Transition Properties of f-electrons in Rare-earth Optical Materials

BY

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Abstract

The main purpose of this thesis is to theoretically study energy levels and intra-electronic transition intensities for various f-electron systems. The f-f electronic dipole transitions are parity-forbidden for a free ion but become non-zero when the ion is subject to a crystal-field. This is commonly described within the framework of Judd-Ofelt theory which accounts for the mixing of odd parity into the wave-functions.

Some refinements and quantitative studies have been made by applying many-body perturbation theory, or the perturbed functions approach, to obtain effective dipole operators due to correlation, spin-orbit and higher order crystal-field effects not included in Judd-Ofelt theory. A software for the computation of f-electron multiplets and Stark levels was implemented and published as well.

The single- and pair-functions used for the evaluation of intensity parameters were obtained by solving various inhomogeneous Schrödinger equations. The wave-functions and energies obtained by diagonalizing an effective Hamiltonian have been used together with the oscillator strength methods to simulate absorption spectrum. Consistent crystal-field parameters applied in some of the papers were obtained by fitting crystal polarizabilities to reflect the experimental Stark levels. The same crystal model was then used to generate odd crystal field parameters needed for the f-f transition intensities. The total effect of these refinements are spectral features that usually agree well with experimental findings. Some of these methods have also been applied and seen to be quite useful for the understanding of optical fiber amplifiers frequently used in today's optical networks.

Finally, a finite-difference approach was applied for the Helium iso-electronic sequence. The exact wave-function was expanded in a sum of partial waves, and accurate ground- and excited state energies were obtained by using the iterative Arnoldi approach.

Keywords: rare-earth ions, oscillator strengths, correlation, crystal field, f-electrons

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List of Papers

This thesis is based on the following papers, which will be referred to in the text by their Roman numerals.


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To Klara and Marie.
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Introduktion (in Swedish)


bra nogrannhet med både relativistiska DFT- och pseudopotentialmetoder [13–15]. Tillvägagångssättet i artikel VIII kan i framtiden kanske visa sig vara framgångsrikt för explicit behandling av de två $f$-elektronerna hos Pr$^{3+}$ förutsatt att den effektiva potential som används, inkluderande bland annat polarisering av elektronerna nära kärnan, visar sig vara en tillräcklig beskrivning av de återstående växelverkningarna.

Approximativa atomära beräkningar kan naturligtvis göras. Emellertid så involverar detta empiriska skalningar hos de elektrostatiska $R^2$-integralerna samt andra tillvägagångssätt som exempelvis manuell förflyttning av konfigurationsenergier till motsvarande experimentella värden. Cowan ger en bra introduktion till dessa typer av beräkningar [16] och för ett bra nutida exempel se Dzuba med flera [17]. Dessa typer av metoder har även använts i artikel VI.


Man kan fråga sig vad som egentligen är meningen med att utföra alla dessa grundläggande undersökningar av atomära/material-egenskaper. Bortsett från den rena nyfikenheten för grundläggande fysik så är jordartsmetallbaserade optiska eller magnetiska material mycket viktiga i många tillämpningar. Till exempel inom informationsteknologi spelar jordartsmetallerna en viktig roll i halvedukare och glas. De är fundamentalt viktiga i många fotoniktillämpningar i dagens moderna samhälle: förstärkare för fiberoptisk kommunikation (EDFA), högeffektsfibrar, lasrar för svetsning, lasrar för signaltransmission, ultrastabila lasrar för kalibrering och noggranna mätningar etc. Alla dessa aktiva joner
har det gemensamt att de är påverkade av kristallfält från de kemiska omgivningarna som i sin tur leder till en variation av optiska eller magnetiska egenskaper. För exempelvis alla jordartsmetallbaserade förstärkare är diverse förlustmekanismer ständigt närvarande: destruktiv uppkonvertering eller energiöverföring (t.ex. för höga dopningskoncentrationer), olycklig degeneration hos energinivåer som leder till ESA (absorption från ett exciterat tillstånd), dåliga radiativa eller icke-radiativa övergångar, ASE (förstärkt spontan emission som leder till brus) etc. Materialet eller de kemiska omgivningarna kan förstås förändras, men i vilken riktning? För en god förståelse krävs fundamentala fysikaliska insikter om elektronstrukturen hos både jordartsmetalljonen själv samt dess kemiska omgivning.
Introduction

An accurate treatment of the electron correlation is generally regarded as a very challenging problem in physics. There exist many approaches to get insights of the electron correlation problem. A few examples are: classical configuration interaction methods (Full CI; see [1]), many-body perturbation theory (MBPT; see [2]), the correlated coupled cluster method (CCSDT1-R12; [3]), Hylleraas methods such as Hy-CI, see [4], numerical methods such as finite differences [5] or splines [6, 7] and Monte-Carlo methods [8] etc. These methods are all designed to accurately treat the many-particle Schrödinger equation. For small systems, the achieved accuracy is excellent if not essentially exact, see Ref. [9] which gives 24 significant figures for the ground state energy of Helium. However, for larger systems, the obtained accuracy is rapidly decreasing, e.g., the ground state energy of Beryllium appear to be accurate to about 6 figures [8]. Beyond 4 electrons, very accurate results are unfortunately not easily achieved. The last paper of this thesis is a study of the finite difference method for two-electron atoms. This work perhaps lists the most accurate L-limit energies for Helium in the literature. In particular, the S-limit ground state energy in Hartrees was calculated to $-2.8790287673192144062$ which can be compared to $-2.87902876731921441$ due to Goldman [10]. It is straightforward to apply the finite difference approach to more than two electrons. However, as in the other approaches, the dimensionality grows rapidly and it is again not expected that very accurate calculations will be possible for more than about 4 electrons.

In the case of f-electron systems, the correlation complexity is overwhelming. There are just a few ab initio attempts to approximately compute the multiplet structure of the $4f^2$ electronic configuration for Pr$^{3+}$. One example of this is the multiconfiguration Dirac-Fock method [11] and another the relativistic coupled cluster approach [12]. Although impressive, these calculations are very time consuming and the typical accuracy is about one part in 10 or slightly better. There are no examples of accurate ab initio calculations of crystal field splitted levels. However, Dolg et al. have calculated various ionization potentials (IP$_1$-IP$_4$) of lanthanides and actinides with quite a good accuracy using both relativistic Dirac-Kohn-Sham DFT as well as relativistic pseudopotential methods [13–15]. The method described in paper VIII might turn out to be useful for an explicit treatment of the correlation between the
two \(f\) electrons in \(\text{Pr}^{3+}\) provided that an effective potential including effects such as core polarization would be a sufficient description for the remaining interactions.

Approximate atomic calculations for the rare-earths can certainly be done but involves empirical scaling of the electrostatic \(R^{k}\) integrals and other procedures such as moving the electronic configurations to their experimental energy difference. Cowan gives a good introduction to those type of calculations [16]. For a current example see Dzuba et al. [17]. Similar methods have been applied in Paper VI.

The complexity of the \(f\) electron structure and their group-theoretical properties were studied already in the 1950s and 1960s with many pioneering papers. The papers that have been a great inspiration for this thesis are those by Judd [18–21], Racah [22–25], Wybourne and Rajnak [26–31], Trees [32, 33], Carnall [34, 35], Smentek [36–39], Reid [40, 41] and others [42–49] etc. These investigations led to the constructions of semi-empirical methods involving effective Hamiltonians with free parameters to be adjusted to experiment and evaluations of oscillator strengths within the 4\(f\)-shell. These approaches have certainly proved themselves in the field of theoretical spectroscopy with e.g. typical errors in the crystal field levels as low as a few parts in \(10^{4}\). An excellent review of the area of theoretical spectroscopy is due to Judd [50]; see also the review by Goldschmidt [51]. Papers I, III, IV and V are directly related to this area. In particular, paper IV and V study the effect of including spin-orbit interactions, higher order crystal field contributions and electron correlation in the calculation of \(f-f\) transition intensities. The quantitative examples are for the host crystal LiYF\(_4\). The overall agreement between calculation and experiment is often encouraging.

One could finally ask what is the point of doing all these fundamental investigations of atomic/material properties? Besides a fundamental curiosity, the rare-earth optical and magnetic materials have many important applications. In for example information technology, rare-earths play a vital role in semiconductors and glasses. Rare-earths are key factors in many photonic devices serving very important applications in today’s modern society: amplifiers for fibre optical communication (EDFA), high power fibre and solid state lasers for cutting and welding, lasers for signal transmission, ultra-stable lasers for calibration and measurement purposes etc. What these active ions all have in common is that the rare-earth ion is in one way or another subject to a crystal field from the chemical environments leading to various optical/magnetic properties. In all rare-earth optical amplifiers there are always potential loss mechanisms such as e.g. destructive up-conversion or energy transfer (e.g. at high Erbium concentrations), accidental degeneracy that can lead to ESA (excited state absorption), bad radiative or nonradiative transitions, ASE (am-
plified spontaneous emission) etc. The material or the chemical environments can of course be changed but in what direction? A good understanding requires fundamental physical knowledge about the electronic structure of the rare-earth ion itself and its chemical environment.
Many-electron systems

3.1 The non-relativistic Schrödinger equation

The main difficulty of theoretical calculations of energy-level structures for rare-earth ions is the electron correlation. The relativistic phenomena such as the spin-orbit interaction and other effects that are due to quantum-field theory are smaller in magnitude and can therefore be treated as perturbations at a later stage. Thus the starting point is the non-relativistic Hamiltonian in the Born-Oppenheimer approximation, here given in Hartrees:

\[ H = \sum_i \left( -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j} \frac{1}{r_{ij}}. \]  \hspace{1cm} (3.1)

Analytical solutions to the Schrödinger equation can readily be obtained for Hydrogen, but unfortunately this is not the case for many-particle problems. This is due to the fact that it is not possible to separate the variables in the Schrödinger equation. Therefore, in order to calculate the energies of these systems, simplifications and/or numerical methods have to be applied.

3.2 The Variational theorem

By expanding an arbitrary \( N \)-electron trial-function \( \Psi \) in the exact eigenfunctions of the Schrödinger equation, using the completeness property, it is readily derived that the Rayleigh quotient

\[ E[\Psi] = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \]  \hspace{1cm} (3.2)

is an upper bound to the exact ground state energy \( E_0 \). This is the all-important Variational theorem, and the methods that rely on Eq. (3.2) are said to be variational. Examples of such methods are Hartree-Fock (HF) methods, multiconfiguration HF and configuration interaction (CI). It should be mentioned that the MBPT and CC-methods to be discussed later are non-variational and such calculations can therefore overshoot the correct value.
3.3 Basis functions

Most of the computational methods in many-electron theory are one-particle methods in nature, that is, the basis set is expanded in a set of spin orbitals $\phi_i(x)$. These are often written in the form

$$\phi_{nalamla msa}(x) = r^{-1}P_{nala}(r)Y_{lamla}(\theta, \phi)\chi_{msa}. \quad (3.3)$$

Here $P_{nala}$ is a radial function, $Y_{lamla}$ is a spherical harmonic and $\chi_{msa}$ is a Pauli spin function. We will in the following use the short-hand notation $a$ for the set of quantum numbers $(nalamla msa)$ and $|\phi_a\rangle$ will be written as $|a\rangle$.

A simple and commonly used antisymmetric function is the Slater determinant:

$$|\alpha\rangle = |\{ab...n\}\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(x_1) & \phi_b(x_1) & \cdots & \phi_n(x_1) \\ \phi_a(x_2) & \phi_b(x_2) & \cdots & \phi_n(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_a(x_N) & \phi_b(x_N) & \cdots & \phi_n(x_N) \end{vmatrix} \quad (3.4)$$

Matrix elements for an $m$-body operator in this basis set can be evaluated using the Slater-Condon rules. The rules for one- and two-body operators are generally known, but the rules for the three-body operators are not so well-known and are therefore listed in Appendix B. If the spin orbitals are not orthonormal, Löwdin’s rules can be applied [52]. Of particular interest are the matrix elements of $\sum_{i<j} r_{ij}^{-1}$, which reduces to a sum of two-electron integrals

$$\langle ab| r_{ij}^{-1} |cd \rangle = \sum_k (ab) \frac{r_k}{r_{ij}+1} C^{(k)}(1) \cdot C^{(k)}(2) |cd\rangle$$

$$= \delta(m_{sa},m_{sc})\delta(m_{sb},m_{sd}) \sum_k \langle l_{a1b1}|C^{(k)}(1)\cdot C^{(k)}(2)|l_{c1d1}\rangle \times R^k(n_{a1a1}n_{b1b1}, n_{c1c1}n_{d1d1}). \quad (3.5)$$

The $R^k$’s are radial integrals defined by

$$R^k(n_{a1a1}n_{b1b1}, n_{c1c1}n_{d1d1}) = \int \int P_a(r_1)P_b(r_2) \frac{r_k}{r_{r_1+1}}P_c(r_1)P_d(r_2)dr_1dr_2. \quad (3.6)$$

and are known as Slater integrals. It is also common to use the $F^k$ and $G^k$ integrals which are given in terms of the $R^k$ as

$$F^k(a,b) = R^k(ab,ab) \quad (3.7)$$

$$G^k(a,b) = R^k(ab,ba). \quad (3.8)$$
For energy calculations of a free ion or atom it is sometimes more advantageous to choose basis functions $|\gamma L S M L M S \rangle$ that are eigenfunctions of $L^2$, $L_z$, $S^2$ and $S_z$. $\gamma$ here denotes the additional quantum numbers, including the electronic configuration, that are needed to uniquely describe the state.

### 3.4 The Hartree-Fock equations

In the restricted HF procedure the spin orbitals are of the form of Eq. (3.3), that is, the radial functions $P_{nl}$ are identical for all electrons in the same $nl$-shell. This is in contrast to the unrestricted HF where the radial functions also depend on the magnetic quantum numbers $m_l m_s$. The functional space which is employed in the variational calculus is limited to a single configuration and the energy functional (3.2) can either represent the average energy of the configuration or a specific $LS$-term. The energy functional can be written in a general form as [2]

$$E[\{P_{nl}\}] = \sum_a q_a I_a + \frac{1}{2} \sum_{abk} q_a q_b \left[ c_k(ab) F^k(a,b) + d_k(ab) G^k(a,b) \right],$$

(3.9)

where $q_a$ is the occupation number of the shell $(n_a l_a)$ and the radial integral $I_a$ is defined by

$$I(a) = \int P_a(r) \left( -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l_a(l_a + 1)}{2r^2} - \frac{Z}{r} + \hat{u}_{HF} \right) P_a(r) dr.$$

(3.10)

In the case of a closed-shell atom or the average energy of a configuration, the coefficients $c_k(ab)$ and $d_k(ab)$ are easily derived without referring to any particular coupling-scheme, see e.g. Refs. [2, 16]. For the energy of an $LS$-term these coefficients be obtained using Racah algebra techniques [53, 54]. From the energy functional and the additional orthogonality constraint that $P_{nl}$ is orthogonal to $P_{n'l}$ for $n \neq n'$, variational calculus yields a set of coupled integro-differential radial equations, one for each occupied shell [16, 55]:

$$\left( -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l_a(l_a + 1)}{2r^2} - \frac{Z}{r} + \hat{u}_{HF} \right) P_a(r) = \epsilon_a P_a(r) + \sum_{b \neq a} q_b \epsilon_{ab} P_b(r).$$

(3.11)

Here the $\epsilon_{ab}$’s are associated with the off-diagonal Lagrange multipliers used to ensure orthogonality. The non-local potential $\hat{u}_{HF}$ can be written in terms of the integrals $Y_k(ab,k)$:
\[ \hat{u}_{\text{HF}} P_a(r) = \sum_{bk} q_b \left[ c_k(ab) \frac{1}{r} Y_k(bb, r) P_a(r) + d_k(ab) \frac{1}{r} Y_k(ab, r) P_b(r) \right] \] (3.12)

\[ Y_k(ab, k) = r \int \frac{r_<^k}{r_>^{k+1}} P_a(r') P_b(r) dr' \] (3.13)

The radial Eqs. (3.11) are coupled, and thus they have to be solved iteratively. This is usually done by an initial guess for the \( \{P_{nl}\} \) which gives an estimate of the potential in Eq. (3.12). The HF-equations are then solved for this potential, giving a new set \( \{P_{nl}\} \), and this procedure is repeated until self-consistency is obtained, see e.g. Refs. [16, 56].

Since the HF-method treats an electron as an independent particle moving in an average field of the other electrons, the wave functions and energies obtained are at best qualitative one-electron estimates of the exact solution. However, they can nevertheless be useful as the point of departure for other methods.

Relativistic effects can also be incorporated into the HF-Hamiltonian; For example, in the RHF-software package of Cowan [16], which is applied in the papers of this thesis, the mass-velocity and Darwin-term are included.

### 3.5 Configuration interaction

It is often stated that the method of configuration interaction (CI) is one of the conceptually simplest methods available to obtain good estimates of the exact eigenvalues and eigenfunctions. Still, the construction of an efficient CI algorithm is not trivial, for a review see Refs. [57–59]. In the CI-method the wave function \( |\Psi\rangle \) is approximated with a linear expansion of the basis functions \( |\psi_i\rangle \).

\[ |\Psi\rangle = \sum_{j=1}^{M} c_j |\psi_j\rangle. \] (3.14)

Inserting this expression into the Schrödinger equation and multiplying with \( |\psi_i\rangle \) gives the generalized eigenvalue equation

\[ Hc = ESc \] (3.15)

where \( H_{ij} = \langle \psi_i | H | \psi_j \rangle \), \( S_{ij} = \langle \psi_i | \psi_j \rangle \) and \( c \) is the vector containing the linear coefficients in the expansion (3.14). If the basis set is orthonormal, the overlap
matrix elements reduce to $S_{ij} = \delta(i, j)$. From the Variational theorem it is seen that the lowest eigenvalue of Eq. (3.15) is an upper bound to the exact ground state energy. Further, if the eigenvalues of Eq. (3.15) are labeled $E'_0 \leq E'_1 \leq E'_2 \ldots$, the Hylleraas-Undheim theorem states that $E'_k$ is an upper bound to the exact value $E_k$.

In the multiconfigurational HF (MCHF)-methods the energy of a specific $LS$-term can be minimized by writing the trial wave function to be optimized as

$$\Psi = \sum_i c_i \psi(\gamma_iLS)$$

(3.16)

where $\gamma_i$ denotes configuration $i$. Note the difference to the ordinary HF wave function, where only one configuration is included. Variation of the energy functional with respect to the radial functions leads to radial equations of HF-type, and the flexibility of the expansion (3.16) leads to a matrix eigenvalue problem

$$Hc = Ec.$$  

(3.17)

Since the radial equations depend on the coefficients $c_i$ obtained from solving Eq. (3.17), an iterative procedure must be applied [56].

### 3.6 MBPT

The many-body perturbation theory (MBPT) rests upon the Rayleigh-Schrödinger (RS) perturbation expansion, for which the functional space of the wave functions can be partitioned into a model space $P$ and an orthogonal space $Q$. The aim is to obtain effective operators $T$ acting within the limited subspace $P$, but producing the same result as the original operator $T$ in the whole Hilbert space. For the rare-earths the model space $P$ is often chosen as the space spanned by all the Slater determinants $|\alpha\rangle$ of [Xe]$4f^N$.

We will here briefly describe the basics of the RS-theory in order to be able to discuss the effective dipole operators in the theory of transition intensities in Chapter 6. As in most perturbative approaches, the Møller-Plesset partition, $H = H_0 + V$, of the Hamiltonian is applied. We also assume that the eigenfunctions $|\gamma\rangle$ of $H_0$ with corresponding energies $E_0^\gamma$ are known. The exact wave functions and energies of the system are denoted $\Psi^\alpha$ and $E^\alpha$, respectively. The projection of an exact wave function $\Psi^\alpha$ onto $P$ is called a model function, denoted by $\Psi_0^\alpha = P\Psi^\alpha$. Here $P$ is the projection operator associated with the model space, and the corresponding operator for the orthogonal space is $Q$. By acting on a model function with a wave operator $\Omega$, which is defined by the relation

$$\Omega \Psi_0^\alpha = (1 + \chi) \Psi_0^\alpha = \Psi^\alpha,$$

(3.18)
the corresponding exact wave function is obtained. The \(i\)th order wave operator \(\Omega^{(i)}\) can be obtained from the RS-expansion of the generalized Bloch-equation [2]:

\[
[\Omega^{(i)}, H_0]P = QV\Omega^{(i-1)}P - \sum_{j=1}^{i-1} \Omega^{(i-j)}PV\Omega^{(j-1)}P.
\] (3.19)

For the first few orders in this expansion, Brueckner showed in 1955 that the so-called unlinked terms vanish [60]. These unlinked terms are proportional to the square of the number of particles and are thus not size consistent. Later Goldstone, using his graphical approach inspired by R. P. Feynman, were able to prove that they vanish to all orders [61], see also Sandars [62] and Lindgren [63]. Thus, Eq. (3.19) can in the general case be written as

\[
[\Omega, H_0]P = (V\Omega P - \chi PV\Omega P)_{\text{linked}}.
\]

It is now possible to construct an effective Hamiltonian, here chosen as

\[
\mathcal{H}_{eff} = PH\Omega P
\]

\[
= PH_0P + PV\Omega P
\] (3.20)

which satisfies

\[
\mathcal{H}_{eff}\Psi^a_0 = E^a\Psi^a_0.
\] (3.21)

As is seen from Eq. (3.21), the model functions \(\Psi^a_0\) are eigenfunctions to \(\mathcal{H}_{eff}\) with the exact energies \(E^a\) as eigenvalues. In order to derive expressions for the linked terms in Eq. (3.19) and the effective Hamiltonian (3.20), we will employ the graphical approach of Goldstone as described by Lindgren and Morrison [2]; Every second-quantized operator is put into normal form with respect to the vacuum state, which for our purposes will be the closed shell Slater determinant of the Xe-configuration. By 'normal form' it is here meant that \(a^+_r a_a\) and \(a^+_a a_r\) appear to the right of \(a^+_a a^+_r\), where \(a\) and \(r\) denotes a core and virtual orbital, respectively. Wick’s theorem [64, 65] then provides the means to express the products of the creation/absorption operators in a summation of terms of normal ordered operators. The algebraic book-keeping of this procedure is rather tiresome, making the graphical form of Wick’s theorem more attractive. This latter approach is also particularly suitable for the separation of an operator into angular and radial parts; Each interaction line of a diagram is associated with a matrix element and possibly an energy denominator. The geometric structure of the Goldstone diagram can be converted into orbital- and spin angular momentum graphs that can be evaluated or recoupled by using the JLV theorems of Jucys et al. [66]. The evaluation of the radial parts of the diagrams can be made by solving inhomogeneous differential equations, which to second order contains single-particle [67–69] and pair-functions [2, 5, 70].
From MBPT to coupled-cluster theory

By inspection of the diagrams obtained from the linked diagram theorem, it is realized that the disconnected diagrams, i.e. the diagrams that consists of two or more separate graphs, can be expressed in terms of products of the connected diagrams of lower order. That is, it is possible to express the wave operator using connected diagrams only. This leads to the coupled-cluster methods where the wave operator can be expressed as $\Omega = \exp\{S\}$. Here $S$, the cluster operator, equals the connected parts of the wave operator. By regarding the term $PV\Omega P$ in Eq. (3.20) as the effective interaction $W$, the coupled-cluster equation can be written in the simple form

$$[S,H_0]P = (V\Omega P - \chi W)_{\text{connected}}.$$

The CC-method is generally regarded as a successful approach to calculate energy levels of atomic and molecular systems.
Correlation of two electrons

The first, and most simple, example of an atomic system for which the presence of electronic correlation prevents an analytical solution of the Schrödinger equation is the Helium atom. Therefore substantial efforts has been made during the years to develop numerical methods and efficient basis sets to obtain accurate estimates for the ground- and excited energies and their corresponding wave functions. For a review, see Ref. [71] and the references in Paper VIII. In fact, the problem is today essentially considered to be solved far beyond reasonable accuracy, as for example Korobov were able to obtain 24 significant digits for the Helium ground state [9].

However, when developing new tools for the calculation of energies of more complex systems, the Helium atom still serves as a benchmark to be able to check that reasonable accuracy can be obtained.

4.1 A finite difference approach

Although the most accurate methods rely on the explicit use of the coordinate $r_{12}$ in the wave function, we adopted a scheme in which the standard partial wave expansion of $r_{12}$ is employed

$$\frac{1}{r_{12}} = \sum_k \frac{r_{12}^k}{r_{12}^{k+1}} C^{(k)}(1) \cdot C^{(k)}(2)$$

and thus we expand the wave function in the following form:

$$\Psi_{LS} = \frac{1}{r_1 r_2} \sum_{l_1 l_2} \Phi_{l_1 l_2}^{LS}(r_1, r_2) \Lambda_{l_1 l_2}^{LM}(1, 2), \quad (4.1)$$

where the angular functions are given by

$$\Lambda_{l_1 l_2}^{LM}(1, 2) = \sum_{m_1 m_2} \langle l_1 m_1, l_2 m_2 | (l_1 l_2)LM \rangle Y_{l_1 m_1}(1) Y_{l_2 m_2}(2)$$

and the $\Phi_{l_1 l_2}^{LS}$ are the radial pair-functions. This ansatz has the advantage that subsequently better approximations are possible depending on where the summation in $l_1$ and $l_2$ is truncated. Although the slow convergence with respect
to $l_1$ and $l_2$ of this expansion is well-known, it can be remedied by use of the asymptotic formulae derived by Hill [72] and further studied by Kutzelnigg and Morgan [73]. For the ground state Hill showed that

$$E_l - E_{l-1} = C_4(l + \frac{1}{2})^{-4} + C_5(l + \frac{1}{2})^{-5} + O(l^{-6}),$$

(4.2)

where the coefficients $C_4$ and $C_5$ are given by integrals over the exact ground state wave function and $l$ denotes the largest value of $l_1$ and $l_2$. These coefficients were accurately evaluated by Freund and Morgan [74,75], here given in atomic units:

$$C_4 = -0.0742257$$

$$C_5 = -0.0309891.$$

Many modern fast eigenvalue-solvers rely on iterative techniques which only require the action of the operator, in this case the Hamiltonian, on a given trial function. That is, in each iteration we compute $H\Psi$, where $\Psi$ is of the form given in Eq. (4.1).

Because numerical basis sets are considered to be very accurate for small systems such as He and Be [1], we chose to discretize the radial functions and apply extrapolation to obtain the continuous grid result, see also the early works of Winter et al. [76,77]. Thus we applied the finite difference formula

$$\left(\frac{d^2}{dr_1^2} + \frac{d^2}{dr_2^2}\right)\Phi = \frac{1}{h^2}(\Phi_{m-1,n} + \Phi_{m+1,n} + \Phi_{m,n-1} + \Phi_{m,n+1} - 4\Phi_{m,n}) + O.$$  \hspace{0.5cm} (4.3)

for the approximate second derivatives. The action of $r_{12}^{-1}$ on a partial wave $(r_1 r_2)^{-1} \Phi_{l_1 l_2}^{LS} \Lambda_{l_1 l_2}^{LM}$ is given by

$$r_{12}^{-1} \frac{1}{r_1 r_2} \Phi_{l_1 l_2}^{LS} \Lambda_{l_1 l_2}^{LM} = \frac{1}{r_1 r_2} \sum_{l_1' l_2'} \sum_{k} \frac{r_{12}^k}{r_{k+1}} \Phi_{l_1 l_2}^{LS} (l_1' l_2' L | C^{(k)} \cdot C^{(k)} | l_1 l_2) \Lambda_{l_1 l_2}^{LM}$$

$$= \frac{1}{r_1 r_2} \sum_{l_1' l_2'} \sum_{k} \frac{r_{12}^k}{r_{k+1}} (-1)^{L+l_1'+l_2'} [l_1, l_2, l_1', l_2']^{1/2} \Phi_{l_1 l_2}^{LS} \Lambda_{l_1 l_2}^{LM}$$

$$\times \left( \begin{array}{ccc} l_1' & k & l_1 \\ 0 & 0 & 0 \\ l_2' & k & l_2 \end{array} \right) \left( \begin{array}{ccc} l_1 & 0 & 0 \\ 0 & 0 & 0 \\ l_2 & l_1 & k \end{array} \right).$$

A computer program designed to efficiently perform the above operations and employ the ARPACK/PARPACK library [78] for the extraction of eigenvalues, was written and submitted to the CPC Program Library, see Paper VIII.
Table 4.1: Energies in Hartrees for the $1^1S$ and $2^{1,3}S$-states. The 'exact' $1^1S$ and $2S$ energies are from Korobov [9] and Drake and Yan [79], respectively.

<table>
<thead>
<tr>
<th>$l$</th>
<th>$1^1S$</th>
<th>$2^{1}S$</th>
<th>$2^{3}S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-2.879028767</td>
<td>-2.174264856</td>
<td>-2.14419727</td>
</tr>
<tr>
<td>1</td>
<td>-2.900516247</td>
<td>-2.175171982</td>
<td>-2.14576662</td>
</tr>
<tr>
<td>2</td>
<td>-2.902766852</td>
<td>-2.175220437</td>
<td>-2.1459148</td>
</tr>
<tr>
<td>3</td>
<td>-2.903321084</td>
<td>-2.175227126</td>
<td>-2.1459494</td>
</tr>
<tr>
<td>4</td>
<td>-2.903518601</td>
<td>-2.175228620</td>
<td>-2.1459615</td>
</tr>
<tr>
<td>5</td>
<td>-2.903605707</td>
<td>-2.175229069</td>
<td>-2.1459669</td>
</tr>
<tr>
<td>6</td>
<td>-2.903649877</td>
<td>-2.175229236</td>
<td>-2.1459695</td>
</tr>
<tr>
<td>7</td>
<td>-2.903674601</td>
<td>-2.175229304</td>
<td>-2.1459709</td>
</tr>
<tr>
<td>8</td>
<td>-2.903689497</td>
<td>-2.17522933</td>
<td>-2.1459718</td>
</tr>
<tr>
<td>9</td>
<td>-2.903698998</td>
<td>-2.17522935</td>
<td>-2.1459722</td>
</tr>
<tr>
<td>10</td>
<td>-2.903705340</td>
<td>-2.17522936</td>
<td>-2.1459727</td>
</tr>
<tr>
<td>$\infty$</td>
<td>-2.90372437</td>
<td>-2.17522938</td>
<td>-2.145974</td>
</tr>
</tbody>
</table>

The results obtained are quite accurate considering that the submitted program runs in double precision only. More accurate results can of course be obtained. If we switch to quadruple precision, we were for example able to obtain -2.8790287673192144062 a.u. for the $S$-limit of the Helium ground state, which can be compared to -2.87902876731921441 a.u. due to Goldman [10]. Table 4.1 summarizes the result for the three lowest $S$-states of Helium for $0 \leq l_{\text{max}} \leq 10$, and also the extrapolated result using the asymptotic formulae for the $l$-dependence of the energies, see Paper VIII.
The Rare-earth series

The rare-earths (RE’s), comprising the atoms with atomic number 58-71, are chiefly trivalent with a Xenon-like core and $N$ 4f-electrons in an open shell. An optical absorption spectrum of a rare-earth ion in a solid or liquid reveals the sharp lines of the intra 4f-transitions. These appear because the localized 4f-shell is efficiently screened from ligand-interactions by the outer 5s and 5p-shells. The result is that an f-electron experiences only a minor part of the crystal field. Calculations and estimates of the shielding effect has been made by e.g. Sternheimer [80]. In contrast to the sharp f-f transitions, the experimentally measured f-d transitions are usually very broad. Here the radial and angular electron density change which induce vibrations in the environment, usually explained well by the configurational-coordinate model. Fig. 5.1 shows the complexity of the many energy levels within the 4f$^N$-shell. This splitting is mostly due to electron correlation and the spin-orbit interaction. Inside a crystal (here LaF$_3$), the levels are also splitted into crystal field levels. This effect is only in the order of 100’s of cm$^{-1}$, further emphasizing the minor influence of the crystal field on the energy structure. Despite this, the environment has a major impact on the electric dipole f-f transitions, which would all be parity forbidden for a free ion.

5.1 Classification of states

For two electrons, an antisymmetric basis function can be unambiguously characterized by the set of quantum numbers $LSM\ell M_S$. This is however not true in general when the number of electrons exceeds two, as for example the $d^3$-configuration contains two $^2D$-terms. However, in a celebrated paper from 1949, Racah introduced the concept of continuous groups to the theory of atomic spectra [25]. In the same way as $L$ and $S$ correspond to irreducible representations (irreps.) of the group $R_3$, Racah recognized that the irreps. of higher groups can provide additional quantum numbers to separate the $LS$-basis functions of the configurations $nd^N$ and $nf^N$. The

$$\binom{4I + 2}{N} = \frac{(4I + 2)!}{N!(4I + 2 - N)!}$$
Figure 5.1: Energies of triply ionized rare-earths in LaF$_3$ in cm$^{-1}$. This calculation was done by using the computer program Lanthanide, see Paper III, using parameters from Carnall et al. [34].

antisymmetrical basis functions of the $4f^N$-configuration form a basis of the irrep. \{$\lambda^N$\} of SU$_{14}$, the special unitary group in 14 dimensions. Two different chains of SU$_{14}$ ⊇ SU$_2 \times$ R$_3$ are widely used for the labeling of $f$-electron states:

\[ SU_{14} \supset SU_2 \times (U_{2l+1} \supset R_{2l+1} \supset G_2 \supset R_3) \]
\[ SU_{14} \supset Sp_{14} \supset SU_2 \times (R_{2l+1} \supset G_2 \supset R_3) \]

The first is used by Judd [21] and the second is Racah’s fractional parentage scheme [25]. Here U is the unitary group, G$_2$ is one of Cartan’s exceptional groups [81], Sp is the symplectic group and R is the group of rotations. In Judd’s scheme, the irreps. \{$\lambda_1 \lambda_2 \lambda_3 \ldots$\} of U$_7$ (note that specifying this irrep. amounts to specify the spin $S$), \(W = (w_1 w_2 w_3)\) of R$_7$, \(U = (u_1 u_2)\) of G$_2$, and \(L\) of R$_3$ are used to define the basis functions of $n^f N$ by:

\[ |f^N \tau W U L S M_L M_S \rangle. \] (5.1)
As can be seen in Table 5-3 of Ref. [21] the irreps. (31) and (40) of \( \mathbf{G}_2 \) contain several identical irreps. of \( \mathbf{R}_3 \). As (31) and (40) can only be obtained from the decomposition of (221) and (222) of \( \mathbf{R}_7 \), an additional arbitrary quantum number \( \tau \) has to be inferred in Eq. (5.1) for \( f^S \cdot f^d \). However, the eigenvectors of the effective Hamiltonian, even in the absence of a crystal field, are not in general of the form (5.1) since the spin-orbit interaction mixes states with different \( L \) and \( S \). Rather, \( \left| f^N \psi JM \right> \) will be used to denote a state for which \( JM \) is a good quantum number. Here \( \psi \) symbolizes the specific linear combination of the basis functions \( f^N \tau^W U L S J M \).

Matrix elements in this basis may be calculated using the coefficients of fractional parentage, as introduced by Racah [24] following an idea of Bacher and Goudsmit [82]. Instead of using these basis functions, the equivalent Slater determinant basis has been applied in all papers. This is clearly a disadvantage for the group-theoretical aspects of the energy levels, but is indeed appealing with regard to the simplicity in calculating matrix elements for any number of electrons.

5.2 The free-ion effective Hamiltonian

Since we are mainly concerned with the energy splittings of the \( 4f^N \) configuration, all contributions that produce a constant shift of all the energies are omitted. The free-ion Hamiltonian that has been applied in this thesis is

\[
\mathcal{H}_{\text{free}} = \mathcal{H}_{\text{es}} + \mathcal{H}_{\text{so}} + \mathcal{H}_{\text{lc}},
\]

(5.2)

and will briefly be discussed in the following subsections.

5.2.1 First order contributions

The first order effective Hamiltonian \( \mathcal{H}^{(1)} \) is given by

\[
\mathcal{H}^{(1)} = PV P
\]

which merely corresponds to the closing of the diagrams of the perturbations \( V \). If only the terms that contribute to the energy splitting are kept, this reduces to the operator

\[
\mathcal{H}_{\text{es}} = \sum_{i<j} \sum_{k=2,4,6} F^k(4f,4f) \mathbf{C}^{(k)}(i) \cdot \mathbf{C}^{(k)}(j),
\]

(5.3)

for the electrostatic interaction. This term is usually interpreted as the correlation between the \( 4f \)-electrons.
In order to more properly describe the experimentally observed energy splittings, relativistic effects must also be considered. In the non-relativistic limit of the Dirac equation the most important correction is obtained, namely the spin-orbit interaction [83]:

$$\mathcal{H}_{so} = \sum_i \zeta_{i} A(i) \cdot s(i) \quad (5.4)$$

Classically, this term corresponds to the interaction of the electron spin with the induced magnetic field due to its motion.

The Slater integral values and the spin-orbit parameter, see Table 5.1, obtained from the Hartree-Fock method are quite poor and largely over-estimate the energy splitting as shown in Fig. 5.2. This is mainly due to the fact that HF integrals are over-estimated. Even by treating the \( F^k \)'s and \( \zeta \) as free parameters a perfect experimental fit cannot be obtained.

**Table 5.1:** Radial HF integrals for \( Pr^{3+} \) in cm\(^{-1}\).

<table>
<thead>
<tr>
<th></th>
<th>( F^2 )</th>
<th>( F^4 )</th>
<th>( F^6 )</th>
<th>( \zeta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>98514</td>
<td>61796</td>
<td>44452</td>
<td>824</td>
</tr>
<tr>
<td>Exp</td>
<td>68878</td>
<td>50347</td>
<td>32901</td>
<td>752</td>
</tr>
</tbody>
</table>

### 5.2.2 Second order contributions

The second order effective Hamiltonian is, from Eq. (3.20),

$$\mathcal{H}^{(2)} = PV\Omega^{(1)} P.$$  

This consists of zero-, one-, two and three-body diagrams, and if the spin-orbit interaction is neglected the two former does not contribute to the energy level splitting.

As for the two-body diagrams, see Fig. 13.7 in Ref. [2], it can be shown that besides modifying the \( F^k \)'s in Eq. (5.3) they also show the need for scalar two-particle operators of odd rank. It was noted empirically by R.E. Trees as early as 1951 [32, 33] that the addition of \( \alpha L^2 \) to the Hamiltonian for the \( d^5s \) configuration of \( Mn^{2+} \) and \( Fe^{2+} \) significantly improved the fitting of the experimental energy levels. This was later justified by Rajnak and Wybourne [26] who showed that scalar two-particle operators of odd rank arises from the perturbing influences on the open shell \( l^N \) from the different configurations.
Figure 5.2: Experimental and HF-energies of a free Pr$^{3+}$ ion.

- $l^{N-2}p^2$ or $l^{N-2}p'p''$
- $l'^4l''^{N+2}$ or $l'^4l''^{N+1}l'^{N+1}$
- $l'^4l''^{N+2}$

The scalar two-body operators of odd rank obtained from these considerations are commonly written as

$$H_{cl} = \alpha L^2 + \beta G(G_2) + \gamma G(R_7).$$  \hspace{2cm} (5.5)

The $\alpha, \beta, \gamma$ are named Trees parameters and the $G(K)$ is the Casimir operator for the group $K$;

$$G(K) = g^{\rho\sigma}(K)X_\rho X_\sigma$$

Here $g^{\rho\sigma}(K)$ is the metric tensor of the group and the $X_\sigma$ are its infinitesimal generators. Since the basis functions $|f^N_{\text{eWULSM}_L M_S}\rangle$ are eigenfunctions to $L^2$, $G(G_2)$ and $G(R_7)$ the matrix elements of Eq. (5.5) are particularly easy to evaluate. However, in the Slater determinantal basis set employed here, the operators $G(G_2)$ and $G(R_7)$ can be expressed as;

$$G(G_2) = \frac{3}{4}U^{(1)} \cdot U^{(1)} + \frac{11}{4}U^{(5)} \cdot U^{(5)}$$  \hspace{2cm} (5.6)
\[ G(\mathbf{R}_T) = \frac{3}{5} \mathbf{U}^{(1)} \cdot \mathbf{U}^{(1)} + \frac{7}{5} \mathbf{U}^{(3)} \cdot \mathbf{U}^{(3)} + \frac{11}{5} \mathbf{U}^{(5)} \cdot \mathbf{U}^{(5)}. \]  

(5.7)

\textit{Ab initio} calculations using perturbation theory to calculate the Trees parameters for Pr\textsuperscript{3+} and Er\textsuperscript{3+} have been performed by Morrison and Rajnak [70, 84] with at least some limited success. However, to get as accurate energies and eigenvectors as possible, these are often regarded as parameters which are adjusted to experiment.

We shall now consider the second order effective Hamiltonian diagrams in Fig. 5.3. The first diagram corresponds to a single excitation of an open-shell electron to an excited configuration, and the second to an excitation of a core electron into the open shell. These types of interactions were also studied by Rajnak and Wybourne [26] and further analyzed by Rajnak [30]. By recoupling the angular diagrams in Fig. 5.3 and using the JLV-theorem for diagrams separable on six lines, it is apparent that these two Goldstone diagrams consist of a summation of terms having the angular structure

\[ V(k_1k_2k_3) = 6 \sum_{i<j<k} \sum_{q_1,q_2,q_3} \begin{pmatrix} k_1 & k_2 & k_3 \\ q_1 & q_2 & q_3 \end{pmatrix} \begin{pmatrix} v^{(k_1)}_{q_1} & v^{(k_2)}_{q_2} & v^{(k_3)}_{q_3} \end{pmatrix}. \]  

(5.8)

For the parametrization of a scalar three-particle operator, it can be shown that \( k_1, k_2 \) and \( k_3 \) consists of the triplets (222), (224), (244), (444), (446), (266), (466) and (666). It was first thought that ten parameters were needed to completely parametrize the scalar three-particle operators. The number could directly be reduced to nine, as it was realized that the triad (226), initially included in the above series, does not contribute due to the triangular condition in Eq. (5.8). In an analogy to the parametrization of the two-particle operators, Judd [19] examined certain linear combinations of the \( V(k_1k_2k_3) \) that
transforms as the representations $WU$:

$$ t(WU) = \sum_{k_1k_2k_3} \langle k_1k_2k_3 | WU \rangle V(k_1k_2k_3). \quad (5.9) $$

Judd was then able to further reduce the number of parameters to six, as it was shown that the effects of $t((000)(00))$ and $t((400)(40))$ are absorbed by the two-particle parameters and that all matrix elements of $t((600)(60))$ identically vanish. A tabulation of the coefficients $\langle k_1k_2k_3 | WU \rangle$ may be found in Table VI of Ref. [19]. In this way the parametrized three-body operators can be written as

$$ \mathcal{H}_{nlci} = \sum_{i=2,3,4,6,7,8} t_i T^i. \quad (5.10) $$

### 5.3 The crystal field

When a rare-earth ion is doped into a host material, parts of the $2J+1$ degenerate $|f^NwJ\rangle$ states will split into so called Stark- or crystal field levels, with energy splittings much smaller than the splitting of the fine structure levels of a free ion. The Stark-level splittings are very sensitive to the specific host material and can therefore serve as a fingerprint of the surrounding crystal structure. Also, when a RE-ion is placed in a solid, intra $f$-shell transitions become allowed because of a mixing of parity due to the crystal field. It is therefore of great importance to take crystal field effects into account in order to predict energies and oscillator strengths.

There are basically two approaches to the crystal field theory, the phenomenological and the \textit{ab initio} approach. In the former approach the crystal

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5.4}
\caption{Energy splitting of the $4I_J$ levels of Nd:LaF$_3$ in cm$^{-1}$.}
\end{figure}
field Hamiltonian is constructed from parametrized linear independent operators to be fitted to experimental findings. For further reading on this topic, see Ref. [85].

5.3.1 The simple electrostatic model

\[ H_{cf} = -eU = - \sum_{i} \sum_{tp} \frac{r_{i}^{l}}{R_{p}^{l+1}} n(R) C_{p}^{(l)}(\alpha, \beta) C_{p}^{(l)}(\theta, \phi) dV \]

where the crystal field parameters \( A_{tp} \) are given by
\[ A_{tp} = (-1)^{t+1} \int \frac{n(R)}{R^{t+1}} C^{(t)}_{-p}(\alpha, \beta) dV. \]  
\hspace{1cm} (5.13)

As long as the energy calculations are concerned, it can be seen from the matrix elements of \( H_{cf} \) that the number of parameters are limited by \( t = 2, 4, ..., 2l \) within an \( nlN \)-shell. However, for intensity calculations the \( A_{tp}'s \) with odd \( t \) are also needed. The 4\( f \)-electrons also experience that the closed shells become polarized by the crystal field. This effect gives rise to a screening of the crystal field and the \( A_{tp} \)-parameters must be multiplied by the factors \( (1 - \sigma) \) for even \( t \) \[80\].

A first approximation is to apply DFT-method to determine \( n(R) \), see e.g. Refs. \[86, 87\]. For very ionic host materials it is natural to expand the charge density of the ligands in multipoles

\[ A_{tp} = (-1)^{t+1} \sum_j [q_j R_j^{-t-1} + \mu_j R_j^{-t-2}(t+1)] + \frac{1}{4} Q_j R_j^{-t-3}(t+2)(t+1) + ... |C^{(t)}_{-p}(\theta_j, \phi_j), \]  
\hspace{1cm} (5.14)

where the multipole moments in general depend on both the electric field and its directional derivatives. Therefore, in order to calculate the \( A_{tp}'s \) using Eq. (5.14) a self-consistent approach has to be employed, see Papers IV, V and Refs. \[49, 88\].

### 5.3.2 Site symmetry

Fortunately, the number of crystal field parameters can be reduced, as the hermiticity of \( H_{cf} \) gives \( A_{tp} = (-1)^{t} A_{-t-p}^{*} \). Also, the RE-site in a crystalline host or molecule often possesses a certain symmetry which forces the crystal field Hamiltonian to be invariant under the operations of the specific point group. We consider as an example the point group \( S_4 \), which is generated by \( \hat{S}_4 \) a rotation by \( \pi/2 \) about the \( z \)-axis followed by an inversion. The remaining three operators of the group are \( \hat{C}_2 = \hat{S}_4^2, \hat{S}_4^3 \) and \( \hat{E} = \hat{S}_4^4 \). We then have for the first operator:

\[
\hat{S}_4 \sum_p A_{tp} C_p^{(t)}(\theta, \phi) = \sum_{p'} \left[ \sum_p \langle tp'|\hat{S}_4|tp \rangle A_{tp} \right] C_{p'}^{(t)}(\theta, \phi) \\
= \sum_p \left[ (-1)^t e^{-i\pi/2} A_{tp} \right] C_{p}^{(t)}(\theta, \phi) \\
= \sum_p A_{tp}' C_{p}^{(t)}(\theta, \phi)
\]
and thus \((-1)^t e^{-ip\pi/2} = 1\). Summarizing the conditions for all four operators we have:
\[ (-1)^t e^{-ip\pi/2} = (-1)^t e^{-ip3\pi/2} = (-1)^p e^{-ip\pi} = 1.\]
This gives that \(p = 4m\) for even \(t\) and \(p = 4m + 2\) for odd \(t\), for \(m \in \mathbb{N}\). For example the \(A_{1p}\)-parameters identically vanishes in this symmetry, implying that the electric field is zero at the RE site. Tables of non-vanishing crystal field parameters for all crystallographic 32 point groups can be found in Ref. [89].

5.3.3 A semi-empirical approach

In order to obtain consistent optimized even and odd crystal field parameters we proposed an unorthodox method in Paper V. There a model cluster was set up for \(\text{Nd:LiYF}_4\) by considering the nearest ligands out to a certain cut off distance \(R_{\text{cut}}\) with the rare-earth ion in the center. Because of the need for computational speed in the optimization, the multipole expansion of Eq. (5.14) was truncated such that only the ligand charge- and dipole moment terms were included. The effective Hamiltonian used for the calculation of energies were
\[
\mathcal{H}_{\text{free}} + \sum_i \sum_p B_{tp} C_p^{(l)}(i)
\]
where \(B_{tp} = \rho_t A_{tp}\) \((t = 2, 4, 6)\). Here the parameters \(\rho_t\) were imposed to account for an effective expansion of the radial \(f\)-function and also shielding. An optimization of the parameters
\[
\xi, F^2, F^4, F^6, \alpha, \beta, \gamma, T^2, T^3, T^4, T^6, T^7, T^8, q_j, \alpha_j, \rho_t
\]
were performed with respect to experimental energy levels by using an adaptive simulated annealing method. In each step a self consistent crystal field calculation, see Eq. (5.14), and an energy matrix diagonalization were made using the parameters proposed from the optimization routine.

As Eq. (5.14) is valid for both even and odd \(A_{1p}\)’s we also obtained a set of odd parameters which are useful for the intensity calculations. It should be mentioned, that although an electrostatic model were used, the applied fitting procedure allows for the inclusion of other interactions into the \(A_{1p}\) parameters. This is certainly beneficial for the energy level structure, but it remains unclear in what way this affects the odd parameters and also the transition amplitudes.
5.4 The 'Lanthanide' software

In order to diagonalize the effective Hamiltonian within a single open shell, a Slater determinant based computer program, 'Lanthanide', was written and later also published in the CPC Program Library, see Paper II. Since then, the package has been substantially revised and extended to calculate absorption spectra, charge and spin densities, configuration interaction etc. It was for example modified to be able to handle several open shells and configurations which then was applied to Manganese in Paper VI.

The program Lanthanide has also been developed in a different direction by Caspary [90] in order to fit energy- and intensity parameters to experiment. He found it particularly useful for fibre laser applications.

In Fig. 5.6 we show the calculated angular $f$-electron charge density $|\Psi|^2$ for the two lowest crystal field levels of the ground state $^4I_{9/2}$ for Nd:LiYF$_4$.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5_6.png}
\caption{The angular $f$-electron charge density for the two lowest states of Nd:LiYF$_4$.}
\end{figure}
Radiative transitions within the f-shell

There are many different suggested mechanisms and methods in use for calculations of f-f transitions. The usual electric-dipole transition is parity forbidden but becomes allowed when account is made to the crystal field. These perturbations mix in opposite parity into the f-states. This mechanism is treated in Judd-Ofelt theory [18, 91], described below, and gives clearly large contributions to the observed transition intensities. Higher order effects such as magnetic dipole or quadrupole transitions are allowed but are usually also small, see e.g. Ref. [92]. Theoretical estimations also confirm that they are several orders of magnitude smaller than the usual electric-dipole effect [93]. Six years after the birth of the JO-theory, third order contributions from the crystal field, spin-orbit interaction and electron correlation to the transition amplitude was discussed by Wybourne [94]. Judd and Pooler also examined the impact from the spin-orbit interaction on the two-photon transitions of Gd:LaF$_3$ [95]. Later, Smentek and Hess presented all third order spin-orbit contributions to the two-photon absorption process [96, 97]. Downer, Burdick, Sardar and Bivas also studied the impact from spin-orbit for one-photon transitions for Gd and Eu [98, 99]. Smentek later examined the contributions from all third order spin-orbit effective dipole operators using the perturbed functions approach [100]. In Paper IV we studied the effect of including spin-orbit interaction perturbations for the host material LiYF$_4$, but the effect was found to be small, see Table IX in Paper IV. Even though the errors in the crystal field parameters are probably large, an unlikely alteration of several orders of magnitude would be required to render the spin-orbit effect significant. In this paper we also examined the effect from including crystal field to higher order but again it was found to give very small contributions to the transition amplitude. Fig. 6.1 shows the experimental and theoretical $\sigma$-polarized spectra for Ho:LiYF$_4$. The overall agreement between the experimental and theoretical spectra is quite satisfactory as most features are reproduced. In Subsection 5.3.2, the $A_{1p}$-parameters was seen to be identically zero for a RE-ion in a perfect $S_4$-symmetry. If that were the case, the hypersensitive $[^{5}I_8] \rightarrow [^5G_6]$ peak, at ~450 nm, would be very small in comparison with experiment. However, if the crystal field parameters are calculated using the positions from an molecular dynamics (MD)-simulation the $A_{1p}$-parameters become non-zero and a larger peak is observed. An effective non-zero value for $A_{1p}$ was therefore
used in Paper IV. It would be interesting to also study this specific transition using the correlated approach of Paper V (keeping $A_{1p} \equiv 0$).

Figure 6.1: Experimental and theoretical $\sigma$-polarized spectra of Ho:LiYF$_4$.

Smentek and co-workers have also studied the effective dipole operators originating from the electron correlation [36–39]. Using the perturbed functions approach it has been shown that these third order contributions modify the standard second order integrals significantly [38,39,101]. In paper V, an attempt was made to study the influence on the oscillator strengths by including electron correlation using the MBPT. Also here the correlation contribution
was seen to be large. It would therefore be interesting to derive and evaluate fourth order effective operators to be able to study the convergence of the perturbation series. However, the mathematical apparatus involving huge algebraic expressions and diagrams makes it extremely tedious to continue to higher orders. Be it as it may, Fig. 6.2 displays an experimental absorption spectrum for Nd:LiYF$_4$ [102]. A theoretical spectrum using the method of paper IV (non-correlated) is shown in Fig. 6.3. It can be seen that the main deviations are located below 600 nm. These bands are less intense than those seen in the experiment. Fig. 6.4 shows the effect of taking correlation into account to third order. The tendency is that the relative band intensities between the groups below and above 600 nm have been improved. It should be noted that many of the transitions below 600 nm have large reduced matrix elements of $U^{(2)}$ occurring in the Judd-Ofelt approximation. The site-symmetry $S_4$ forces the crystal field parameters $A_{1p}$ to be zero which also could explain the low band intensities below 600 nm in the non-correlated spectrum, see Fig. 6.3. In a dynamical model the local environments can break this symmetry resulting in effective non-zero $A_{1p}$’s. A decisive conclusion is thus hard to make.

![Absorption spectrum](image)

**Figure 6.2:** Experimental unpolarized spectrum for Nd:LiYF$_4$.

Other suggested mechanisms that contribute to the transition amplitude are the effect of an inhomogeneous dielectricum for which the radiation fields induce oscillating dipoles in the ligands [103], and the so-called dynamic coupling proposed by Mason et al. [104]. Judd showed that these seemingly differ-
ent mechanisms are in fact identical [103]. The effect of an inhomogeneous dielectricum is particularly useful for the explanation of so-called hypersensitive transitions (i.e. those transitions usually having large reduced matrix elements of $U^{(2)}$). Reid et al. have shown that the dynamic coupling model is able to reproduce the correct relative signs of the intensity parameters $A_{\lambda+1,p}^2$ [105].
Yet another dynamic mechanism, the vibronic coupling, was suggested by Judd [106]. This corresponds to a non-zero phonon transition and was also designed as a possible explanation of the hypersensitivity phenomenon. The dynamics of the surrounding atoms might also be important in a different way; because of the dynamics of the various rare-earth environments, the rare-earth ions experience different crystal fields at different sites. When the radiation field is turned on, absorptions take place for many different environments leading to inhomogeneous broadening and variations in the oscillator strengths. In a static model, assuming that shielding is not complete, it has been argued that potentials of the type $Y_{1p}$ connected to $U^{(2)}$, would be unphysical since the ion would not be in equilibrium. In a dynamical picture this problem disappears. These dynamical effects were for example studied earlier by Wolf et al. [107]. The charge-transfer mechanism has also been investigated as a possible source of hypersensitivity [108, 109], but it was later stated by Peacock that its impact probably is negligible [110].

A recent development within the framework of $f-f$ transitions is the relativistic approach [111–114], where the effective operators are constructed from double unit tensor operators $W^{(k)\lambda}$, which acts within the spin-orbital space of the $4f$-shell. The standard parametrization for the line strength of $f-f$ transitions is thus replaced with

$$S_{f\rightarrow i} = \sum_{\lambda} \sum_{k\ell} \Omega_{(k\ell)\lambda} \langle \Psi_f | W^{(k)\lambda} | \Psi_i \rangle^2.$$

6.1 An outline of the Judd-Ofelt theory

The Judd-Ofelt (JO) theory has played an important role in the understanding of rare-earth spectra, and its 40th year anniversary was celebrated with a special issue of *Molecular Physics* [115] which were presented during a workshop held in Karpacz, Poland. The theory was independently developed by Judd [18] and Ofelt [91], and has since then been applied in a vast number of publications to describe the optical properties of rare-earth ions in solids and liquids. For a review of the JO-theory, see Ref. [116].

The oscillator strength for a dipole transition from state $i$ to $f$ is given by

$$P = \chi \frac{8\pi m \nu}{\hbar} \left| \langle i | D^{(1)}_q | f \rangle \right|^2$$

(6.1)

where $\chi$ is the Lorentz local field correction, $m$ is the electron mass and $\nu$ is
the transition frequency. The dipole operator $D_q^{(1)}$ is defined by

$$D_q^{(1)} = \sum_i r_i^0 C_q^{(i)}(\theta_i, \phi_i). \quad (6.2)$$

for $t = 1$. If the initial and final states are written

$$\langle A \rangle = \sum_M \langle \langle n^N \psi J M | a_M \rangle$$

$$\langle A' \rangle = \sum_{M'} \langle \langle n^N \psi J' M' | a'_{M'} \rangle,$$

it is seen that the oscillator strength in Eq. (6.1) identically vanishes, due to that the states $|A\rangle$ and $|A'\rangle$ have the same parity. However, when the rare-earth ion is subject to an external field which breaks the spherical symmetry, the wave functions will no longer have a definite parity and intra-shell transitions become allowed. Note that this does not apply to all symmetries, as all odd crystal field parameter are zero for the point groups $C_l, C_{2h}, C_{4h}, C_{6h}, D_{2h}, D_{4h}, D_{6h}, D_{3d}, S_6, O, O_h$ and $T_h$.

Following Judd [18], the states $|A\rangle$ and $|A'\rangle$ can according to first order perturbation theory, under the influence of a static crystal field, be expanded into

$$\langle B \rangle = \sum_M a_M \langle \langle n^N \psi J M | H_{cf} | l^{N-1}(n't') \psi'' J'' M'' \rangle$$

$$\times \langle l^{N-1}(n't') \psi'' J'' M'' | [E(\psi J') - E(n't', \psi'' J'')] \rangle \quad (6.3)$$

$$\langle B' \rangle = \sum_{M'} a'_{M'} \langle \langle n^N \psi J' M' | H_{cf} | l^{N-1}(n't') \psi'' J'' M'' \rangle$$

$$\times \langle l^{N-1}(n't') \psi'' J'' M'' | [E(\psi J') - E(n't', \psi'' J'')] \rangle \quad (6.4)$$

where $|l^{N-1}(n't') \psi'' J'' M''\rangle$ represents a state reached by a single excitation from the $n^N$ configuration. This leads to

$$\langle B | D_q^{(1)} | B' \rangle = \sum a_M a'_{M'} A_{\alpha \beta} \langle \langle n^N \psi J M | D_q^{(1)} | l^{N-1}(n't') \psi'' J'' M'' \rangle$$

$$\times \langle l^{N-1}(n't') \psi'' J'' M'' | D_q^{(1)} | l^{N-1}(n't') \psi'' J'' M'' \rangle | E(\psi J') - E(n't', \psi'' J'')] \rangle$$

$$\langle B | D_q^{(1)} | B' \rangle = \sum a_M a'_{M'} A_{\alpha \beta} \langle \langle n^N \psi J M | D_q^{(1)} | l^{N-1}(n't') \psi'' J'' M'' \rangle$$

$$\times \langle l^{N-1}(n't') \psi'' J'' M'' | D_q^{(1)} | l^{N-1}(n't') \psi'' J'' M'' \rangle | E(\psi J') - E(n't', \psi'' J'')] \rangle$$

The presence of

$$|l^{N-1}(n't') \psi'' J'' M''\rangle \langle l^{N-1}(n't') \psi'' J'' M'' |$$

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suggests that a closure procedure [117] could be performed in some way. This would then allow for expressing $D_q^{(1)}$ and $D_p^{(1)}$ as a single operator acting within the $f$-shell. Under the approximations that the energies of the excited configuration are degenerate with respect to $n', l', \psi'', J''$, and that the energy denominators of Eqs. (6.3) and (6.4) are equal, Judd arrived at

$$
\langle B | D_q^{(1)} | B' \rangle = \sum_{\lambda} \sum_{tq} [\lambda] (-1)^{p+q} A_{tp} \left( \begin{array}{ccc} 1 & \lambda & t \\ q & -p-q & p \end{array} \right) \langle A | U_p^{(\lambda)} | A' \rangle \Xi(t, \lambda)
$$

(6.5)

where

$$
\Xi(t, \lambda) = 2 \sum_{t'q' \lambda} \frac{\langle nl|r'tl'||nl'|nl\rangle \langle ll'||C^{(1)}||l'l'\rangle \langle l'||C^{(1)}||l\rangle}{\epsilon_{nl} - \epsilon_{t'q'}}
$$

(6.9)

6.2 Parametrizations

J-J multiplet transitions

For the calculation of oscillator strengths for RE’s in liquid solutions, Judd averaged over the components $-1, 0, 1$ of $D_q^{(1)}$ and further made the approximation that the states $|lN\psi JM\rangle$ were degenerate with respect to $M$, and finally arrived at

$$
P = \sum_{\lambda=2,4,6} T_{\lambda} \langle lN\psi J||U^{(\lambda)}||lN\psi' J' \rangle^2
$$

(6.6)

where

$$
T_{\lambda} = \chi \frac{8\pi^2 m [\lambda]}{3h[J]} \sum_{tq} \frac{\Xi(t, \lambda)}{[t]} |A_{tp}|^2.
$$

(6.7)

However, more common in literature is the corresponding parametrization of Axe [118] who proposed

$$
P = \chi \frac{8\pi^2 mv}{3h[J]} \sum_{\lambda=2,4,6} \Omega_{\lambda} \langle lN\psi J||U^{(\lambda)}||lN\psi' J' \rangle^2
$$

(6.8)

with the intensity parameters $\Omega_{\lambda}$, not to be confused with the wave operator, defined by

$$
\Omega_{\lambda} = [\lambda] \sum_{tq} \frac{|\Xi(t, \lambda)A_{tp}|^2}{[t]}.
$$

(6.9)
Much of the success of the JO-theory may be ascribed to the relative simplicity of Eqs. (6.6) and (6.9); Since they are linear in the intensity parameters, fittings to experiment can easily be made. Although the JO-theory was originally derived for the mixing of odd parity wave functions due to an electrostatic crystal field, the parametrization (6.8) has been shown to be able to absorb contributions also from electron correlation of the static and dynamic models, spin-orbit interactions, mass polarization and other relativistic effects [113].

Transitions between crystal field levels

In the same way as Eq. (6.5) can be regarded as the matrix element of an effective dipole operator between \( J \)-multiplets, effective dipole operators can be constructed to act between individual crystal field or Zeeman levels. A spin-independent one-electron effective dipole operator is restricted by hermiticity and time-reversal symmetry to consist of linear combinations of even rank operators [85]. This means that such an operator can be written as

\[
\mathcal{D}_1 = \sum_{\lambda l} B^{(\lambda)}_{l q} U^{(\lambda)}_l
\]

where \( \lambda = 2, 4, 6 \) for \( f \)-electrons, and the subscript 1 denotes that this is a one-particle operator. The operator \( U^{(0)}_0 \) is a scalar operator which do not contribute to the transition amplitude, and is therefore excluded in the above summation.

The parametrization of Reid and Richardson [40]:

\[
\mathcal{D}_1 = \sum_{\lambda lp} A^{(\lambda)}_{lp} (-1)^q U^{(\lambda)}_{p+q} (\lambda(p + q), 1 - q|tp)
\]

is however more widely used both in \textit{ab initio} and phenomenological approaches. As is seen from the Clebsh-Gordan coefficient, \( t \) is restricted to \( \lambda \) and \( \lambda \pm 1 \). The intensity parameters \( \Omega_{\lambda} \) of Axe can also be expressed in terms of the \( A^{(\lambda)}_{lp} \):

\[
\Omega_{\lambda} = \sum_{lp} \frac{|A^{(\lambda)}_{lp}|^2}{|\lambda|} \quad (6.11)
\]

The two-particle operators can also be parametrized in much the same way, giving:

\[
\mathcal{D}_2 = \sum_{k_1 k_2 lp} A^{(k_1 k_2 \lambda)}_{lp} (-1)^q \{ u^{(k_1)} (1) u^{(k_2)} (2) \} \langle \lambda(p + q), 1 - q|tp \rangle \quad (6.12)
\]

with \( |k_1 - k_2| \leq \lambda \leq k_1 + k_2 \), \( 0 \leq k_1, k_2 \leq 6 \).
To actually calculate the transition amplitudes (Paper V), we use the model functions $\Psi_0^i$ obtained from the diagonalization of the effective Hamiltonian $H_{\text{eff}}$. These are expressed in Slater determinants of the $[\text{Xe}]4f^N$-configuration and can be written as

$$\Psi_0^i = \sum_j c_j^i \{|abc...g\}_j\),$$

and the transition amplitude becomes

$$\langle \Psi_0^i | D_1 + D_2 | \Psi_0^j \rangle = \sum_{jk} c_j^i c_k^j \langle \{|abc...g\}_j| D_1 + D_2 | \{|abc...g\}_k \rangle. \quad (6.13)$$

6.3 Effective operators using MBPT

In order to derive explicit expressions for the effective dipole operator we follow the approach of Duan and Reid [119], where the non-hermitean effective operator, to be used with eigenvectors obtained from a diagonalization of $H_{\text{eff}}$, is:

$$D = (\Omega^\dagger \Omega)^{-1} \Omega^\dagger D \Omega. \quad (6.14)$$

By using the expansion $\Omega = \sum_{i=0}^\infty \Omega^{(i)}$, the non-vanishing terms up to third order are

$$D^{(2)} = D \Omega^{(1)} + \Omega^{(1)\dagger} D \quad (6.15)$$
$$D^{(3)} = \Omega^{(1)\dagger} D \Omega^{(1)} + \Omega^{(2)\dagger} D + D \Omega^{(2)}. \quad (6.16)$$

To construct the wave operators $\Omega$ from Eq. (3.19) we will consider the perturbation

$$V = H_{cf} + V'$$

where the ansatz $\sum_{ip} r^i A_{ip} C_p^{(j)}$ for the crystal field Hamiltonian is applied and $V'$ denotes additional perturbations. If $V'$ conserves parity, then a non-vanishing effective dipole operator must contain at least one interaction with the odd part of the crystal field.

The Goldstone diagrams of $D^{(2)}$ are shown in Fig. 6.5. The diagrams $(a)$ and $(b)$ correspond to $D \Omega_{cf}^{(1)}$ and $(c)$ and $(d)$ to $\Omega^{(1)\dagger} D$. It can also be seen that $(a)$ and $(c)$ represent the interaction of an excitation $nf^{N-1}n'l'$ with $nf^N$, which is the mechanism described by the original Judd-Ofelt theory. Diagrams $(b)$ and $(d)$ represent an excitation of a core electron to the open $f$-shell. In algebraic form the second order diagrams can be written...
\[ D \Omega_{cf}^{(1)} = \sum_{mn} a_m^\dagger a_n \left[ \sum_{r \neq 4f} \langle m | d | r \rangle \langle r | h_{cf} | n \rangle \epsilon_{4f} - \epsilon_r + \sum_a \langle m | h_{cf} | a \rangle \langle a | d | n \rangle \epsilon_{4f} - \epsilon_a \right] \] (6.17)

\[ \Omega_{cf}^{(1)\dagger} D = \sum_{mn} a_m^\dagger a_n \left[ \sum_{r \neq 4f} \langle m | h_{cf} | r \rangle \langle r | d | n \rangle \epsilon_{4f} - \epsilon_r + \sum_a \langle m | d | a \rangle \langle a | h_{cf} | n \rangle \epsilon_{4f} - \epsilon_a \right] \] (6.18)

Figure 6.5: First order contributions to $\mathcal{D}$

Following the convention that $a, b, ...$ denotes core-, $r, s, ...$ virtual- and $m, n, ...$ open-shell orbitals. By applying the JLV4-theorem to the angular diagrams obtained from these, the contribution to the intensity parameters $A_{lp}^{t}$ can be derived. For the diagrams $(a) + (c)$ we have

\[ \Delta A_{lp}^{t} = -2 \sum_{l'_{fl'}} [t_{l'}^* l_{l_{fl'}}^{t} ] \left( \Omega_{lp} \right) \left( \Xi_{t, \lambda} A_{lp} \right) \] (6.19)

which was to be expected from the beginning, since this contribution to $\Omega_{lp}$ is

\[ \Omega_{lp} = |\lambda| \sum_{t_{lp}} \frac{|\Xi(t, \lambda) A_{lp}|^2}{[t]_{lj}}. \]

Since the diagrams $(b)$ and $(d)$ have the same angular structure as $(a)$ and $(c)$, they modify the $A_{lp}^{t}$ in a similar way as Eq. (6.19); the only difference being that the summation instead is taken over the occupied $(n'l')$.

Turning the attention to the third order effective dipole operator, and limiting the discussion to diagrams having at most one interaction with the crystal field we have

\[ \mathcal{D}^{(3)} = \Omega_{cf}^{(1)\dagger} D \Omega_{cf}^{(1)} + \Omega_{cf}^{(1)\dagger} D \Omega_{cf}^{(1)} + \Omega_{cf}^{(2)\dagger} D + \Omega_{cf}^{(2)\dagger} D \] (6.20)
which lead to a huge amount of zero-, one- and two-body diagrams. The zero-body diagrams only contribute in the uninteresting case of \( i = f \) in Eq. (6.13), and are therefore discarded. The remaining operators can, if \( V' \) is spin-independent, be recoupled to give contributions to the parameters \( A_{tp}^k \) and \( A_{tp}^{(k,k)\lambda} \) of Eqs. (6.10) and (6.12), respectively, see Paper V.

Besides the angular structure of the diagrams, the radial parts are also of great interest. If the perturbation \( V' \) is chosen as the electrostatic interaction \( r^{-1} \), the radial parts of the diagrams of \( D^{(3)} \) that do not contain an interaction with the effective potential can be written as

\[
\sum R^k H^r H^s, \Delta E_1 \Delta E_2,
\]

where \( H^r(a,b) = \int P_a P_r r dr \). The evaluation of such terms can be done, as demonstrated by Lindgren and Morrison [2], by introducing certain single- and pair-functions which makes the integration and summations straightforward. This can be illustrated by considering the expression

\[
\sum \frac{\rho^k(4f \rightarrow l_r; r)H^r(4f, r)H^s(a, s)}{(\varepsilon_{4f} + \varepsilon_a - \varepsilon_r - \varepsilon_s)(\varepsilon_{4f} - \varepsilon_r)} = \sum \int \rho^k(r_1, r_2) \rho^l(r_2) P_a(r_1) r_1 dr_1 dr_2, \quad (6.21)
\]

where

\[
\rho^l(4f \rightarrow l_r; r) = \sum P_{l_r}(r_2) \frac{H^r(4f, r')}{\varepsilon_{4f} - \varepsilon_{r'}} \quad (6.22)
\]

\[
\rho^k(4f, n_{al} \rightarrow l_{lr}; r_1, r_2) = \sum P_{l_r}(r_1) P_{l_r}(r_2) \frac{R^k(s_r, 4fa)}{\varepsilon_{4f} + \varepsilon_a - \varepsilon_r - \varepsilon_s}. \quad (6.23)
\]

The functions \( \rho^l(4f \rightarrow l_r) \) and \( \rho^k(4f, n_{al} \rightarrow l_{lr}) \) can be obtained by solving two inhomogeneous differential equations, first applied by Sternheimer [67, 68], and later by several authors [69, 70, 120] for energy calculations and introduced into the field of theoretical spectroscopy by Jankowski, Smentek and Sokolowski [121]. The more direct way, which was applied in Paper V, is to use the eigenfunctions and energies of a discretized one-particle Hamiltonian [5]:

\[
\left[ \frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} + u(r) \right] P_{nl} = \varepsilon_{nl} P_{nl}.
\]

By evaluating Eq. (6.21) for a few grid spacings it is then possible to use Richardson extrapolation to obtain the continuous grid result. This procedure is then repeated for all diagrams of Eqs. (6.17), (6.18) and (6.20), in order to evaluate the transition amplitudes of Eq. (6.13).
6.4 Notes on the perturbed functions approach

In Papers II and IV the so-called perturbed functions approach (PFA) were applied for the calculation of polarizabilities and oscillator strengths. The perturbation theory used in this work can be thought of as a one-body theory applied to a many-electron system and thus it is not as general or as straightforward as the MBPT, as will be shown below. Instead of using the CI-like expansion employed in MBPT

\[
\Psi = \left( 1 + \sum_{ar} c_{ra} a_r^\dagger a_a + \sum_{abrs} c_{rab} a_r^\dagger a_s^\dagger a_b a_a + \ldots \right) |\alpha\rangle,
\]

here written for a closed shell system for simplicity, the Slater determinants are constructed from the first order corrections \( \varphi_1 \) to the spin orbitals \( \varphi^0 \) due to a perturbation \( h' \);

\[
|\{ \varphi^0_0 \varphi^0_0 \ldots \varphi^0_g \} \rangle \rightarrow |\{ (\varphi^0_0 + \varphi^1_0) (\varphi^0_0 + \varphi^1_0) \ldots (\varphi^0_g + \varphi^1_g) \} \rangle.
\]

If the perturbation \( h' \) is chosen as \( h' = h_{cf} + h_{so} \), the perturbed functions can to first order be written as

\[
\varphi^1_a = \varphi^1_{a,cf} + \varphi^1_{a,so}.
\]

Provided the modified basis set \( \{ \varphi^0 + \varphi^1 \} \) is orthonormal, the transition amplitude of Eq. (6.13) reduces by use of the Slater-Condon rules to a sum over terms of the kind

\[
\langle \varphi^0_m + \varphi^1_m | D^{(1)}_q | \varphi^0_n + \varphi^1_n \rangle.
\]

It is thus seen that the following terms are of interest;

\[
d_{cf-0} = \langle \varphi^1_{m,cf} D^{(1)}_q | \varphi^0_n \rangle + \langle \varphi^0_m D^{(1)}_q | \varphi^1_{n,cf} \rangle \quad (6.24)
\]

\[
d_{cf-cf} = \langle \varphi^1_{m,cf} D^{(1)}_q | \varphi^1_{n,cf} \rangle \quad (6.25)
\]

\[
d_{cf-so} = \langle \varphi^1_{m,cf} D^{(1)}_q | \varphi^1_{n,so} \rangle + \langle \varphi^1_{m,so} D^{(1)}_q | \varphi^1_{n,cf} \rangle. \quad (6.26)
\]

Here the second order corrections to the spin orbitals which should be added to Eqs. (6.25) and (6.26) are omitted, as they were not studied in Paper IV. Thus the statement (1) in Paper IV should be read with this in mind. Further, Eq. (6.24) is equivalent to diagrams (a) and (c) of Fig. 6.5 which was shown to lead to the JO-expressions. This implies that the approximations made in the JO-theory are here made implicitly. Also, it can be noted that no core excitations are present in Eqs. (6.24), (6.25) and (6.26) and this constitutes an inherent weakness of this approach. Thus, the diagrams (b) and (d) of Fig. 6.5 are not accounted for here, and the only third order diagrams obtained are of the type shown in Fig. 6.6, where \( h_1 \) and \( h_2 \) may denote \( h_{cf} \) and \( h_{so} \).

In conclusion, although this approach seems attractive in the sense that it allows for an intuitive picture of modified spin orbitals, its limitations in comparison with MBPT restricts further developments.
Figure 6.6: Third order diagram for two perturbations.
Mn XAS spectra

In order to study the electronic structure of the technologically important alloy La$_{0.7}$Sr$_{0.3}$MnO$_3$, several XAS spectra of the Mn L edge were recorded and interpreted in terms of atomic theory as standard band structure calculations fail in describing its features, see Paper VII. The relative population of the two possible charge states Mn$^{3+}$ and Mn$^{4+}$ were a priori unknown and therefore both cases were studied. The specific transitions studied for Mn$^{3+}$ and Mn$^{4+}$ were

$$\frac{2p^63d^3}{[21_{10}C_0^4(i)]} \rightarrow \frac{2p^53d^5}{[2S'+1L'J']} \Gamma_i$$

$$\frac{2p^63d^3}{[4F_{3/2,5/2,7/2,9/2}] \Gamma_i} \rightarrow \frac{2p^53d^4}{[2S''+1L''J'']} \Gamma_j$$

were $\Gamma$ denotes a Stark-level as the ions were supposed to be confined in a cubic field whose strength is determined by the parameter 10Dq. The Hamiltonian employed in these energy calculations was chosen as

$$H = \sum_{i<j} \sum_k \frac{\rho_n}{r_{ij}} C^i(i) \cdot C^k(j) + \sum_i \zeta_{nl} l(i) \cdot s(i) + 10Dq \sum_i \left[ \frac{21}{10} C_0^{(4)}(i) + \frac{3}{10} \sqrt{\frac{35}{2}} (C_4^{(4)}(i) + C_4^{(4)}(i)) \right].$$

The Slater and spin-orbit parameters were obtained from the relativistic HF program of Cowan. Also, since it is well known that the electrostatic HF Slater parameters are too large, they were scaled with a factor of 0.8, which is a well-known, although somewhat crude, approach [16, 122].

It should be noted, as it is not entirely obvious in Paper VI, that the energy calculations were actually performed in two steps; Since we neglect the interaction between the two configurations, justified by the large separation in energy, the matrix can be divided into two smaller matrices which can be diagonalized one at a time using a modification of the software Lanthanide, see Paper III.

The dipole transitions were then calculated using

$$I(i \rightarrow f) \propto (E_f - E_i) \sum_{deg(i)} \sum_{k=1}^{deg(i)} \sum_{l=1}^{deg(f)} |\langle \Psi_k | r C_q^{(1)} | \Psi_f \rangle|^2 \frac{e^{-\frac{E_i}{kT}}}{\sum_f e^{-\frac{E_f}{kT}}},$$

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for different values of $10Dq$, see Figure 7.1 for the case of Mn$^{3+}$.

It is interesting to study the splitting of the energies as a function of the spin-orbit parameters $\zeta_{nl}$. Fig. 7.2 (top) shows the most intense transitions for a free Mn$^{4+}$ ion ($10Dq = 0$), originating from the lowest ground state level $^4F_{3/2}$. The middle part of the figure shows how these levels originate from transitions having zero intensity in the limit of vanishing spin-orbit interaction (bottom). The transitions seen in this part of the figure obey the standard selection rules $\Delta L = 0, \pm 1, \Delta S = 0$ as expected in the extreme $LS$-limit. As the spin-orbit interaction is increased, there is a mixing of states with different $L$ and $S$ which make the transitions allowed. It is also seen that the physical origin of the splitting of the two main bands centered at 656 eV and 666 eV is equally due to electron correlation and the spin-orbit interaction.

A comparison of the experimental and theoretical spectra is displayed in Fig. 7.3. The atomic spectrum mimics the experimental quite nicely, while for the LDA and LDA+U spectra the position, width and structure are in disagreement.
Figure 7.2: Energy splitting as a function of the spin-orbit constant $\zeta$ for Mn$^{4+}$.

Figure 7.3: Experimental and theoretical L$_{III}$-edge XAS spectrum of the alloy La$_{0.7}$Sr$_{0.3}$MnO$_3$. 

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Conclusions and some thoughts for the future

During the last five years, I have only started to touch the surface of the vast area of rare-earth physics. This subject covers many different parts of physics, e.g., theoretical atomic physics, crystal field theory, group theory, DFT, molecular dynamics, optical spectroscopy, microwave spectroscopy, IR, NMR, methods for structural determination such as X-ray diffraction etc. From a theoretical point of view, not only a good understanding of the physics and mathematics is required, but also numerical skills and programming abilities, such as the application of optimization techniques and parallelization, are needed.

The physics of $f$-electrons is difficult and there remain many problems that need attention. There is a gap between ab initio calculations and semi-empirical parametrization models. Parameters that are adjusted to experimental measurements can certainly absorb several different physical effects whose relative contributions are difficult to distinguish. Ab initio calculations can be very beneficial for the physical understanding provided that reasonable accuracy can be obtained. There are particularly severe problems with regard to crystal field and electron correlation calculations. These uncertainties presently necessitates a mixed ab initio-parametrization approach which largely has been used in this work.

As the perturbation theory becomes unwieldy at high orders, it would be interesting to return to more manageable approaches such as the configuration interaction method. Algorithms developed by Siegbahn, Roos and others shows good promise in the area of large CI calculations. Numerical basis sets and iterative methods are also interesting. The coupled cluster approach used by Eliav, Kaldor and Ishikawa [12] showed promise in a energy structure calculation of $4f^2$ for a free Pr$^{3+}$. These type of calculations would also be interesting to investigate further. It is, however, difficult to predict their usefulness concerning calculations of reliable $f$-$f$ transition intensities.

The crystal field influencing the rare-earth ion has proved difficult to calculate. There are many physical contributions that ideally should be included in an ab initio study: the electron densities, correlation effects, covalency and overlap, exchange effects, charge transfer, etc. It is empirically found that most of these effects can be absorbed by the crystal field hamiltonian. The correla-
tion crystal field hamiltonian has also been investigated, but usually only gives a minor effect in the crystal field levels. It is worthwhile to mention some interesting crystal field calculations in the literature. For example, in the early studies of Hummler, Fähnle and Richter [86, 87] the DFT method for the calculation of the crystal field parameters was applied. These type of calculations are certainly very interesting.
Some useful relations

Throughout this thesis the abbreviation

\[ [a, b, \ldots] = (2a + 1)(2b + 1) \ldots \]

is made. An irreducible tensor operator \( t_q^{(k)} \) with the \( 2k + 1 \) components \( q = -k, \ldots, k \) is defined through the commutator relations

\[ [j_z, t_q^{(k)}] = q_q^{(k)} \]
\[ [j_\pm, t_q^{(k)}] = (k(k + 1) - q(q + 1))^{1/2} t_q^{(k)} \]

Matrix elements of tensor operators are often simplified by using the Wigner-Eckart in \( \mathbb{R}_3 \):

\[ \langle \gamma jm | t_q^{(k)} | \gamma j' m' \rangle = (-1)^{j - m + k} \langle \gamma | t_q^{(k)} | \gamma \rangle \delta(j''j') \delta(m''m') \]

where \( \langle \gamma | t_q^{(k)} | \gamma \rangle \) is a reduced matrix element. The standard unit tensor operator is defined by

\[ \langle nl | u_q^{(k)} | n'l' \rangle = \delta(n'n) \delta(l'l) \]

and the corresponding unit tensor operator of Judd is

\[ v_q^{(k)} = \sqrt{k} u_q^{(k)} \]

For many-particle wave functions the unit tensor is written as

\[ U_q^{(k)} = \sum_i u_q^{(k)}(i) \]

Two tensor operators of rank \( k_1 \) and \( k_2 \), respectively, can be coupled to form a tensor of rank \( K \) by:

\[ \{ u_q^{(k_1)} u_q^{(k_2)} \}^{(K)}_Q = \sum_{q_1q_2} u_q^{(k_1)}(k_1) u_q^{(k_2)}(k_2) \langle k_1 q_1, k_2 q_2 | K Q \rangle. \]

The scalar product of two tensors of rank \( k \) is related to \( \{ u_q^{(k)} u_q^{(k)} \}^{(0)}_0 \) by

\[ u_q^{(k)} \cdot u_q^{(k)} = \sum_q (-1)^q u_q^{(k)} u_{-q}^{(k)} \]
\[ = (-1)^k [k]^{1/2} \{ u_q^{(k)} u_q^{(k)} \}^{(0)}_0. \]
Three-particle operators

Suppose we have a three-particle operator

\[ K = \sum_{i<j<k} k(i,j,k) \]

and want to evaluate the matrix element \( \langle \alpha|K|\alpha' \rangle \) of two Slater determinants \( |\alpha\rangle \) and \( |\alpha'\rangle \). If we assume that \( |\alpha\rangle = |\{abc...n\}\rangle \) then the following rules apply:

1. \( |\alpha'\rangle = |\alpha\rangle \)
   \[ \langle \alpha|K|\alpha \rangle = \sum_{a<b<c} \langle \{abc\}|k|\{abc\} \rangle \] (B.1)

2. \( |\alpha'\rangle = a_a^\dagger a_a |\alpha\rangle \) and \( r \neq a \)
   \[ \langle \alpha|K|\alpha' \rangle = \sum_{b<c} \langle \{abc\}|k|\{rbc\} \rangle \] (B.2)

3. \( |\alpha'\rangle = a_a^\dagger a_b^\dagger a_c a_d |\alpha\rangle \) where none of \( abrs \) are equal
   \[ \langle \alpha|K|\alpha' \rangle = \sum_c \langle \{abc\}|k|\{rsc\} \rangle \] (B.3)

4. \( |\alpha'\rangle = a_a^\dagger a_a^\dagger a_b^\dagger a_c a_d a_e |\alpha\rangle \) where none of \( abcrst \) are equal
   \[ \langle \alpha|K|\alpha' \rangle = \langle \{abc\}|k|\{rst\} \rangle \] (B.4)

|\alpha'\rangle \) differs from \( |\alpha\rangle \) in more than three spin orbitals
   \[ \langle \alpha|K|\alpha' \rangle = 0 \] (B.5)
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Daniel Åberg, Sundsvall, February 2004
References


A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series *Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology*. (Prior to October, 1993, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science”.)