnetic states.

The QUASST basic message can be defined also in a way that for the physically adequate description of electronic and magnetic properties of 3d-/4f-/5f-/atom compounds the CEF interactions, completed with the intra-atomic-spin-orbit coupling, have to be determined the first.
6.3 The need for formulation of QUASST

One can ask: "Is this atomistic idea a new one in the solid-state physics?" Yes and no. No, as most of experimentalists naturally discuss their results in terms of local properties. Yes, as according to our knowledge none has been able to resist to presently-in-fashion solid-state physics theories that simply ignore the existence of the atom in a solid arguing that a solid is so many-body object and that there are so strong intersite correlations that the individuality of atoms is lost. In the standard band-structure calculations the f and d electrons are taken as itinerant forming a band. In the band there is a continuum of the energy states within 1-5 eV. In our model there are discrete states with energy separations even less than 1000 times smaller (1 meV, but 0 in case of Kramers ions). No, as there are some text-books written about the crystal field, let mention a book of Abragam and Bleaney [27], of Ballhausen [28] and others [29, 30]. Yes, as they applied the CEF approach to some diluted 3d systems, not to the concentrated ones, i.e. not to a crystalline solid. Yes, as they have not been consequent enough and they largely washed up the original idea. Yes, as there are still very popular text-books and review articles that show very schematic description of 3d states [1, 2, 33, 64] making use of the single-electron picture. One should note that in the strong CEF approach the 3d electrons are treated as largely independent, i.e. they do not form the strongly-correlated 3d system in contrary to QUASST. QUASST corresponds to the intermediate (3d) or weak (4f) crystal-field approach, but we point out the fundamental importance of the intra-atomic spin-orbit coupling, despite of its relative weakness for the 3d ions. Also yes, as at present this atomic-like picture is enormously prohibited in the leading physical journals and a little is said about the discrete states at the magnetic and annual strongly-correlated electron system (SCES) conferences.

We would like to add, preceding unfounded critics, that we do not claim that everything can be explained only by single atoms but our point is that the proper, i.e. physically adequate starting point for the discussion of properties of a solid containing the open-shell atoms is the consideration of its atomic-like states in the local surroundings, i.e. in the lattice crystal field. Our numerous computer experiments point out that e.g. the orbital moment has to be unquenched in the solid-state physics of 3d-ion containing compounds and our approach enables it. For instance, we have derived the orbital moment in NiO to be 0.54 $\mu_B$ what amounts to 20% of the total moment (2.53 $\mu_B$) [38]. Moreover, one should not consider our approach as the treatment of an isolated atom - we start the discussion of NiO from the consideration of the cation octahedra NiO$_6$ (more exactly - the Ni$^{2+}$ ion in the octahedral crystal field). The whole NaCl structure of NiO is built up from the edge sharing cation octahedra. The perovskite structure, for instance, is built up from the corner (and the edge) sharing cation octahedra along the c direction (in the a-b plane). Thus, such octahedra cover the whole macroscopic 3D body provided the perfect translational symmetry. The CEF parameters contain information about the interaction of the single ion with the whole charge surroundings.
Our approach is in agreement with the general conviction about the importance of the electron correlations in description of open-shell compounds - in our approach we start from the very strongly-correlated limit in contrary to a weak correlation limit of the LSDA approach.

For the better illustration of our point of view the reader is asked to look into recent Phys. Rev. Lett. papers. In Ref. [65] authors, considering states of two 3d electrons of the V$^{3+}$ ion in V$_2$O$_3$, came out with the continuous electronic structure spread over 2.5 eV (Figs 2 and 3 of Ref. [65]). In Ref. [66] two d electrons of the V$^{3+}$ ion are considered to be largely independent. It shows that our quite reasonable atomic-like approach is far from being accepted in presently-in-fashion theoretical approaches. In Ref. [67] the continuous electronic structure for six 3d electrons in FeO spreads over 8 eV (Fig. 8 of Ref. [67]). In Refs [65, 66, 67] the orbital moment and the spin-orbit coupling is completely ignored. These examples prove that our call for the "unquenching" of the orbital moment and taking into account the spin-orbit coupling is fully justified. We are convinced that in all called papers d electrons form the crystal-field discrete energy states with the importance of the s-o coupling. In FeO, in the paramagnetic state, we expect a quite similar structure to that presented in Fig. 8. Also magnetism develops analogically to that discussed here for FeBr$_2$, Fig. 9, though FeO exhibits much higher value of $T_N$. The electronic structure of the V$^{3+}$ ion in V$_2$O$_3$ within the strongly-correlated crystal-field approach has been derived by us in Ref. [68].

### 7 Some further problems

#### 7.1 CEF and QUASST vs ab-initio calculations

Numerous successes of the CEF approach indicate that so subtle effect as charge quadrupolar and octupolar interactions, with energies smaller than 1 meV, have to be incorporated into each modern solid-state theory. In QUASST the real space description is used in contrast to the reciprocal space used in band theories.

Many-electron states and many-electron wavefunctions discussed in CEF and in QUASST contrast single-electron states and single-electron wavefunctions considered in the band theories. They are also completely different from single-electron CEF d-orbitals $t_{2g}$ and $e_g$. In general, the wavefunction and the energy of the whole atomic-like 3d$^n$ many-electron system can be constructed from single-electron wavefunctions of d-orbitals $[l, l_z]$, with $l = 2$, and $l_z = \pm 2, \pm 1, \text{and} \ 0$. Undoubt successes of the CEF and QUASST description of many 3d-/4f-/5f-atom compounds indicate that this construction from single-electron wavefunctions $l, l_z$ have to be oriented in order to reproduce the atomic-like eigenstates and wavefunctions of the desired ion. Other words, ambitious solid-state theories starting the description of a 3d solid from a (gaseous) jellium of independent electrons must put such conditions and such potentials and mutual electron interactions into their theories in order
to get 3d atoms or 3d ions and to reproduce the spectral term structure, known from the atomic physics. In QUASST we take the existence of atoms or ions as the physical fact that is not necessary to prove. Their existence in the reality confirms the validity of our assumption. We treat the problem of the description of atoms or ions, in fact the description of the term electronic structure, as the subject of the atomic physics.

The preservation in a solid of the atomic-like 3d\textsuperscript{n} configuration is the manifestation of strong electron correlations. The developed by us the QUASST theory is, according to us, the physical realization of the general idea of Sir Nevill Mott that it is strong electron correlations that make electrons in the incomplete 3d shell to stay rather localized than itinerant in 3d oxides. The 3d oxides are known at present as Mott insulators.

Crystal-field parameters can be, in general, calculated \textit{ab initio} as the multipolar potentials of the total charge distribution in a solid. The total charge distribution is related to all charges in a solid; all nuclei and all electrons. This first-glance hopeless task becomes, however, tractable in a crystalline solid thanks the translational and local symmetry. Such calculations, direct \textit{ab initio} electrostatic multipolar potentials of the 3D surroundings, have been demonstrated by Hutchings \cite{Hutchings} by considering point charges of the octahedral and tetrahedral symmetries. Calculations by Hutchings concern the crystal field for rare-earth ions but the calculations are the same for 3d ions if one replaces J by L quantum number. For the octahedral symmetry of the 3d-ion cation in the oxygen octahedron the CEF coefficient A\textsubscript{4} can be calculated \textit{ab initio} by consideration of electrostatics like Eqn 6. The single-ion prediction of the variation of the B\textsubscript{4} parameter enables study of CEF interactions across the whole isostructural series and somehow to predict physical properties of a compound knowing the local symmetry and the involved cation. The reversal of the electronic structure for the Ni\textsuperscript{2+} and Co\textsuperscript{2+} ions (d\textsuperscript{7} and d\textsuperscript{8} configurations) have been noticed already by Van Vleck \cite{VanVleck}.

Although the calculated \textit{ab initio} value of the B\textsubscript{4} parameter in LaCoO\textsubscript{3} for the nearest oxygen octahedron, see section 4.2, is eight times smaller than the recent evaluation of 260 K it is extremely important that this \textit{ab initio} calculation provides the proper sign of B\textsubscript{4} parameter because this sign determines the ground state in the oxygen octahedron. There is a hope that taking into calculations all charges and other physical effects bridges both values. However, we point out that by the recent experimental evaluation of the strength of crystal-field interactions it turns out that the commonly used strong crystal-field approach, with breaking the atomic-like correlations, is not justified. In fact, turns out to be useless.

In fact, QUASST is indeed \textit{ab initio} theory - it takes profit of the atomic physics with the spectral term electronic structure and later \textit{ab initio} calculates the electronic structure of the given magnetic ion in a crystalline solid, taking into account the crystal field potentials and the spin-orbit coupling. The electronic structure from \textit{first principles} by means of the statistical physics provides both zero-temperatures
properties and thermodynamics.

We think that the largest error in the ab initio CEF calculations of $B_\text{3}$, mentioned in section 4.2, is associated with the determination of the charge distribution in the crystal and the theoretical evaluation of the ionic octupolar moment of the 3d cation, in particular with the value of $< r^4 >$. Our preliminary studies indicate that there is no strong dependence of $< r^4 >$ across the 3d series as values in Fig. 7 show.

7.2 One-term vs all-terms fine electronic structure

Of course, the QUASST calculations should be performed within all-terms space involving the $\binom{10}{n}$ states allowed by the Pauli principle. Of course, it would be better to take into consideration all interactions known to exist in a solid. However, more parameters more difficult to get physically adequate results is. Physics is the science of approximations - the most important is to catch the most essential physical ingredient(s) and made only physically proper approximations. We are convinced that by taking into account the atomic physics and the spin-orbit coupling we have caught the most essential physical ingredients. Surely we have the physically adequate number of states involved in the low-energy electronic structure like it was shown for FeBr$_2$. For the V$^{4+}$ ion in Na$_2$V$_3$O$_7$ there is only one term, $^2$D. Thus calculations for the d$^1$ configuration for the V$^{4+}$ and Ti$^{3+}$ ions are equivalent to all-terms calculations. The performing all-terms calculations, provided that there is no term reorganization as occurs in LaCoO$_3$, will lead to only small changes in energies and eigenfunctions compared to Hund’s rules ground term calculations, but the number of electronic states will be preserved.

It is important as the number of available low-energy states determines the overall behavior of thermodynamical properties, like the total entropy. In LaCoO$_3$ the sub-term reorganization occurs and the $^1A_1$ subterm becomes the ground subterm, but it proceeds in the fully-controlled and in the fully-understood way.

Thus, all-terms calculations do not introduce changes in the physical description of properties in comparison to the one-term calculation. It is in contrast to the revolutionary change of physics going from the orbital-only states to the spin-orbit states discussed in the strongly-correlated crystal-field approach and in QUASST. But it is Nature that chooses the physically adequate approach.

7.3 Towards 4d and 5d atom containing compounds

We hope that the discrete states also are present in 4d-/5d-atom containing compounds. Calculated electronic structure for the Ru$^{4+}$ ion in Sr$_2$RuO$_4$ has been presented in Ref. [70]. In 4d and 5d ions the spin-orbit coupling is much stronger than in case of 3d ions. The j-j coupling should be rather more applicable than the Russell-Saunders coupling used for the description of 3d ions. The substantial applicability of the strongly-correlated CEF approach to 5f-atom compounds have been demonstrated for UPd$_2$Al$_3$, UGa$_2$ and NpGa$_2$ [25, 71]. Magnetic and electronic
properties of UPd$_2$Al$_3$ and UGa$_2$ turn out to be related to the $5f^3$ configuration like in the U$^{3+}$ ion.

### 7.4 Testing of the quantum mechanics

Accepting the CEF and QUASST theory one can say that the crystalline solid provides the wide possibility to study the Stark and Zeeman effect on paramagnetic ions, their discrete states, in very complicated multipolar electrostatic fields and in extremal magnetic fields, unavailable presently in the laboratory.

In deriving the states, their energy and eigenfunction, an important problem of the atomic physics, the applicability of the Russell-Saunders or j-j coupling can be effectively studied. From this point of view the perfect description of the $g$ tensor of the Co$^{3+}$ ion [18] and the behavior of its localized states observed in the ESR experiment on single crystalline LaCoO$_3$ in magnetic fields up to 30 T along different crystallographic directions we take to be of a remarkable scientific importance.

It is also very important from the unification point of view that the single-ion Hamiltonian widely used in the analysis of electron-paramagnetic resonance spectra of 3d-ion doped systems has been successfully used for systems, where the 3d atoms are the full part of the crystal.

### 8 CONCLUSIONS

We have presented the crystal-field approach with strong electron correlations, extended to the Quantum Atomistic Solid-State theory (QUASST), as a physically relevant theoretical model for the description of electronic and magnetic properties of 3d-atom compounds. Its applicability has been illustrated for LaCoO$_3$, FeBr$_2$ and Na$_2$V$_3$O$_7$. According to the QUASST theory in compounds containing open 3d-/4f-/5f-shell atoms the discrete atomic-like low-energy electronic structure survives also when the 3d atom becomes the full part of a solid matter. This low-energy atomic-like electronic structure, being determined by local crystal-field interactions and the intra-atomic spin-orbit coupling, predominantly determines electronic and magnetic properties of the whole compound. It should not mean that other mechanisms than CEF and the spin-orbit coupling are not present in a solid, but we are convinced that analysis of electronic and magnetic properties of 3d-/4f-/5f-atom compounds is necessary to start from the determination of the crystal-field interactions and of the localized CEF-like states.

We understand our theoretical research as a continuation of the Van Vleck’s studies on the localized magnetism. We point out, however, the importance of the orbital magnetism and the intra-atomic spin-orbit coupling for the physically adequate description of real 3d-ion compounds. Our studies clearly indicate that it is the highest time to "unquench" the orbital moment in solid-state physics in description of 3d-atom containing compounds.
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