Erbium in an SiO₂ Crystal

PROJECT WRITTEN

BY

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May 28, 2008

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Abstract

Silicon is practically not represented in optoelectronic applications mainly due to its inability to efficiently emit light due to its indirect bandgap. Silicon can be made into a light emitter however, by doping it with another material. In this respect the rare earth elements, and in particular Erbium, deserve special attention because their properties are weakly dependent on the surrounding environment. The ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition in Erbium lies at around 1.54 μ m which is compatible with the minimum losses of silica based optical fibers. In this work the isolated Erbium ion Er^{3+} is analyzed theoretically to determine the energy levels due to the spin-orbit coupling. The analysis is based on the Hartree-Fock method which is suggested for calculating the change in transition energies due to this potential. It is found that the Hartree-Fock method gives qualitatively correct results for the excited states but that electron correlation effects and the fact that Hartree-Fock is a ground state theory causes the results to be quantitatively unsatisfactory.

Preface

Together with Fortran and Mathematica programs used for calculations this report is the product of the 8th semester project period at Aalborg University, Denmark. It has been written by René Petersen, a nano-physics student at Aalborg University.

Throughout the text vectors are typeset as \boldsymbol{a} , matrices as \hat{A} and operators as \hat{A} . Most of the time matrices are written in uppercase and vectors in lowercase. Atomic units are adopted. In this unit system angular momentum is measured in units of \hbar , length in Bohr radii a_B , masses in electron masses m_e and charge in electron charges e so that all these constants all become equal to one. Also, in this unit system the electrostatic force constant $1/4\pi\epsilon_0$ equals one. Energies in this system are measured in units of Hartrees.

The text begins with an introduction which provides background information and motivation for subsequent chapters. The two chapters "Hartree-Fock Theory" and "Excited States" describe the theory behind the Hartree-Fock method and how the Hartree-Fock calculations can be used to determine energies of excited states. "Influence of the Crystal Potential" describes how the influence of the crystal potential on the energy levels can be calculated. "Implementation & Results" presents the results of the calculations of excited states. The appendices provide additional information on some of the concepts introduced throughout the report and also Mathematica code for calculation of the matrix elements used in the Hartree-Fock method.

René Petersen, May 28, 2008

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Chapter 1

Introduction

1.1 Silicon as a Light Emitter

Today silicon (Si) is used in practically every electronic device. Other semiconductors are available, for example germanium (Ge) or gallium arsenide (GaAs), but Si is used because it remains a semiconductor at higher temperatures than Ge and its native oxide is easily grown in a furnace and forms a better semiconductor/dielectric interface than any other material [1]. In addition, Si is available in large amounts, is easily accessible and is nontoxic as opposed to As which is very toxic.

When it comes to optoelectronic applications Si is hardly represented, first of all, due to its inability to emit light efficiently. This is mainly due to its indirect bandgap and the resulting low probability of radiative recombination. In such applications other more appropriate materials like the direct bandgap semiconductor GaAs are used. Since the Si industry is so well established and since Si is found in almost every electronic device, it is of great interest to be able to use Si for light emitting applications as well. It would be particularly interesting if the emission was at a wavelength of 1.5 μ m as this matches the minimum losses of the silica based fibers used in optical communications.

One way of obtaining light emission from Si is by forming nanostructures of Si. Silicon nanocrystals (Si-nc) and porous Si are examples of such structures. Porous Si can be thought of as Si nanowires and DFT calculations on Si nanowires reveal a direct bandgap as opposed to the indirect bandgap in bulk Si. The calculations also reveal a peak in the imaginary part of the dielectric constant (related to absorption) which is dependent on the diameter of the nanowires [2]. This suggests that the light emission wavelength can be controlled by varying the nanowire diameter.

Another way to achieve light emission from Si is to dope it with another material which has the desired optical properties. In this respect the rare earth element erbium (Er) deserves special attention. Er belongs to the group of lanthanoids which are the elements with atomic numbers between 58 and 71. All the lanthanoids, except for Lutetium, are f-block elements and have a complete $5s^25p^66s^2$ shell and an incomplete 4f shell. The complete shell serves as an efficient screening of the incomplete 4f shell and therefore the properties of the 4f electrons are only weakly dependent on the environment [3]. Thus, when a lanthanoide element is inside another material the energy of intra 4f-shell transitions is almost independent of the host matrix. This is very convenient because the properties of the 4f electrons in a lanthanoide inside the host

matrix then resemble closely the properties of the isolated atom. In order to include the effect of the host matrix one can use perturbation theory.

When Er is located inside another material such as SiO_2 it gives up three of its electrons to the SiO_2 matrix and effectively becomes an Er^{3+} ion. Therefore one has to calculate the properties of this Er ion instead of neutral erbium.

Er is number 68 in the periodic system which means that electrons close to the nucleus move at large velocities which are comparable to the speed of light (due to the large nuclear charge and subsequent large centripetal acceleration of the electrons). This means that the effect of spin-orbit coupling becomes important. The transition between the two lowest spin-orbit levels of Er^{3+} , ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$, occurs at approximately 1.54 μ m (0.81 eV) which is coincident with the minimum losses of silica based fibres [3].

In Fig. 1.1 experimental data of the photoluminescence (PL) of Er and Si-nc in SiO₂ as measured by [4] are shown. The pumping wavelength is 488 nm. The figure shows that for Er in SiO₂ without Si-nc present (dashed line) a peak shows up at about 1.54 μ m. This peak is due to the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition in Er. For Si-nc in SiO₂ without Er present (dotted line) a peak is observed at about 0.85 μ m. This peak is due to the creation of an electron-hole pair in Si-nc and subsequent emission of light upon recombination. The solid line shows PL from SiO₂ in which both Si-nc and Er is present and it is seen that the peak at 1.54 μ m is almost two orders of magnitude larger than for SiO₂ with Er alone. In addition to the increase of the 1.54 μ m peak two more features are observed: the appearance of a peak at about 0.98 μ m and the disappearance of the 1.54 μ m peak indicates that the energy which was responsible for the emission of 0.85 μ m photons is now somehow transferred to Er³⁺ effectively increasing the absorption cross section of Er³⁺. The appearance of the 0.98 μ m peak, which is caused by the ${}^{4}I_{11/2} \rightarrow {}^{4}I_{15/2}$ transition, also supports the idea of energy transfer from Si-nc to the Er ion since more energy is transferred to the Er ion.

In Fig. 1.2 a result from a further investigation of the energy transfer from Si-nc to the Er ion made by [5] is shown. The Er ion concentration is varied between 0 and 0.11 at.% and the Si-nc concentration is held constant at about 5 vol. %. It is seen that the PL(0.8 μ m) decreases and the PL(1.54 μ m) increases when the Er ion concentration is increased. The method of energy transfer is suggested to be as follows: The excitation light is absorbed primarily by Si-nc and electron hole pairs are created in the nanocrystals. A part of the recombination energy of the electron-hole recombination is transferred to the Er ion and the amount transferred increases as the concentration of the Er ion increases [5].

The results shown here show that light emission from SiO_2 can be made possible by doping the material with Er and incorporating Si-nc into the material. This project will focus on the properties of isolated Er^{3+} .

1.2 Purpose of the Project

The focus of this project will be on the optical properties of isolated Er^{3+} . The effect of having Si-nc in the SiO₂ matrix will not be treated. In order to understand the light emission from Er^{3+} it is necessary to calculate the ground state energy and the energy of excited states taking into account spin-orbit coupling. The calculation of ground state energy and of the atomic orbitals will be made by using the Hartree-Fock method. From the calculated atomic orbitals the excited states will be calculated within the Russell-Saunders coupling scheme.



Figure 1.1: Room temperature photoluminescence spectra of Si-nc alone, of Er in the presence of Si-nc and of Er in SiO₂. The excitation pump power and wavelength are 100 mW and 488 nm respectively. The Er concentration is 6.5×10^{20} cm⁻³ [4]

Since the 1.54 μ m emission is due to transitions between two spin-orbit states the effect of spin-orbit has to be included. This can be done by treating it as a perturbation instead of doing the full calculation. Furthermore, a method is suggested for calculating the effect of the SiO₂ host matrix on the optical properties of the Er³⁺ ion.



Figure 1.2: Photoluminescence spectra of SiO₂ films containing nc-Si and Er. The inset is an expansion of the region between 1.46 and 1.61 μm [5].

Chapter 2

Hartree-Fock Theory

2.1 The Hartree-Fock Equations

When dealing with many-body systems such as those of atoms and molecules it becomes impossible to solve the Schrödinger equation (SE) analytically. Only a few problems in quantum mechanics is exactly solvable, for instance the hydrogen atom and the harmonic oscillator. Common to both of these problems is that they both involve a single particle in a potential which is only dependent on the distance to some fixed point. For the hydrogen atom this distance is the distance to the nucleus. This makes the problem to be solved quite simple and most importantly, exactly solvable. For situations involving several interacting particles, for example that of the helium atom, the problem becomes more complicated. Now the potential does not only depend on the distance to the nucleus but also on the distance to the other electron. This complicates the problem considerably and makes it necessary to use approximations in order to solve the problem.

One way of solving the problem is by using the Hartree-Fock (HF) method [6] [7]. In the HF method the idea is to assume that the total wavefunction can be written as a Slater type determinant of the form

$$\Psi(x_1, x_2, \dots, x_N) = \sqrt{\frac{1}{N!}} \begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \dots & \psi_1(x_N) \\ \psi_2(x_1) & \psi_2(x_2) & \dots & \psi_2(x_N) \\ \dots & \dots & \dots & \dots \\ \psi_N(x_1) & \psi_N(x_2) & \dots & \psi_N(x_N) \end{vmatrix}$$
(2.1)

where N is the total number of electrons. The spin-orbitals ψ_i should be chosen to make the expectation value of the Hamiltonian an absolute minimum in accordance with the variational theorem. This theorem states that the true wavefunction of the system is the one which minimizes the expectation value of the Hamiltonian of the system. Intuitively this makes good sense. If a wavefunction is chosen which does not minimize the energy this must be an unstable state because there is no reason why the system should not fall into a state with a lower lying energy. The spin-orbitals which minimize the energy are the HF orbitals. Thus, the idea is to consider a small variation in the total wavefunction and adjust the orbitals until a minimum is found. The condition for minimum is

$$\delta \langle \Psi | \hat{H} | \Psi \rangle = 0 \tag{2.2}$$

The left side of this equation involves the matrix element between two Slater determinants. Operations on Slater determinants are described in App. A. The expectation value of the Hamiltonian is

$$\langle \Psi | \hat{H} | \Psi \rangle = \sum_{i=1}^{N} h'_i + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left(J'_{ij} - K'_{ij} \right)$$
(2.3)

with h'_i , J'_{ij} and K'_{ij} given in App. A. To express the variation in the expectation value each spin orbital ψ is replaced by $\psi + \delta \psi$. By writing out the expressions for h'_i , J'_{ij} and K'_{ij} and keeping only terms linear in the variation the following expression is obtained

$$\delta \langle \Psi | \hat{H} | \Psi \rangle = \sum_{i=1}^{N} \langle \delta \psi_i | \hat{h} | \psi_i \rangle + \sum_{i=1}^{N} \sum_{j=1}^{N} \left[\langle \delta \psi_i \psi_j | \frac{1}{r_{12}} | \psi_i \psi_j \rangle - \langle \delta \psi_i \psi_j | \frac{1}{r_{12}} | \psi_j \psi_i \rangle \right] + \sum_{i=1}^{N} \langle \psi_i | \hat{h} | \delta \psi_i \rangle + \sum_{i=1}^{N} \sum_{j=1}^{N} \left[\langle \psi_i \psi_j | \frac{1}{r_{12}} | \delta \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_j \delta \psi_i \rangle \right]$$

$$(2.4)$$

For this expression to be valid it is a requirement that the spin orbitals are orthogonal and are kept orthogonal during the variation. Thus, the variation in the inner product between ψ_i and ψ_j has to be zero

$$\delta \langle \psi_i | \psi_j \rangle = \langle \delta \psi_i | \psi_j \rangle + \langle \psi_i | \delta \psi_j \rangle = 0 \tag{2.5}$$

The expression Eqn. 2.4 can be rewritten by introducing the Fock operator

$$\hat{F} = \hat{h}' + \sum_{j=1}^{N} \left(\hat{J}'_j - \hat{K}'_j \right)$$
(2.6)

where

$$\hat{J}'_{j}\psi(x_{1}) = \int \psi_{j}(x_{2})^{*}\psi_{j}(x_{2})\frac{1}{r_{12}}dx_{2}\psi(x_{1})$$
(2.7)

$$\hat{K}'_{j}\psi(x_{1}) = \int \psi_{j}(x_{2})^{*}\psi(x_{2})\frac{1}{r_{12}}dx_{2}\psi_{j}(x_{1})$$
(2.8)

These two operators are called the Coulomb and the exchange operators and the prime is meant to indicate that the spin integration has not been done. They describe the Coulomb and exchange interaction between an electron in orbital ψ_i and an electron in orbital ψ , so that when the matrix elements $\langle \psi | \hat{J}'_j | \psi \rangle$ and $\langle \psi | \hat{K}'_j | \psi \rangle$ are formed they give the Coulomb and exchange interaction between an electron in orbital ψ_j and one in orbital ψ respectively. Using the Fock operator Eqn. 2.4 becomes

$$\delta \langle \Psi | \hat{H} | \Psi \rangle = \sum_{i=1}^{N} \left[\langle \delta \psi_i | \hat{F} | \psi_i \rangle + \langle \psi_i | \hat{F} | \delta \psi_i \rangle \right] = 0$$
(2.9)

Considering now a variation of the form

$$\delta\psi_j = c\psi_j^u, \qquad \delta\psi_k = 0 \tag{2.10}$$

where this expression means that all variations other than the j'th are zero. The j'th spin orbital is therefore changed in the direction along ψ_j^u and ψ_j^u belongs to the subspace of "unoccupied" orbitals. Inserting this variation in Eqn. 2.9 gives

$$c^* \left\langle \psi_i^u \right| \hat{F} \left| \psi_i^o \right\rangle + c \left\langle \psi_i^o \right| \hat{F} \left| \psi_i^u \right\rangle = 0 \tag{2.11}$$

$$c^* \langle \psi_i^u | \hat{F} | \psi_i^o \rangle - c \langle \psi_i^o | \hat{F} | \psi_i^u \rangle = 0$$
(2.12)

where the second equation has been obtained by making the substitution $c \rightarrow ic$ and multiplying by *i*. This can be done since *c* is not determined. Adding and subtracting these two equations gives

$$\langle \psi_i^u | \hat{F} | \psi_i^o \rangle = 0 \qquad \langle \psi_i^o | \hat{F} | \psi_i^u \rangle = 0 \tag{2.13}$$

If the ψ 's are chosen to form a complete orthonormal set, the action of the Fock operator on one of the "occupied" orbitals can be expanded in this set so that

$$\hat{F}\psi_i^o = \sum_{k=1}^N \epsilon_{ki}\psi_k^o + \sum_{l=N+1}^\infty \epsilon_{li}\psi_l^u$$
(2.14)

The coefficients in this expansion are given by

$$\epsilon_{mi} = \langle \psi_m^o | \hat{F} | \psi_i^o \rangle \qquad \epsilon_{li} = \langle \psi_l^u | \hat{F} | \psi_j^o \rangle \tag{2.15}$$

From Eqn. 2.13 it can be seen that $\epsilon_{li} = 0$ and thus that Eqn. 2.14 must terminate after the N'th term. In addition to this the matrix ϵ_{ki} can be diagonalized by a unitary transformation so that the following equation in the unknown occupied orbitals ψ_i can be obtained

$$\hat{F}\psi_i = \epsilon_i \psi_i \tag{2.16}$$

If it is assumed that the spin orbitals are eigenfunctions of \hat{s}_z and that the Slater determinant is on the form

$$\Psi(x_1, x_2, ..., x_n) = | \psi_1^+ \psi_2^+ ... \psi_{n-1}^+ \psi_n^+ \psi_{n+1}^- ... \psi_N |$$
(2.17)

so that the n first orbitals are spin up orbitals and the N - n next orbitals are spin down orbitals, the spin integrations in the expressions for the Coulomb and exchange operators can be made and the following expressions obtained

$$\hat{J}'_{i}\psi_{i}(x_{1}) = \hat{J}_{j}\psi_{i}(x_{1}) \qquad \hat{K}'_{i}\psi_{i}(x_{1}) = \delta(m_{si}, m_{sj})\hat{K}_{j}\psi_{i}(x_{1})$$
(2.18)

where the prime has been dropped to indicate that the spin integration has been made. It is seen that $\hat{K}_j \psi_i$ vanish when electron *i* and *j* have opposite spins. This corresponds to the fact that there is no exchange interaction between two electrons of opposite spin. Thus, when the Fock operator defined in Eqn. 2.6 operates on a spin up orbital the exchange operator contributes only for the first *n* terms and when the Fock operator operates on a spin down orbital only the last N - (n + 1) terms contribute to the exchange term. Thus, two equations can be expressed, one in the spin up orbitals and one in the spin down orbitals

$$\hat{F}^{\uparrow}\psi_i = \epsilon_i\psi_i, \qquad i = 1, 2, ..., n \tag{2.19}$$

$$\hat{F}^{\downarrow}\psi_j = \epsilon_j\psi_j, \qquad j = n+1, n+2, ..., N$$
(2.20)

These two equations are the Hartree-Fock equations under spin restrictions. The two Fock operators \hat{F}^{\uparrow} and \hat{F}^{\downarrow} are given by

$$\hat{F}^{\uparrow} = \hat{h} + \sum_{j=1}^{N} \hat{J}_j - \sum_{j=1}^{n} \hat{K}_j$$
(2.21)

$$\hat{F}^{\downarrow} = \hat{h} + \sum_{j=1}^{N} \hat{J}_j - \sum_{j=n+1}^{N} \hat{K}_j$$
(2.22)

where \hat{J}_j is the Coulomb operator which describes the Coulomb interaction between the electron in orbital j and the electron in the orbital on which the operator is operating. \hat{K}_j is the exchange operator which describes the exchange interaction between the two electrons.

When solving the Hartree-Fock equations Eqn. 2.19 and Eqn. 2.20 one does not obtain the energy directly. Instead the eigenvalue ϵ is obtained. The energy can however be obtained easily once the eigenvalue is known

$$E = \frac{1}{2} \sum_{i=1}^{N} \left(\epsilon_i + \langle \psi_i | \hat{h} | \psi_i \rangle \right)$$
(2.23)

The goal in the Hartree-Fock method is to obtain all the spin orbitals ψ_i and this can be done by solving the eigenvalue problems Eqn. 2.19 and Eqn. 2.20. The problem is complicated by the fact the unknown spin orbitals have to be known in order to construct the Fock operator. Therefore the solution has to be found by an iterative process. The idea is to start with a reasonable guess for the spin orbitals, construct the Fock operator and then solve the eigenvalue equations in order to obtain a better guess. This process is continued until convergence is achieved. How this is done in practice is described in the next section.

2.2 Solving the Hartree-Fock Equations

In order to solve the Hartree-Fock equations the spin orbitals are written as atomic hydrogen orbitals with a stretchable radial part . The electrons are filled into hydrogen like orbitals one after one. This could easily mislead one into thinking that the electrons are being distinguished but this is not the case. Also, an electron in for example a 1s orbital does not have the probability distribution of a hydrogenic 1s orbital. The probability distribution of the electrons is determined by the total wavefunction Ψ .

The spin orbitals are written as

$$\psi_{\mu} = \sum_{i} c_{i\mu} \phi_{i\mu}(r, \theta, \phi) \tag{2.24}$$

where

$$\phi_{i\mu}(r,\theta,\phi) = Y_{lm}(\theta,\phi)R_{nl}(r) = Y_{lm}(\theta,\phi)r^l \exp(-b_{i,nl}r^2)$$
(2.25)

and μ is the set of quantum numbers n, l and m. Thus, the radial part of the spin orbitals is expanded in a basis of Gaussian functions. The goal here is to determine the coefficients c_i and this is done by rewriting the problem into a matrix problem. The action of the Fock operator on a particular spin orbital is given by

$$\hat{F}^{\uparrow}\psi_{\mu} = \hat{h}\psi_{\mu} + \sum_{i=1}^{N} \hat{J}_{i}\psi_{\mu} - \sum_{i=1}^{n} \hat{K}_{i}\psi_{\mu} = \epsilon_{\mu}\psi_{\mu}$$
(2.26)

where

$$\hat{h} = -\frac{1}{2}\boldsymbol{\nabla}^2 - \frac{Z}{r} \tag{2.27}$$

is the Hamiltonian of a single electron in the potential field of a nucleus of charge Z in atomic units . Left multiplication by $\phi_{p\mu}$ in Eqn. 2.26 and subsequent integration over all space gives

$$\langle \phi_{p\mu} | \hat{h} | \psi_{\mu} \rangle + \sum_{i=1}^{N} \langle \phi_{p\mu} | \hat{J}_{i} | \psi_{\mu} \rangle - \sum_{i=1}^{n} \langle \phi_{p\mu} | \hat{K}_{i} | \psi_{\mu} \rangle = \epsilon_{\mu} \langle \phi_{p\mu} | \psi_{\mu} \rangle$$
(2.28)

Using Eqn. 2.24 to write out ψ_{μ} gives

$$\sum_{q} c_{q\mu} \langle \phi_{p\mu} | \hat{h} | \phi_{q\mu} \rangle + \sum_{q} \sum_{i=1}^{N} c_{q\mu} \langle \phi_{p\mu} | \hat{J}_{i} | \phi_{q\mu} \rangle - \sum_{q} \sum_{i=1}^{n} c_{q\mu} \langle \phi_{p\mu} | \hat{K}_{i} | \phi_{q\mu} \rangle = \epsilon_{\mu} \sum_{q} c_{q\mu} \langle \phi_{p\mu} | \phi_{q\mu} \rangle \quad (2.29)$$

Introducing now the following matrix elements

$$h^{pq}_{\mu} = \langle \phi_{p\mu} | \, \hat{h} \, | \phi_{q\mu} \rangle \tag{2.30}$$

$$J^{pq}_{\mu} = \sum_{i=1}^{N} \langle \phi_{p\mu} | \hat{J}_i | \phi_{q\mu} \rangle$$
(2.31)

$$K^{pq}_{\mu} = \sum_{i=1}^{n} \langle \phi_{p\mu} | \hat{K}_i | \phi_{q\mu} \rangle \tag{2.32}$$

$$S^{pq}_{\mu} = \langle \phi_{p\mu} | \phi_{q\mu} \rangle \tag{2.33}$$

(2.34)

By inserting these matrix elements Eqn. 2.29 becomes

$$\sum_{q} c_{q\mu} h^{pg}_{\mu} + \sum_{q} c_{q\mu} J^{pq}_{\mu} - \sum_{q} c_{q\mu} K^{pq}_{\mu} = \epsilon_{\mu} \sum_{q} c_{q\mu} S^{pq}_{\mu}$$
(2.35)

Each choice of p gives a new equation. This set of equations can be written in matrix form in the following way

$$\hat{\mathsf{H}}_{\mu} \cdot \boldsymbol{c}_{\mu} = \epsilon_{\mu} \hat{\mathsf{S}}_{\mu} \cdot \boldsymbol{c}_{\mu} \tag{2.36}$$

where $\hat{H}_{\mu} = (\hat{h}_{\mu} + \hat{J}_{\mu} - \hat{K}_{\mu})$. The problem has now been formulated as a generalized eigenvalue problem. Just as in the original Hartree-Fock equations knowledge of the eigenvectors is needed in order to construct the \hat{H} matrix. Therefore the problem has to be solved iteratively.

Since Eqn. 2.36 only determines the eigenvectors to within a phase factor the eigenvectors has to be properly normalized. This is done by requiring that the probability of finding the electron in the respective orbital somewhere in space is unity. This gives the following condition

$$\boldsymbol{c}_{\mu} \cdot \hat{\boldsymbol{S}}_{\mu} \cdot \boldsymbol{c}_{\mu} = 1 \tag{2.37}$$

By introducing this additional condition the eigenvectors are still only determined up to a sign. If subsequent calculations only involve eigenvectors from the same state, for example calculations of transitions within the same shell or transitions between two spin-orbit states, this additional condition is sufficient.

2.3 Calculation of Matrix Elements

In order to construct the \hat{H} matrix the matrix elements have to be calculated. The determination of \hat{h} and \hat{S} matrix elements is straightforward so only the results are given here

$$h_{\mu}^{pq} = -\frac{1}{2} (b_{i,nl} + b_{j,nl})^{-(2l+5)/2} \left[Z(b_{i,nl} + b_{j,nl})^{3/2} \Gamma(l+1) - 2b_{i,nl} b_{j,nl} \Gamma\left(\frac{2l+5}{2}\right) \right]$$
(2.38)

$$S^{pq}_{\mu} = \frac{1}{2} (b_{i,nl} + b_{j,nl})^{-(3+2l)/2} \Gamma \left[\frac{3+2l}{2} \right]$$
(2.39)

The \hat{J} and \hat{K} matrix elements are more complicated because of the $1/r_{12}$ term. The integrals to be evaluated are

$$J^{pq}_{\mu\lambda} = \sum_{i,j} c_{i\lambda}c_{j\lambda} \int r_1^{2l_1} r_2^{2l_2} \exp\left[-(b_{p,n_1l_1} + b_{q,n_1l_1})r_1^2\right] \exp\left[-(b_{i,n_2l_2} + b_{j,n_2l_2})r_2^2\right] \times Y^*_{l_1m_1}(\theta_1,\phi_1)Y_{l_1,m_1}(\theta_1,\phi_1)Y^*_{l_2m_2}(\theta_2,\phi_2)Y_{l_2m_2}(\theta_2,\phi_2)\frac{1}{r_{12}}dv_1dv_2 \quad (2.40)$$

$$K^{pq}_{\mu\lambda} = \sum_{i,j} c_{i\lambda} c_{j\lambda} \int r_1^{l_1+l_2} r_2^{l_1+l_2} \exp\left[-(b_{p,n_1l_1} + b_{j,n_2l_2})r_1^2\right] \exp\left[-(b_{i,n_2l_2} + b_{q,n_1l_1})r_2^2\right] \times Y^*_{l_1m_1}(\theta_1,\phi_1)Y_{l_2m_2}(\theta_1,\phi_1)Y^*_{l_2m_2}(\theta_2,\phi_2)Y_{l_1m_1}(\theta_2,\phi_2)\frac{1}{r_{12}}dv_1dv_2 \quad (2.41)$$

where $J_{\mu\lambda}^{pq} = \langle \phi_{p\mu} | \hat{J} | \phi_{q\mu} \rangle$ and $K_{\mu\lambda}^{pq} = \langle \phi_{p\mu} | \hat{K} | \phi_{q\mu} \rangle$ are Coulomb and exchange matrix elements between an electron in a state μ and one in a state λ . The quantum numbers for the state μ will be referred to as n_1 , l_1 and m_1 and those for λ will be referred to as n_2 , l_2 and m_2 . In order to continue the evaluation of these integrals the reciprocal electron-electron distance $1/r_{12}$ has to be expressed in terms of the integration variables. A convenient way to do this is to use the result that the reciprocal distance can be expressed in terms of spherical harmonics [6] [8]

$$\frac{1}{|\boldsymbol{r_1} - \boldsymbol{r_2}|} = \sum_{l,m} \frac{4\pi}{2l+1} Y_{lm}^*(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2) \frac{r_{<}^l}{r_{>}^{l+1}}$$
(2.42)

where $r_{\leq} = \min(r_1, r_2)$ and $r_{>} = \max(r_1, r_2)$. By using this result in Eqn. 2.40 and Eqn. 2.41 the following two expressions are obtained

$$J_{\mu\lambda}^{pq} = \sum_{i,j} c_{i\lambda} c_{j\lambda} \sum_{l,m} \frac{4\pi}{2l+1} \langle Y_{l_1m_1} | Y_{lm}^* | Y_{l_1m_1} \rangle \langle Y_{l_2m_2} | Y_{lm} | Y_{l_2m_2} \rangle F_l$$
(2.43)

$$K_{\mu\lambda}^{pq} = \sum_{i,j} c_{i\lambda} c_{j\lambda} \sum_{l,m} \frac{4\pi}{2l+1} \langle Y_{l_1m_1} | Y_{lm}^* | Y_{l_2m_2} \rangle \langle Y_{l_2m_2} | Y_{lm} | Y_{l_1m_1} \rangle G_l$$
(2.44)

where F_l and G_l are the radial parts of the matrix elements given by

$$F_{l} = \int_{0}^{\infty} \int_{0}^{\infty} r_{1}^{2l_{1}+2} r_{2}^{2l_{2}+2} \exp\left[-(b_{p,n_{1}l_{1}}+b_{q,n_{1}l_{1}})r_{1}^{2}\right] \exp\left[-(b_{i,n_{2}l_{2}}+b_{j,n_{2}l_{2}})r_{2}^{2}\right] \frac{r_{<}^{l}}{r_{>}^{l+1}} dr_{1} dr_{2}$$

$$(2.45)$$

$$G_{l} = \int_{0}^{\infty} \int_{0}^{\infty} r_{1}^{l_{1}+l_{2}+2} r_{2}^{l_{1}+l_{2}+2} \exp\left[-(b_{p,n_{1}l_{1}}+b_{j,n_{2}l_{2}})r_{1}^{2}\right] \exp\left[-(b_{i,n_{2}l_{2}}+b_{q,n_{1}l_{1}})r_{2}^{2}\right] \frac{r_{<}^{l}}{r_{>}^{l+1}} dr_{1} dr_{2}$$

$$(2.46)$$

The radial integrals are easily evaluated by splitting the integral over for example r_2 into two integrals, one running from 0 to r_1 and another running from r_1 to ∞ . In that way $r_> = r_1$ and $r_< = r_2$ in the first integral and $r_> = r_2$ and $r_< = r_1$ in the other integral. Therefore, generally one obtains

$$\int_{0}^{\infty} \int_{0}^{\infty} r_{1}^{a_{1}} r_{2}^{a_{2}} \exp\left[-b_{1} r_{1}^{2}\right] \exp\left[-b_{2} r_{2}^{2}\right] \frac{r_{<}^{m}}{r_{>}^{m+1}} dr_{1} dr_{2} = \int_{0}^{\infty} r_{1}^{a_{1}} \exp\left[-b_{1} r_{1}^{2}\right] \times \left\{ \int_{0}^{r_{1}} r_{2}^{a_{2}} \exp\left[-b_{2} r_{2}^{2}\right] \frac{r_{<}^{m}}{r_{1}^{m+1}} dr_{2} + \int_{r_{1}}^{\infty} r_{2}^{a_{2}} \exp\left[-b_{2} r_{2}^{2}\right] \frac{r_{1}^{m}}{r_{2}^{m+1}} dr_{2} \right\} dr_{1}$$

$$(2.47)$$

In this way the integrals have been reduced to integrals of the form

$$\int_{A}^{B} r^{a} \exp[-br^{2}] dr \tag{2.48}$$

for which one can find tabulated expressions. In this way all the radial integrals can be evaluated.

The polar integrals in Eqn. 2.43 and Eqn. 2.44 are more complicated as they involve integrals over a product of three spherical harmonics. To perform these integrations the fact that spherical harmonics can be expressed in terms of associated Legendre polynomials in the following way is used

$$Y_{lm}(\theta,\phi) = \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos\theta) e^{im\phi}$$
(2.49)

where P_l^m is an associated Legendre polynomial. The problem is to evaluate the integral of the product of three associated Legendre polynomials. In the following the spherical harmonics will be written without the arguments because they are always functions of θ and ϕ . The associated Legendre polynomials are written as $P_n(x)$ when m = 0 which corresponds to a Legendre

polynomial. In order to evaluate the product of three associated Legendre polynomials the recurrence formula for associated Legendre polynomials can be used

$$(n+1-m)P_{n+1}^m(x) - (2n+1)xP_n^m(x) + (n+m)P_{n-1}^m(x) = 0$$
(2.50)

This relation makes it possible to write the product of two associated Legendre polynomials as a sum of associated Legendre polynomials. Thereby the product of three associated Legendre polynomials can be written as a product of two, and the integral over this product can be evaluated. Consider for example the evaluation of the integral $\langle Y_{10} | Y_{30} | Y_{20} \rangle$. This expression involves the product $P_2(x)P_3(x)$. Since $P_2(x) = \frac{1}{2}(3x^2 - 1)$ this product gives

$$P_2(x)P_3(x) = \frac{1}{2}(3x^2 - 1)P_3(x)$$
(2.51)

An expression for $x^2 P_3(x)$ is needed in order to express the product as a sum. This expression can be obtained by multiplying the recurrence formula Eqn. 2.50 by x and using the recurrence formula in its original form to express the $x P_{n+1}^m$ and $x P_{n-1}^m$ terms to obtain

$$x^{2}P_{n}^{m}(x) = \frac{n-m+1}{2n+1} \left[\frac{n-m+2}{2n+3} P_{n+2}^{m}(x) + \frac{n+m+2}{2n+3} P_{n}^{m}(x) \right] + \frac{n+m}{2n+1} \left[\frac{n-m}{2n-1} P_{n}^{m}(x) + \frac{n+m-1}{2n-1} P_{n-2}^{m}(x) \right]$$
(2.52)

Using this the product Eqn. 2.51 can be evaluated and the result is

$$P_2(x)P_3(x) = \frac{9}{35}P_1(x) + \frac{4}{15}P_3(x) + \frac{10}{21}P_5(x)$$
(2.53)

By using Eqn. 2.49 this sum can be expressed in terms of spherical harmonics as

$$P_2(\cos\theta)P_3(\cos\theta) = \frac{9}{35}\sqrt{\frac{4\pi}{3}}Y_{10} + \frac{4}{15}\sqrt{\frac{4\pi}{7}}Y_{30} + \frac{10}{21}\sqrt{\frac{4\pi}{11}}Y_{50}$$
(2.54)

By using Eqn. 2.49 again

$$Y_{20}Y_{30} = \frac{\sqrt{35}}{4\pi} P_2(\cos\theta) P_3(\cos\theta) = \frac{\sqrt{35}}{4\pi} \left(\frac{9}{35}\sqrt{\frac{4\pi}{3}}Y_{10} + \frac{4}{15}\sqrt{\frac{4\pi}{7}}Y_{30} + \frac{10}{21}\sqrt{\frac{4\pi}{11}}Y_{50}\right) \quad (2.55)$$

The integral $\langle Y_{10} | Y_{30} | Y_{20} \rangle$ can now be evaluated by exploiting the orthonormality of spherical harmonics i.e.

$$\int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} Y_{lm} Y_{l'm'} \sin \theta d\theta d\phi = \delta_{ll'} \delta_{mm'}$$
(2.56)

Only the first term in Eqn. 2.55 contributes, the other terms vanish due to orthogonality. The result is

$$\langle Y_{10} | Y_{30} | Y_{20} \rangle = \sqrt{\frac{27}{140\pi}}$$
 (2.57)

Using this procedure all integrals between three spherical harmonics can be evaluated. For higher order spherical harmonics though, the calculations become very cumbersome because the recurrence formula has to be applied several times. A more general approach for calculating integrals over products of three spherical harmonics is preferred and in this respect Gaunts formula is convenient [8]

$$\langle Y_{l_1m_1} | Y_{l_2m_2} | Y_{l_3m_3} \rangle = (-1)^{m_1} \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \times \begin{pmatrix} l_1 & l_2 & l_3 \\ -m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}$$
(2.58)

where the quantities in parentheses are so called Wigner-3j symbols or just 3j-symbols. The 3j-symbol vanish unless the following conditions are satisfied

$$-m_1 + m_2 + m_3 = 0,$$

$$l_1 + l_2 - l_3 \ge 0, \tag{2.59}$$

$$l_1 - l_2 + l_2 \ge 0 \tag{2.60}$$

$$\begin{array}{c} l_1 & l_2 + l_3 \ge 0, \\ -l_1 + l_2 + l_3 \ge 0, \end{array} \tag{2.60}$$

$$l_1 + l_2 + l_3$$
 is an even integer (2.62)

These conditions are collectively called the triangular conditions and the symbol $\Delta(l_1 l_2 l_3)$ is used to denote that $l_1 l_2 l_3$ fulfill these conditions. General formulas for the 3j-symbols are quite complicated. They can be found in [8] or [9] and is often implemented in mathematics software, for example in Mathematica as ThreeJSymbol.

In App. C Mathematica code for calculating all matrix elements is given along with matrix elements up to $l_1 = l_2 = 2$ for \hat{h} , \hat{S} , \hat{J} and \hat{K} .

Chapter 3

Excited States

3.1 Atomic Term Determination

So far the treatment of atomic energy levels has focused only on the ground state energy. In order to discuss the optical properties of atoms knowledge about the energy levels of the excited states is needed. To determine the excited states one has to find out which atomic term symbols arise from the given configuration. Atomic term symbols are described in App. B. This section has been written using [6].

V^{3+}

As a simple example the terms arising from triply ionized vanadium will be considered. This section on the Va ion only serves the purpose of illustrating the concepts and no further calculations will be done on the Va ion. The ground state electron configuration of V^{3+} is $Ar[3d^2]$ with the two d electrons having spin up [10]. Complete shells do not contribute to the atomic term since the sums of angular momentum and spin projections are zero. Therefore only the outermost electrons, the two d electrons, need to be considered and in the following the notation will show only the configuration of the incomplete shells. The total spin is 1 because the two electrons are spin up electrons. The orbital angular momenta of the two electrons can be combined in the following ways

| m ₁ | 2 | 2 | 2 | 2 | 1 | 1 | 1 | 0 | 0 | -1 |
|----------------|---|---|----|----|---|----|----|----|----|----|
| m_2 | 1 | 0 | -1 | -2 | 0 | -1 | -2 | -1 | -2 | -2 |
| М | 3 | 2 | 1 | 0 | 1 | 0 | -1 | -1 | -2 | -3 |

Table 3.1: The possible combinations of m quantum numbers for two spin up electrons in a d orbital and the resulting total angular momentum projection M.

The possibility $m_1 = m_2$ is not allowed due to the Pauli principle because both electrons would then be in the same state since they are of same spin. By investigation of the table it is seen that two terms arise, namely ³F and ³P. From Hund's rules the ³F term is expected to be lowest in energy. In the following the notation $|^{2S+1}L, M\rangle$ is used to denote the state belonging to the term ^{2S+1}L with total angular momentum projection M. From the table it can be seen that the $|^{3}F, 3\rangle$ state can be constructed in one way only, since only one combination of the electrons gives a state of M = 3, thus

$$|{}^{3}F,3\rangle = |{}^{++}_{21}| \tag{3.1}$$

The $|{}^{3}P, 1\rangle$ state can be constructed as

$$|{}^{3}P,1\rangle = c_{1}|\overset{++}{2}\overset{++}{_{-}}| + c_{2}|\overset{++}{1}\overset{+}{_{0}}|$$
(3.2)

since two possible combinations of the electrons give a state of M = 1. The horizontal bar below 1 means that this m_l is negative, thus

$$\begin{vmatrix} \dot{2} \\ \dot{2} \\ - \end{vmatrix} = \begin{vmatrix} \dot{2} \\ - 1 \end{vmatrix}$$
(3.3)

It is not possible to determine the coefficients c_1 and c_2 from the table above alone. Instead, one exploits the orthonormality of the states. This means that $\langle {}^{3}P, 1 | {}^{3}P, 1 \rangle = 1$ and $\langle {}^{3}P, 1 | {}^{3}F, 1 \rangle = 0$. From the first condition one gets $c_1^2 + c_2^2 = 1$. The second relation involves the state $|{}^{3}F, 1 \rangle$. To determine this state the step down operator is applied to $|{}^{3}F, 3 \rangle$ twice to obtain the $|{}^{3}F, 1 \rangle$ state. For a general angular momentum the action of the step up and step down operators is given by

$$\hat{J}_{+}|J,M\rangle = \sqrt{(J-M)(J+M+1)}|J,M+1\rangle,$$
(3.4)

$$\hat{J}_{-}|J,M\rangle = \sqrt{(J+M)(J-M+1)}|J,M-1\rangle.$$
 (3.5)

For V³⁺ the outermost electrons are d-electrons and therefore J = 2 when operating on the determinants since the determinants represent the outer electrons only. The first operation of the step down operator to $|{}^{3}F, 3\rangle$ gives

$$|{}^{3}F,2\rangle = \frac{1}{\sqrt{6}} \left(\hat{l}_{1-} + \hat{l}_{2-} \right) |{}^{++}_{21}| = \frac{1}{\sqrt{6}} \left(\sqrt{4} |{}^{++}_{11}| + \sqrt{6} |{}^{++}_{20}| \right) = |{}^{++}_{20}|$$
(3.6)

where the last step follows from the fact that any determinant with linearly dependent rows or columns is zero. This result could have been obtained immediately since there is only one state of M = 2 in Tbl. 3.1. Applying the step down operator again

$$|{}^{3}F,1\rangle = \frac{1}{\sqrt{10}} \left(\hat{l}_{1-} + \hat{l}_{2-} \right) |{}^{++}_{20}| = \frac{1}{\sqrt{10}} \left(\sqrt{4} |{}^{++}_{10}| + \sqrt{6} |{}^{++}_{2-}| \right) = \sqrt{\frac{2}{5}} |{}^{++}_{10}| + \sqrt{\frac{3}{5}} |{}^{++}_{2-}|$$
(3.7)

From the orthogonality condition the state $|{}^{3}P, 1\rangle$ can now be obtained. The result is

$$|{}^{3}P,1\rangle = \frac{\sqrt{15}}{5}|{}^{++}_{10}| - \frac{\sqrt{10}}{5}|{}^{++}_{2}|$$
(3.8)

If the two electrons are of opposite spins the combinations where $m_1 = m_2$ are now allowed. This means that in addition to the combinations of Tbl. 3.1 there are 5 more combinations. All the combinations are listed in Tbl. 3.2

| m ₁ | 2 | 2 | 2 | 2 | 2 | 1 | 1 | 1 | 0 | 0 | -1 | 1 | 0 | -1 | -2 |
|----------------|---|---|---|----|----|---|----|----|----|----|----|---|---|----|----|
| m ₂ | 2 | 1 | 0 | -1 | -2 | 0 | -1 | -2 | -1 | -2 | -2 | 1 | 0 | -1 | -2 |
| M | 4 | 3 | 2 | 1 | 0 | 1 | 0 | -1 | -1 | -2 | -3 | 2 | 0 | -2 | -4 |

Table 3.2: The possible combinations of m quantum numbers for two d electrons of opposite spin and the resulting total angular momentum projection M.

These combinations give rise to additional terms namely ¹G, ¹D and ¹S. Only one combination gives a total angular momentum of 4, therefore

$$|{}^{1}G,4\rangle = |{}^{+-}_{22}|$$
 (3.9)

The $|^{1}D, 2\rangle$ can be constructed from two determinants but the weighing of each determinant is not obvious. It can, however, be determined by the orthogonality condition between $|^{1}G, 2\rangle$ and $|^{1}D, 2\rangle$ where $|^{1}G, 2\rangle$ is determined by using the step down operators.

 \mathbf{Er}^{3+}

Triply ionized erbium has 11 electrons in an incomplete f shell. The electron configuration of the Er ion is Xe[4f¹¹] with the configuration of the f-electrons being seven spin up and 4 spin down (see Chp. 5). The problem of determining the atomic terms arising from this configuration is thus more complicated than that of the vanadium ion, but it is eased by the equivalence of electrons and holes. Thus, instead of determining the terms arising from the electrons one can determine the terms arising from the holes. If the three holes are considered to be spin up the terms ⁴I, ⁴G, ⁴F, ⁴D and ⁴S are found. With two spin up and one spin down hole the terms ²P, ²D, ²F, ²G, ²H, ²I, ²K, ²L are obtained.

According to Hund's rules the ${}^{4}I$ term is the ground state since it has maximum spin and maximum L. It is not possible to say anything about the energy of the state of second lowest energy from Hund's rules because these rules apply only to the lowest energy state. Therefore, in principle a calculation of the energy of all atomic terms is needed to determine the order of the terms.

The other states can be determined by the same method which was illustrated for the vanadium ion. Even though Hund's rules do not say anything about which state lies next lowest in energy, one could suspect that the state of next lowest energy is the ⁴G state. By construction of a table of all different combinations of angular momenta for the three holes it is found that the $|{}^4G, 4\rangle$ state is given by

$$|{}^{4}G,4\rangle = c_{1}|{}^{+++}_{321}| + c_{2}|{}^{+++}_{310}|.$$
(3.10)

As for the vanadium ion, the coefficients can be determined by demanding that $\langle {}^{4}G, 4 | {}^{4}G, 4 \rangle = 1$ and $\langle {}^{4}I, 4 | {}^{4}G, 4 \rangle = 0$. The state $| {}^{4}I, 6 \rangle$ is given uniquely by

$$|{}^{4}I,6\rangle = |{}^{+++}_{321}|, \tag{3.11}$$

since only one determinant has a $M_L = 6$. By using the step down operator twice the state $|{}^4I, 4\rangle$ can be determined

$$|{}^{4}I,4\rangle = \sqrt{\frac{5}{11}} |{}^{+++}_{310}| + \sqrt{\frac{6}{11}} |{}^{+++}_{321}|.$$
(3.12)

From the orthonormality condition one gets the following for the $|{}^4G, 4\rangle$ state

$$|{}^{4}G,4\rangle = \sqrt{\frac{5}{11}} |{}^{+++}_{32}| - \sqrt{\frac{6}{11}} |{}^{+++}_{310}|.$$
(3.13)

The $|{}^4F, 3\rangle$ is determined in much the same way, the only difference being that is has to be orthogonal to both $|{}^4G, 3\rangle$ and $|{}^4I, 3\rangle$. Thus, one has to determine these two states and this is again done using the step down operator. The states are found to be

$$|{}^{4}I,3\rangle = \sqrt{\frac{2}{11}}|{}^{+++}_{3}2{}^{+}_{2}| + \sqrt{\frac{8}{11}}|{}^{+++}_{3}| + \sqrt{\frac{1}{11}}|{}^{+++}_{2}|{}^{+++}_{1}|$$
(3.14)

$$|{}^{4}G,3\rangle = \sqrt{\frac{25}{44}} |{}^{+++}_{322}| - \sqrt{\frac{1}{44}} |{}^{+++}_{311}| - \sqrt{\frac{9}{22}} |{}^{+++}_{210}|$$
(3.15)

From the orthonormality condition the $|{}^4F, 3\rangle$ state is obtained as

$$|{}^{4}F,3\rangle = \frac{1}{2}|{}^{+++}_{3}22| - \frac{1}{2}|{}^{++++}_{3}1| + \sqrt{\frac{1}{2}}|{}^{++++}_{2}10|$$
(3.16)

(3.17)

3.2 Energy of Atomic Terms

The atomic terms arising from the configuration of the electrons in the incomplete shells have now been determined. To get the energy of an atomic term the expectation value of the Hamiltonian of that term has to be evaluated. For example, for the $|{}^{3}P, 1\rangle$ state of V^{3+} it is necessary to evaluate

$$E({}^{3}P) = \langle {}^{3}P, 1 | \hat{H} | {}^{3}P, 1 \rangle.$$
(3.18)

To calculate the difference in energy between $|{}^{3}F, 1\rangle$ and $|{}^{3}P, 1\rangle$ it is not necessary to calculate the expectation value of the full Hamiltonian for the following reasons. (1) The h_i 's are independent of M_L and M_S , (2) the interaction between two electrons in complete shells are independent of M_L and M_S and (3) the interaction between one electron in a complete shell and one electron in an incomplete shell is independent of M_L and M_S . Therefore, for calculation of energy differences, one needs only consider interactions within the incomplete shell. This is described in more detail in App. B. The energy of an atomic term is given by (Eqn. B.20)

$$\langle LM_L SM_S; \lambda | \hat{H} | LM_L SM_S, \lambda' \rangle =$$

$$I + \frac{1}{2} \sum_{\alpha} c^*_{\alpha\lambda} c_{\alpha\lambda'} \sum_{\substack{i,j \\ \text{incomplete}}} \left[\langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_j \psi_i \rangle \right] +$$

$$\sum_{\alpha,\beta} c^*_{\alpha\lambda} c_{\beta\lambda'} \left[\langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_j \psi_i \rangle \right]$$

$$(3.19)$$

where I is the part of the energy which stems from the M_L and M_S independent part of the energy, that is, the contribution from complete shells and interaction of incomplete shells with complete shells.

For the $|{}^4G, 4\rangle$ state of the erbium ion one obtains the following expression for the energy

$$E({}^{4}G) = \langle {}^{4}G, 4|\hat{H}|{}^{4}G, 4\rangle = I + \frac{5}{11} |\frac{1}{32} |\frac{1}{r_{12}}| |\frac{1}{32} |\frac{1}{r_{12}}| |\frac{1}{32} |\frac{1}{r_{12}}| |\frac{1}{310}| |\frac{1}{r_{12}}| |\frac{1}{310}| - \frac{2\sqrt{30}}{11} |\frac{1}{32} |\frac{1}{r_{12}}| |\frac{1}{310}| - (3.20)$$

where the notation $|\overset{+++}{321}|\overset{+++}{r_{12}}|\overset{+++}{321}|$ means the matrix element between the two determinants and $E(^4G)$ is the energy of the 4G term. The first two matrix elements in Eqn. 3.20 correspond to the first sum in Eqn. 3.19 and the last matrix element corresponds to the last sum in Eqn. 3.19. The matrix elements between determinants are given by

$$\begin{vmatrix} \dot{3}2 \stackrel{+}{1} \\ \dot{3}2 \stackrel{+}{1} \\ \dot{1} \\ \dot{7}_{12} \end{vmatrix} \begin{vmatrix} \dot{3}+ 1 \\ \dot{7}_{12} \end{vmatrix} \begin{vmatrix} \dot{3}+ 1 \\ \dot{7}_{12} \end{vmatrix} = 3F_0 - \frac{8}{45}F_2 - \frac{37}{363}F_4 - \frac{100}{1089}F_6 \\ \begin{vmatrix} \dot{3}+ 1 \\ \dot{7}_{12} \end{vmatrix} \begin{vmatrix} \dot{1} \\ \dot{7}_{12} \end{vmatrix} \begin{vmatrix} \dot{3}+ 1 \\ \dot{7}_{12} \end{vmatrix} = 3F_0 - \frac{7}{45}F_2 - \frac{35}{363}F_4 - \frac{1457}{14157}F_6 \\ \begin{vmatrix} \dot{3}+ 1 \\ \dot{7}_{12} \end{vmatrix} \begin{vmatrix} \dot{1} \\ \dot{7}_{12} \end{vmatrix} = \frac{\sqrt{2/15}}{4719} (1573F_2 + 390F_4 - 875F_6)$$
(3.21)

In these expressions F_l is a two electron integral given by

$$F_l(n_1l_1, n_2l_2) = \int_0^\infty \int_0^\infty |R_{n_1l_1}(r_1)|^2 |R_{n_2l_2}(r_2)|^2 \frac{r_{<}^l}{r_{>}^{l+1}} r_1^2 r_2^2 dr_1 dr_2$$
(3.22)

$$G_l(n_1l_1, n_2l_2) = \int_0^\infty \int_0^\infty R_{n_1l_1}(r_1) R_{n_2l_2}(r_2) R_{n_2l_2}(r_1) R_{n_1l_1}(r_2) \frac{r_{<}^l}{r_{>}^{l+1}} r_1^2 r_2^2 dr_1 dr_2$$
(3.23)

 F_l is the radial part of a Coulomb integral and G_l is the radial part of an exchange integral. In principle one should use G_l for the exchange integrals involved, but since the electrons considered all lie in the same shell (n = 4, l = 3) and only differ in their m_l quantum number $G_l = F_l$. Also, the $F_l = F_l(n_1l_1, n_2l_2)$ differ only in the value of l since $n_1 = n_2$ and $l_1 = l_2$. At this point it is possible to calculate the energy of the excited state if the radial functions are known. Therefore, by using the radial functions determined from the Hartree-Fock calculation it is possible to determine the excited state energy.

From Eqn. 3.20 and Eqn. 3.21 the energy can be expressed as

$$E({}^{4}G) = I + 3F_{0} - \frac{2}{45}F_{2} - \frac{25}{363}F_{4} - \frac{2350}{14157}F_{6}$$
(3.24)

The energy of the excited state relative to the ground state energy is given by $E({}^{4}I \rightarrow {}^{4}G) = E({}^{4}G) - E({}^{4}I)$. $|{}^{4}I, 6\rangle$ is the ground state of the erbium ion so that the ground state energy is given by

$$E(^{4}I) = \langle ^{4}I, 6|\hat{H}|^{4}I, 6\rangle = I + |\overset{+++}{321}|_{\frac{1}{r_{12}}}|\overset{+++}{321}| = 3F_{0} - \frac{13}{45}F_{2} - \frac{47}{363}F_{4} - \frac{425}{14157}F_{6}$$
(3.25)

and therefore

$$E({}^{4}I \to {}^{4}G) = \frac{11}{45}F_2 + \frac{2}{33}F_4 - \frac{175}{1287}F_6$$
(3.26)

The calculation of the energy of the $|{}^4F,3\rangle$ term is done in the same way. From Eqn. 3.19 one obtains

In this expression one could naively believe that the two determinants in the second term differs in all three spin orbitals, but by interchanging the first two spin orbitals in the left determinant the determinant changes sign so that

$$|\overset{+++}{322}|_{\frac{1}{r_{12}}}|\overset{+++}{210}| = -|\overset{+++}{232}|_{\frac{1}{r_{12}}}|\overset{+++}{210}|$$
(3.28)

and it is seen that these two determinants differ in only two spin orbitals. The matrix elements are given by

$$|\overset{+++}{322}|_{\frac{1}{r_{12}}}|\overset{+++}{322}| = 3F_0 - \frac{1}{9}F_2 - \frac{31}{363}F_4 - \frac{1825}{14157}F_6$$
(3.29)

$$|\overset{+++}{210}|_{\frac{1}{r_{12}}}|\overset{+++}{210}| = 3F_0 - \frac{1}{9}F_2 - \frac{31}{363}F_4 - \frac{1825}{14157}F_6$$
(3.30)

$$|\overset{+++}{31}\overset{+}{_{12}}|\overset{+++}{31}\overset{+}{_{12}}| = 3F_0 - \frac{11}{45}F_2 - \frac{43}{363}F_4 - \frac{775}{14157}F_6$$
(3.31)

$$\begin{vmatrix} +++\\ |322\\ -|\\ r_{12} \end{vmatrix} \begin{vmatrix} +++\\ 210 \end{vmatrix} = -\frac{\sqrt{8}}{45}F_2 - \frac{\sqrt{32}}{363}F_4 + \frac{350\sqrt{2}}{14157}F_6$$
(3.32)

$$\overset{+++}{322} |_{\frac{1}{r_{12}}}|| \overset{+++}{311}| = -\frac{1}{15}F_2 - \frac{2}{121}F_4 + \frac{175}{4719}F_6$$

$$(3.33)$$

$$|\overset{+++}{210}|_{\frac{1}{r_{12}}}|\overset{+++}{311}| = -\frac{\sqrt{2}}{45}F_2 - \frac{\sqrt{8}}{363}F_4 + \frac{175\sqrt{2}}{14157}F_6$$
(3.34)

and the energy of the ${}^4I \rightarrow {}^4F$ transition is then

$$E({}^{4}I \to {}^{4}F) = \frac{7}{45}F_2 + \frac{14}{363}F_4 - \frac{1225}{14157}F_6.$$
(3.35)

3.3 Spin-orbit Coupling

The 1.54 μ m transition in the Er³⁺ ion which is of interest in optical communication, due to the minimum losses in silica fibers at this particular wavelength, is a transition between two spin-orbit states namely ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$. Obviously one has to take spin-orbit coupling into account in order to calculate the energy of this transition.

Spin-orbit coupling is an entirely relativistic effect so that only Dirac theory can give a complete analysis. A pseudo derivation based on classical reasoning can be made though. If an electron is moving with velocity \boldsymbol{v} with respect to the entire atomic configuration, the other electrons and the nucleus are moving with $-\boldsymbol{v}$ when viewed from the rest frame of the electron. These other electrons and the nucleus set up a moving electric field at the point of the electron and associated with this moving electric field is a magnetic field given by

$$\boldsymbol{B} = \frac{1}{c^2} \boldsymbol{E} \times \boldsymbol{v} \tag{3.36}$$

In electrostatics the electric field is given by $\boldsymbol{E} = -\boldsymbol{\nabla}\phi = \frac{1}{e}\boldsymbol{\nabla}V$ so that

$$\boldsymbol{B} = \frac{1}{ec^2} \boldsymbol{\nabla} V \times \boldsymbol{v} = \frac{1}{em_e c^2} \boldsymbol{\nabla} V \times \boldsymbol{p}$$
(3.37)

If the potential is assumed to be spherically symmetric the θ and ϕ derivatives in the gradient operator vanish and only the radial derivative contributes

$$\boldsymbol{B} = \frac{1}{em_e c^2} \frac{\partial V}{\partial r} \frac{\boldsymbol{r}}{r} \times \boldsymbol{p} = \frac{1}{em_e c^2} \frac{1}{r} \frac{\partial V}{\partial r} \boldsymbol{l}$$
(3.38)

where l is the orbital angular momentum of the one electron considered. This electron interacts with the magnetic field through its spin magnetic moment which is given by

$$\boldsymbol{\mu}_s = -\frac{2\mu_B}{\hbar} \, \boldsymbol{s} \tag{3.39}$$

where $\mu_B = e\hbar/2m_e$ is the Bohr magneton. This expression is of course not rigorously true since the spin is in fact an operator with no classical representation. The interaction energy due to the magnetic field set up by the other electrons and the nucleus is

$$H_{\rm SO} = -\boldsymbol{B} \cdot \boldsymbol{\mu}_s = \frac{1}{c^2 m_e^2 r} \frac{\partial V}{\partial r} \boldsymbol{l} \cdot \boldsymbol{s}$$
(3.40)

where s is the spin of the considered electron. This result is not entirely correct though. If the analysis was made starting from Dirac theory one would have found that this derivation is missing a factor of $\frac{1}{2}$. This extra factor is known as Thomas precession. Thus, the correct result for the spin-orbit interaction is

$$H_{\rm SO} = \frac{1}{2c^2 m_e^2 r} \frac{\partial V}{\partial r} \boldsymbol{l} \cdot \boldsymbol{s}$$
(3.41)

For several electrons the interaction energy becomes

$$H_{\rm SO} = \frac{1}{2c^2 m_e^2 r} \sum_i \frac{\partial V_i}{\partial r} \boldsymbol{l}_i \cdot \boldsymbol{s}_i \tag{3.42}$$

In order to translate this interaction energy into an energy operator the substitutions $l_i \rightarrow \hat{l}_i$ and $s_i \rightarrow \hat{s}_i$ are made. Again, the spin has no classical analog so the translation should not be taken too seriosly since there is no classical representation of \hat{s} . The index on the potential in the above formula is there because every electron does not see the same magnetic field (and the magnetic field stems from the potential). For example an electron in a 1s orbital will see a different potential than an electron in a 2p orbital because each electron does not contribute to the potential at its own position. The spin-orbit operator is seen to be a one electron operator, and therefore matrix elements of this operator between two Slater determinants are nonzero only in two cases: (1) the two determinants differ in exactly one spin orbital (2) the two determinants are the same. In the first case the matrix elements involve only the two differing spin-orbitals lie in the incomplete shell). Also in the second case it can be shown that the matrix element is independent of the complete shell [6] so that only the incomplete shell needs to be considered. If one chooses to start out working in the $m_l m_s$ (uncoupled) representation the matrix elements to be evaluated are

$$H_{\rm SO} = \langle m_{l1} m_{s1} \dots m_{lN} m_{sN}(\alpha) | \hat{H}_{\rm SO} | m_{l1} m_{s1} \dots m_{lN} m_{sN}(\beta) \rangle \tag{3.43}$$

where α and β represent a particular configuration of electrons in the incomplete shell. In evaluating this matrix element integrals of the following type have to be evaluated

$$\int \psi \hat{H}_{\rm SO} \psi' dv = \langle n l m_l m_s | \, \hat{H}_{\rm SO} \, | n l m'_l m'_s \rangle \tag{3.44}$$

where the prime indicates that the $m_l m_s$ configuration of the initial and final states are not necessarily the same. Now, by extracting the radial part of the integral one obtains (remember that $|nlm_sm_s\rangle = R_{nl}Y_{lm} |m_s\rangle = R_{nl} |lm_lm_s\rangle$)

$$\langle nlm_lm_s | \hat{H}_{\rm SO} | nlm'_lm'_s \rangle = \frac{1}{2m_e^2 c^2} \int_0^\infty \frac{\partial V}{\partial r} |R_{nl}|^2 r dr \langle lm_lm_s | \hat{\boldsymbol{l}} \cdot \hat{\boldsymbol{s}} | lm'_lm'_s \rangle$$
$$= \frac{1}{2m_e^2 c^2} \xi_{nl} \langle lm_lm_s | \hat{\boldsymbol{l}} \cdot \hat{\boldsymbol{s}} | lm'_lm'_s \rangle$$
(3.45)

where ξ represents the radial part of the matrix element

$$\xi_{nl} = \int_{0}^{\infty} \frac{\partial V}{\partial r} \left| R_{nl} \right|^2 r dr$$
(3.46)

Thus, from Eqn. 3.45 and the fact that complete shells contribute nothing to the matrix element, so that they may be ignored, the spin-orbit operator is replaced by

$$\hat{H}_{\rm SO}' = \frac{1}{2c^2 m_e^2} \xi_{nl} \sum_i \hat{\boldsymbol{l}} \cdot \hat{\boldsymbol{s}}$$
(3.47)

where the sum now extends only over the electrons of the incomplete shell n, l. It is assumed that ξ_{nl} is the same for all electrons in a shell characterized by n and l, even though there might be small differences because the radial function is in general not the same for spin up and spin down electrons or for electrons of different m_l . The spin-orbit coupling can be calculated by treating it as a perturbation so that the total Hamiltonian is given by

$$\hat{H} = \hat{H}_{\rm HF} + \hat{H}'_{\rm SO} \tag{3.48}$$

where $\hat{H}_{\rm HF}$ is the Hartree-Fock Hamiltonian which was used to calculate the spin-orbitals. The goal is to calculate the matrix elements of $\hat{H}'_{\rm SO}$. For multielectron systems it was found that (App. B) the operators \hat{l}^2 and \hat{l}_z no longer commute with the Hamiltonian, but the total angular momentum operators \hat{L}^2 and \hat{L}_z do. Similarly, when $\hat{H}'_{\rm SO}$ is included in the Hamiltonian the operators \hat{L}_z and \hat{S}_z no longer commute with the Hamiltonian but the combined angular momentum operators $\hat{J}^2 = (\hat{L} + \hat{S})^2$ and $\hat{J}_z = \hat{L}_z + \hat{S}_z$ do. Consider the commutator

$$[\hat{L}_{z}, \, \hat{l}_{i} \cdot \hat{s}_{i}] = \sum_{j} [\hat{l}_{jz}, \, \hat{l}_{ix} \hat{s}_{ix} + \hat{l}_{iy} \hat{s}_{iy} + \hat{l}_{iz} \hat{s}_{iz}] = \sum_{j} [\hat{l}_{jz}, \, \hat{l}_{ix} \hat{s}_{ix}] + \sum_{j} [\hat{l}_{jz}, \, \hat{l}_{iy} \hat{s}_{iy}] + \sum_{j} [\hat{l}_{jz}, \, \hat{l}_{iz} \hat{s}_{iz}]$$
(3.49)

Since the orbital angular momentum commutes with spin angular momentum, $[\hat{l}_i, \hat{s}_j] = 0 \forall i, j$ and since, for a general angular momentum \hat{L} , $[\hat{L}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{L}_k$ where ε_{ijk} is the Levi-Civita symbol and i, j, k is any permutation of x, y and z, the following is obtained

$$\begin{aligned} [\hat{L}_z, \, \hat{\boldsymbol{l}}_i \cdot \hat{\boldsymbol{s}}_i] &= [\hat{l}_{iz}, \, \hat{l}_{ix} \hat{s}_{ix}] + [\hat{l}_{iz}, \, \hat{l}_{iy} \hat{s}_{iy}] \\ &= i\hbar \hat{l}_{iy} \hat{s}_{ix} - i\hbar \hat{l}_{ix} \hat{s}_{iy} \\ &= -i\hbar \left(\hat{\boldsymbol{l}} \times \hat{\boldsymbol{s}} \right) \end{aligned}$$
(3.50)

and it is seen that \hat{L}_z does not commute with $\hat{l} \cdot \hat{s}$. Consider instead the commutator of the combined angular momentum with $\hat{l} \cdot \hat{s}$

$$[\hat{L}_z + \hat{S}_z, \, \hat{l}_i \cdot \hat{s}_i] = [\hat{L}_z, \, \hat{l}_i \cdot \hat{s}_i] + [\hat{S}_z, \, \hat{l}_i \cdot \hat{s}_i]$$
(3.51)

The first commutator on the right side is given by Eqn. 3.50 and the second commutator on the right side can be calculated in the same way as shown above for the first commutator. The result for the second commutator is

$$[\hat{S}_z, \, \hat{l}_i \cdot \hat{s}_i] = i\hbar \left(\hat{l} \times \hat{s} \right), \qquad (3.52)$$

and it is seen that the sum of the two is zero

$$[\hat{L}_z + \hat{S}_z, \, \hat{\boldsymbol{l}}_i \cdot \hat{\boldsymbol{s}}_i] = 0 \tag{3.53}$$

which shows that the combined angular momentum commutes with the operator $\hat{l} \cdot \hat{s}$. Using this result it can be shown that \hat{J}^2 also commutes with $\hat{l} \cdot \hat{s}$. Thus, in the combined representation L, S, J and M_J are good quantum numbers. A state of combined spin and angular momentum is expressed by using the Clebsch-Gordan coefficients

$$|LSJM_J\rangle = \sum_{\substack{M_L, M_S\\M_J = M_L + M_S}} C(LM_L, SM_S; JM_J) |LM_LSM_S\rangle$$
(3.54)

where the $C(LM_L, SM_S; JM_J)$ are the Clebsch-Gordan coefficients and the sum extends only over the M_L and M_S values for which $M_L + M_S = M_J$ (or one could just ignore this constraint since the Clebsch-Gordan coefficients vanish for $M_L + M_S \neq M_J$).

The different spin-orbit states are distinguished by their value of J so that the energy of a particular spin-orbit state is given by

$$E_{\rm SO}(^{2S+1}L_J) = \langle LSJM_J | \hat{H}'_{\rm SO} | LSJM_J \rangle = \sum_{\substack{M'_L, M'_S, M_L, M_S \\ M_J = M'_L + M'_S = M_L + M_S}} C^*(LM'_L, SM'_S; JM_J) \times C(LM_L, SM_S; JM_J) \langle LM'_L SM'_S | \hat{H}'_{\rm SO} | LM_L SM_S \rangle$$
(3.55)

The matrix element on the right hand side can be evaluated by making use of the Wigner-Eckart theorem. Skipping the details of this calculation the following is obtained

$$\langle LSJM_J | \hat{H}'_{SO} | LSJM_J \rangle = \frac{1}{2m_e^2 c^2} \xi_{nl} \sum_i \alpha_i \beta_i \langle LSJM_J | \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} | LSJM_J \rangle$$
(3.56)

where α and β depend only on L and S so that they are constants within the same shell. Motivated by Eqn. 3.56 a new operator can be introduced as

$$\hat{H}_{\rm SO}^{\prime\prime} = \frac{1}{2m_e^2 c^2} \xi_{nl} \gamma_{LS} \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}$$
(3.57)

where

$$\gamma = \sum_{i} \alpha_i \beta_i \tag{3.58}$$

By making use of the operator identity

$$2\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}} = \hat{\boldsymbol{J}}^2 - \hat{\boldsymbol{L}}^2 - \hat{\boldsymbol{S}}^2$$
(3.59)

a simple expression for matrix elements between states in the combined representation $(L, S, J \text{ and } M_J)$ is obtained

$$E_{\rm SO}(^{2S+1}L_J) = \langle LSJM_J | \hat{H}_{\rm SO}'' | LSJM_J \rangle = \frac{\xi_{nl}\gamma_{LS}\hbar}{4m_e^2c^2} \left[J(J+1) - L(L+1) - S(S+1) \right]$$
(3.60)

From this result a simple rule for the separation of two states J and J-1 belonging to the same L, S can be derived

$$E_{\rm SO}(^{2S+1}L_J) - E_{\rm SO}(^{2S+1}L_{J-1}) = \frac{J\xi_{nl}\gamma_{LS}\hbar}{2m_e^2c^2}$$
(3.61)

It can be shown that if S is maximum, i.e. if all $m_s = \frac{1}{2}$, the constant γ attains the value

$$\gamma_{LS} = \frac{1}{2S} \qquad (\text{maximum S}) \tag{3.62}$$

For more than half-full shells the following rule is convenient: A sum over states belonging to a particular shell can be split into two as

$$\sum_{\substack{i \\ \text{filled states}}} \alpha_i \beta_i = \left(\sum_{\substack{i \\ \text{whole shell}}} - \sum_{\substack{i \\ \text{empty states}}} \right) \alpha_i \beta_i \tag{3.63}$$

The first summation is zero because it extends over an equal number of positive and negative values and therefore

$$\sum_{\substack{i \\ \text{filled states}}} \alpha_i \beta_i = -\sum_{\substack{i \\ \text{empty shell}}} \alpha_i \beta_i \qquad \text{(more than half-full shells)}$$
(3.64)

Therefore, for a more than half-full shell

$$\gamma_{LS} = -\frac{1}{2S} \qquad \begin{pmatrix} \text{maximum S, more} \\ \text{than half-full shell} \end{pmatrix}$$
(3.65)

For a less than half-full shell γ_{LS} is given by Eqn. 3.62, i.e. without the minus sign. Hence, from Eqn. 3.61 it is seen that for a less than half-full shell higher J corresponds to higher energy since γ_{LS} is positive, whereas for more than half-full shells higher J corresponds to lower energy since γ_{LS} is negative. Combining the equations one obtains, for an incomplete more than half-full shell characterized by n and l and with maximum S, the spin-orbit splitting between two adjacent J levels

$$E_{\rm SO}(^{2S+1}L_J) - E_{\rm SO}(^{2S+1}L_{J-1}) = \frac{-J\xi_{nl}\hbar}{4Sm_e^2c^2}$$
(3.66)

In atomic units \hbar and m_e both equal one and $c = \alpha^{-1} \approx 137.036$, where α is the (dimensionless) fine structure constant, so that this formula becomes

$$E_{\rm SO}(^{2S+1}L_J) - E_{\rm SO}(^{2S+1}L_{J-1}) = \frac{-J\xi_{nl}\alpha^2}{4S}$$
(3.67)

This formula will be used for the calculation of spin-orbit energy levels in Er^{3+} .

Chapter 4

Influence of the Crystal Potential

4.1 Determining the Crystal Potential

When an Er atom is located inside a crystal its properties are modified relative to the isolated Er atom due to the presence of the crystal potential. The crystal potential is the potential setup by the constituent atoms of the crystal. In Er doped SiO_2 each Er atom is surrounded by 6 O atoms [11] and the Cartesian coordinates of these atoms can be calculated to be

$$\begin{aligned} & \boldsymbol{v_1} = [-3, -1, -1] & \boldsymbol{v_2} = [-1, -3, -1] & \boldsymbol{v_3} = [1, 3, -1] \\ & \boldsymbol{v_4} = [3, 1, -1] & \boldsymbol{v_5} = [1, -1, 3] & \boldsymbol{v_6} = [-1, 1, 3] & (4.1) \end{aligned}$$

The additional potential at the position of Er due to the surrounding O atoms is given by

$$V_{\rm CP} = \sum_{i=1}^{6} \frac{1}{|\boldsymbol{r} - \boldsymbol{R}_i|} \tag{4.2}$$

By using Eqn. 2.42 the reciprocal distance can be expressed in terms of spherical harmonics as

$$V_{\rm CP} = \sum_{i=1}^{6} \sum_{l,m} \frac{4\pi}{2l+1} Y_{lm}^* \left(\theta_r, \phi_r\right) Y_{lm} \left(\theta_{R_i}, \phi_{R_i}\right) \frac{r_{<}^l}{r_{>}^{l+1}}$$
(4.3)

where $r_{<} = \min(r, R_i)$ and $r_{>} = \max(r, R_i)$. Since each of the 6 O atoms lie at the same distance of $R = R_i = 4.31 a_B$ from the Er atom, a distance much larger than the extent of the 4f radial function, it is safe to assume that $r_{<} = r$ and $r_{>} = R_i$. The above formula can then be reformulated as

$$V_{\rm CP} = \sum_{m,l} \frac{4\pi}{2l+1} Y_{lm}^*(\theta_r, \phi_r) \frac{r^l}{R^{l+1}} \left[\sum_{i=1}^6 Y_{lm}(\theta_{R_i}, \phi_{R_i}) \right]$$
(4.4)

This expression for the potential can be viewed as a Taylor series of Eqn. 4.3 around r = 0. Since the positions of the O atoms are known in Cartesian coordinates it is easier to rewrite the spherical harmonics into functions of Cartesian coordinates as well. The spherical harmonics can be expressed in terms of Legendre polynomials

$$Y_{lm}(\theta,\phi) = \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos\theta) e^{im\phi}$$
(4.5)

and since

$$\cos \theta = \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

$$e^{i\phi} = \cos\phi + i\sin\phi = \frac{x + iy}{\sqrt{x^2 + y^2}}$$
(4.6)

the spherical harmonics in Cartesian coordinates become

$$Y_{lm}(x,y,z) = \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m \left(\frac{z}{\sqrt{x^2 + y^2 + z^2}}\right) \left(\frac{x+iy}{\sqrt{x^2 + y^2}}\right)^m$$

In Eqn. 4.4 the factor in brackets does not contribute for all m, l values. Up to the fourth power of r the terms in the potential distinguished by their power of r are given by

$$r^{0}: 12\sqrt{\frac{\pi}{11}}Y_{00}^{*}$$

$$r^{1}: \frac{4}{11}\sqrt{\frac{\pi}{33}}Y_{10}^{*}r$$

$$r^{2}: -i\frac{2}{121}\sqrt{\frac{30\pi}{11}}\left(Y_{2-2}^{*}-Y_{22}^{*}\right)r^{2}$$

$$r^{3}: \frac{2}{1331}\sqrt{\frac{\pi}{77}}\left(92Y_{30}^{*}+i9\sqrt{30}\left(Y_{3-2}^{*}-Y_{32}^{*}\right)\right)r^{3}$$

$$r^{4}: \frac{1}{43923}\sqrt{\frac{\pi}{11}}\left(13\sqrt{70}\left(Y_{4-4}^{*}+Y_{44}^{*}\right)+182Y_{40}^{*}+i76\sqrt{10}\left(Y_{4-2}^{*}-Y_{42}^{*}\right)\right)r^{4}$$
(4.7)

where the spherical harmonics above are all functions of θ_r and ϕ_r . Since the potential must of course be real valued for all r, each of the above terms have to be real. At first sight it might seem that the term proportional to r^2 is imaginary, but the difference $Y_{2-2}^* - Y_{22}^*$ is purely imaginary so that the term overall becomes a real quantity. By similar arguments the r^3 and r^4 terms are also real.

4.2 Energy Splitting due to the Crystal Potential

When calculating the energy due to spin-orbit coupling the calculation was done be treating the spin-orbit operator as a perturbation to the total Hamiltonian. The same method can be used to calculate the energy splitting due to the crystal potential. When the crystal potential is introduced the energy levels are no longer degenerate with respect to M_J , the z-projection of J. Thus, all states ${}^4I_{J,M_J}$ with $M_J \in \left\{\frac{15}{2}, \frac{13}{2}, \ldots, \frac{-13}{2}, \frac{-15}{2}\right\}$ has to be determined. The ground state ${}^4I_{15/2,15/2}$ has been determined and is given by

$${}^{4}I_{15/2,15/2} = | {}^{+++}_{321} | \tag{4.8}$$

since there is only one Slater determinant with maximum L, S, J and M_J . To determine the ${}^4I_{15/2,13/2}$ state the step down operator $\hat{J}_{-} = \hat{L}_{-} + \hat{S}_{-}$ is applied once giving

$${}^{4}I_{15/2,13/2} = \sqrt{\frac{1}{15}} \left(\sqrt{12} |\overset{+++}{320}| + |\overset{-++}{321}| + |\overset{+-+}{321}| + |\overset{++-}{321}| \right)$$
(4.9)

Subsequent states are determined in the same way but the calculations are very cumbersome. The ${}^4I_{15/2,11/2}$ state for example, will contain 18 terms and subsequent calculations only get worse.

In order to calculate the energy one has to form matrix elements of the form

$$V_{\rm CP}^{ij} = \langle {}^4I_{15/2,M_{J,i}} | V_{\rm CP} | {}^4I_{15/2,M_{J,j}} \rangle \tag{4.10}$$

but there is no guarantee that this matrix will be diagonal. When calculating the energy of spin-orbit states the combined representation was chosen because $\hat{L} \cdot \hat{S}$ is diagonal in that representation and this greatly simplified the calculations. The relation between the coupled representation $(|LSM_LM_S\rangle)$ and the combined representation $(|LSJM_J\rangle)$ was simply related by the Clebsch-Gordan coefficients. If a representation exists in which $V_{\rm CP}$ is diagonal there is no easy way of reaching it. Instead, one has to setup the full matrix $\hat{V}_{\rm CP}$ and diagonalize this matrix in order to determine the energy eigenvalues.

Chapter 5

Implementation & Results

5.1 Ground State

The method of solving the Hartree-Fock equations has been implemented in a Fortran95 program and in this chapter the results from the calculations are presented. In order to ease the calculations a simplification have been made. All states of same l-quantum number but with different m_l are treated as the same state, and this same state is an average of all m_l states. Mathematically this can be stated as

$$|Y_{lm}\rangle \approx \sqrt{\frac{1}{2l+1}} \sum_{m'=-l}^{l} |Y_{lm'}\rangle \tag{5.1}$$

and the Coulomb and exchange matrix elements Eqn. 2.43 and Eqn. 2.44 becomes

$$J_{\mu\lambda}^{pq} = \sum_{i,j} c_{i\lambda} c_{j\lambda} \sum_{m_2=-l_2}^{l_2} \frac{1}{2l_2+1} \sum_{l,m} \frac{4\pi}{2l+1} \langle Y_{l_1m_1} | Y_{lm}^* | Y_{l_1m_1} \rangle \langle Y_{l_2m_2} | Y_{lm} | Y_{l_2m_2} \rangle F_l \quad (5.2)$$

$$K_{\mu\lambda}^{pq} = \sum_{i,j} c_{i\lambda} c_{j\lambda} \sum_{m_2=-l_2}^{l_2} \frac{1}{2l_2+1} \sum_{l,m} \frac{4\pi}{2l+1} \left\langle Y_{l_1m_1} | Y_{l_m}^* | Y_{l_2m_2} \right\rangle \left\langle Y_{l_2m_2} | Y_{l_m} | Y_{l_1m_1} \right\rangle G_l \quad (5.3)$$

In this way the matrix elements depend only on l_1 , l_2 and m_1 . But now the choice of m_1 does not matter because of the spherical average. The average represents a sum of all the possible orientations of the orbitals with quantum number l and therefore the interaction with another orbital is the same no matter its orientation.

The electrons are filled into atomic orbitals according to the Madelung rule. According to this rule the electrons are filled into orbitals in the order of increasing n + l. For fixed values of n + l orbitals of lower n are filled first.

For the actual calculations the coefficients b in the basis functions have to be known. These coefficients are taken from [12] which provides non-relativistic optimized basis sets for atoms H to Lr.

In the model it is possible to remove specific electrons. In this way ionized states can be treated easily by removing electrons. It is not obvious which electrons should be removed though, therefore different combinations are tried until the one which gives the lowest energy is found. The ground state energy has been calculated for neutral erbium, singly ionized erbium and triply ionized erbium. The results of these calculations are

 $E_0(Er) = -12497.2949\,{\rm Ha}$ $E_0(Er^+) = -12497.1219\,{\rm Ha}$
 $E_0(Er^{3+}) = -12495.6525\,{\rm Ha}$

The ground state electron configuration of Er^+ was found to be Xe[4f¹²6s¹] where the outermost 6s spin down electron has been removed. The ground state configuration of Er^{3+} was found to be Xe[4f¹¹] where the 6s spin down and spin up electrons and a 4f spin down electron are removed. The ionized states lie at a higher energy than the neutral state as expected. It is peculiar that it is removal of the 6s electrons instead of the 4f electrons which gives the lowest energy for the ionized states. A possible explanation is that the 4f shield is nearly a closed shell so that electrons in this shell have to give up exchange interaction with many other electrons. The ionization potential of neutral erbium is given by the difference in energy between the singly ionized state and the neutral state. For neutral erbium the calculated ionization potential is found to be 0.173 Ha. The experimental value is 0.224 Ha [10]. The large difference might be due to the effect of spin-orbit coupling which has not been included so far. The spherical averaging could also be the cause of the discrepancy.

In Fig. 5.1 the radial eigenfunctions are plotted for the 6s and 4f electrons in erbium and in Fig. 5.2 the 5s, 4s, 5p and 4f radial eigenfunctions are plotted for triply ionized erbium. In all the graphs the x-scale is logarithmic. Only for the f-electrons is there a noticeable difference between spin up and spin down electrons. For the p-electrons in Er^{3+} there is a small difference. The f-electrons are very localized at about $0.3a_B$ whereas the 5s and 5p electrons are not localized and their radial function has a peak at between 0.8 and 2.0 a_B . This is the origin of the efficient screening of the f-electrons and the reason that the intra f-shell transitions are not very dependent on the environment.



Figure 5.1: The radial function for the spin up and spin down 6s and 4f states in neutral erbium. The x-scale is logarithmic.

From the calculated orbitals the electron density can be determined. The probability density of an electron in a particular spin orbital μ is given by $|\psi_{\mu}(r,\theta,\phi)|^2$ where μ is a combination



Figure 5.2: The radial function for a spin up and spin down 5s, 4s, 5p and 4f state in triply ionized erbium. The x-scale is logarithmic

of quantum numbers n, l, m_l and m_s . The electron density at some point is the sum of the contribution from every spin orbital

$$\rho(r,\theta,\phi) = \sum_{\mu} |\psi_{\mu}(r,\theta,\phi)|^2 = \sum_{\mu} |R_{nl}(r)|^2 |Y_{lm}(\theta,\phi)|^2.$$
(5.4)

By multiplying r^2 and integrating over the polar angles θ and ϕ the radial distribution function is obtained. The radial distribution function gives the probability per unit length that an electron is found at a distance r from the nucleus. In Fig. 5.3 the radial distribution function is plotted for the Er^{3+} ion in its ground state.

5.2 Excited States

For calculating the energy of the ${}^{4}G$ and the ${}^{4}F$ states in the Er ion relative to the ground state energy the expressions Eqn. 3.35 and Eqn. 3.26 are used. The radial integrals F_{l} are calculated using the radial part of the orbitals obtained in the Hartree-Fock calculation. The F_{l} integrals are thus given by



Figure 5.3: The radial distribution function for Er^{3+} in its ground state.

$$F_{l} = F_{l}(l'n', l'n') = \sum_{ijkm} c_{i}c_{j}c_{k}c_{m} \int_{0}^{\infty} \int_{0}^{\infty} r_{1}^{2l'+2}r_{2}^{2l'+2} \exp\left[-(b_{i}+b_{j})r_{1}^{2}\right] \exp\left[-(b_{k}+b_{m})r_{2}^{2}\right] \frac{r_{<}^{l}}{r_{>}^{l+1}} dr_{1}dr_{2} \quad (5.5)$$

where l' is the angular momentum quantum number of the electrons so that l' = 3 for the energy states studied here, c_i are the calculated eigenvectors for the (n = 4, l = 3) states and b_i are the basis for the f-electrons in Er. Since the transitions ${}^4G \rightarrow {}^4I$ and ${}^4F \rightarrow {}^4I$ are both intra f-shell transitions the initial and final states in the F_l are the same (see the general definition of the F_l , Eqn. 3.22). The results of the calculations are

$$E({}^{4}I \rightarrow {}^{4}G) = 0.139 \text{ Ha} = 3.794 \text{ eV}$$

 $E({}^{4}I \rightarrow {}^{4}F) = 0.089 \text{ Ha} = 2.414 \text{ eV}$

From these results it is seen that the energy of the ${}^{4}F$ term actually lies lower in energy than the ${}^{4}G$ term even though ${}^{4}F$ has lower total angular momentum. The general rule of thumb that the term energy decreases in order of increasing S and L therefore does not hold in this case. The energy of the ${}^{4}G$ transition has been measured to be 3.3 eV [13] and the energy of the ${}^{4}F$ transition has been measured to be 1.88 eV [10]. These measurements show that it is an experimental fact that the ${}^{4}G$ term lies higher in energy than the ${}^{4}F$ term. Thus, the values calculated here are quantitatively not satisfactory, but qualitatively correct as they predict the correct order of the energy terms.

The calculations made here tend to overestimate the transition energy, meaning that the calculated energy of the excited states lie too high. There are at least two possible explanations to this (1) The spin-orbitals used deviates too much from the correct spin-orbitals due to the spherical average (2) The effect of spin-orbit coupling has still not been included. Another and

more fundamental cause of the discrepancy is the limitation of the Hartree-Fock method since not all electron correlation effects are included in the HF method.

5.3 Spin-orbit States

To calculate the spin-orbit energy splitting an expression for the potential is needed in order to determine the constant ξ . This is not a trivial problem because the potential consists of both a nuclear potential, a Hartree potential (the Coulomb potential due the electron-electron repulsion) and an exchange potential

$$\hat{V}(r) = -\frac{Z}{r} + V_H + \hat{V}_X$$
 (5.6)

The exchange potential is a nonlocal potential and therefore not easy to determine. However, since the exchange potential is much smaller than the Hartree potential, it can be ignored as a first approximation. Then only the nuclear potential and the Hartree potential persist. The latter is given by

$$V_H(\boldsymbol{r}) = \int \frac{\rho(\boldsymbol{r'})}{|\boldsymbol{r} - \boldsymbol{r'}|} dv'$$
(5.7)

where $\rho(\mathbf{r})$ is the electron density at the position \mathbf{r} (Eqn. 5.4). In the derivation of the spinorbit operator \hat{H}_{SO} spherical symmetry of the potential was assumed. Therefore the Hartree potential has to be spherically symmetric too and this in turn requires the electron density to be spherically symmetric, i.e., it has to depend only on the distance from the nucleus. If Eqn. 5.4 is integrated over the polar angles one obtains

$$\rho(r) = \frac{1}{4\pi} \sum_{\mu} |R_{nl}(r)|^2 \tag{5.8}$$

Inserting this into the expression for the Hartree potential and using Eqn. 2.42 to express the reciprocal distance r - r' in terms of spherical harmonics

$$V_{H}(\boldsymbol{r}) = \frac{1}{4\pi} \sum_{\mu} \sum_{l'm'} \frac{4\pi}{2l+1} \int |R_{nl}(r')|^2 Y_{l'm'}^*(\theta,\phi) Y_{l'm'}(\theta',\phi') \frac{r_{<}^l}{r_{>}^{l+1}} r'^2 dr' \sin\theta' d\theta' d\phi' \quad (5.9)$$

The integration over the polar angles vanish for l' or m' different from zero, therefore

$$V_H(r) = \sum_{\mu} \int_0^\infty |R_{nl}(r')|^2 \frac{1}{r_{>}} r'^2 dr' = \int_0^\infty D(r') \frac{1}{r_{>}} dr'$$
(5.10)

where D(r) is the radial distribution function which has been calculated and is shown in Fig. 5.3. By splitting the integral into two an expression for the Hartree potential suitable for numerical integration is obtained

$$V_H(r) = \int_0^r \frac{D(r')}{r} dr' + \int_r^\infty \frac{D(r')}{r'} dr'$$
(5.11)

The Hartree potential calculated from this expression is shown in Fig. 5.4. In Eqn. 3.46 however, it is not the Hartree potential which is needed, but its derivative. In principle it is possible to calculate numerically the derivative of the Hartree potential but this involves then two numerical operations, first a numerical integration to determine the Hartree potential and then a numerical differentiation. This is subject to precision errors. Instead the derivative of the Hartree potential is found before the numerical integration and it is given by

$$\frac{dV_H(r)}{dr} = -\frac{1}{r^2} \int_0^r D(r')dr'$$
(5.12)

By integrating this expression numerically the Hartree potential derivative can be found directly and Eqn. 3.46 can be used to determine the constant ξ . The value of ξ is found to be 499.07 Ha. Inserting this value in Eqn. 3.67 the energy of the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition is calculated to be

$$E({}^{4}I_{15/2} \to {}^{4}I_{13/2}) = 0.904 \,\mathrm{eV} \qquad (1.37 \mu\mathrm{m})$$
 (5.13)

The experimentally determined value of this transition is 0.8034 eV (1.54 μ m)[10]. Since the exchange potential was neglected in the expression for the potential it is not surprising that the calculated value lies higher than the experimental one since the exchange potential tends to lower the energy. From DFT the exchange potential is given by

$$V_{\rm X} = \left(\frac{3}{\pi}\rho(r)\right)^{1/3} \tag{5.14}$$

where $\rho(r)$ is the electron density averaged over angles. By including this potential in Eqn. 5.6 it is found that the energy is lowered by an amount of 0.058 eV so that the transition energy when using the DFT exchange potential is

$$E({}^{4}I_{15/2} \to {}^{4}I_{13/2}) = 0.846 \,\mathrm{eV} \qquad (1.47 \,\mu\mathrm{m})$$
 (5.15)

which is closer to the experimental value as expected.



Figure 5.4: The Hartree potential for Er^{3+} .

Chapter 6

Discussion & Conclusion

In this work the Hartree-Fock method has been described and applied to an isolated Er^{3+} ion. The method has been used to calculate ground state energy and spin-orbitals of this particular ion and the spin-orbitals have been used to calculate the energies of excited states using perturbation theory.

The calculated results are in qualitative agreement with experimentally obtained results. The order of the terms is predicted correctly, i.e., the energy of the ${}^{4}F$ term is found to be lower than the energy of the ${}^{4}G$ term, but quantitatively the energies do not agree well. The energy of the ${}^{4}I_{15/2} \rightarrow {}^{4}I_{13/2}$ transition agrees quite well with the experimental value differing only by 12.5% when the exchange potential is ignored. If the DFT exchange potential is included the difference is only 5.4%. This result shows that it is a fair approximation to ignore the exchange potential.

One of the primary reasons for the deviation of calculated energies from experimental values is the Hartree-Fock method itself which does not fully take into account electron correlation. In order to obtain better results the wave function can be expanded in multiple Slater determinants insted of just a single determinant. One could also use DFT instead.

Another problem, which is also related to the Hartree-Fock method itself, is that the method is essentially a ground-state theory. The method is based on the requirement that the variation in the ground state energy with the spin-orbitals is zero. No guarantee about excited states is provided in the Hartree-Fock method.

From this work it can be concluded that it is possible to employ a relatively simple model in order to calculate properties of isolated atoms. For optical applications the results are not very satisfactory though.

Appendix A

Matrix Elements Between Slater Determinants

In this appendix the action of one and two electron operators operating on Slater determinants of the form

$$\Psi = \sqrt{\frac{1}{N!}} \begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \dots & \psi_1(x_N) \\ \psi_2(x_1) & \psi_2(x_2) & \dots & \psi_2(x_N) \\ \dots & \dots & \dots & \dots \\ \psi_N(x_1) & \psi_N(x_2) & \dots & \psi_N(x_N) \end{vmatrix}$$
(A.1)

will be considered and expressions for evaluating the matrix elements between Slater determinants will be given. The orbitals ψ_i are called spin-orbitals because they consist of a spatial part and a spin part. Thus, each spin-orbital is on the form

$$\psi_i(x) = \phi(\mathbf{r}) \begin{cases} \alpha(\varsigma) & \psi_i \text{ is a spin-up orbital} \\ \beta(\varsigma) & \psi_i \text{ is a spin down orbital} \end{cases}$$
(A.2)

They form an orthonormal set so that

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \tag{A.3}$$

The Slater determinant can be rewritten in the form

$$\Psi = \sqrt{\frac{1}{N!}} \sum_{P} (-1)^{P} \psi_1(Px_1) \psi_2(Px_2) \dots \psi_N(Px_N)$$
(A.4)

where P denotes a permutation of the arguments. By writing out the determinant it can be seen that a Slater determinant is exactly such a sum over products of the constituent wavefunctions with permuted arguments. Thus, an operator called an antisymmetrizer can be defined as

$$\hat{A} = \sqrt{\frac{1}{N!}} \sum_{P} (-1)^{P} \hat{P},$$
 (A.5)

so that $\hat{A}\Phi = \Psi$ where $\Phi = \psi_1(x_1)\psi_2(x_2)\dots\psi_N(x_N)$.

Introducing now an operator \hat{B} which is symmetric in all N electrons. The fact that \hat{B} is symmetric means that it does not matter which electron is in which orbital and this implies

$$[\hat{B}, \hat{A}] = 0 \tag{A.6}$$

Consider now the case where \hat{B} is a symmetric sum of one electron operators

$$\hat{B} = \sum_{i} \hat{b}_{i}.$$
(A.7)

Operating on a Slater determinant with this operator gives

$$\hat{B}\Psi = \hat{B}\hat{A}\Phi = \hat{A}\hat{B}\Phi = \hat{A}\sum_{i}\hat{b}_{i}\Phi$$
(A.8)

In the special case that each ψ_i is an eigenfunction of \hat{b}_i so that $\hat{b}_i\psi_i = b_i\psi_i$, the right hand side becomes

$$\hat{A}\sum_{i}\hat{b}_{i}\Phi = (b_{1}+b_{2}+\ldots+b_{N})\hat{A}\Phi = B\Psi,$$
 (A.9)

where $B = \sum b_i$ is the sum of all the individual eigenvalues. This result implies that if the constituent orbitals are eigenfunctions of for example \hat{l}^2 and \hat{l}_z with eigenvalue l and m_l respectively, the Slater determinant will be an eigenfunction of $\hat{L}^2 = \sum \hat{l}_i^2$ and $\hat{L}_z = \sum \hat{l}_i$ with eigenvalues L and M_L .

Turning now to the evaluation of matrix elements between two different Slater determinants. The purpose is to find expressions for evaluating matrix elements of the form

$$F_{\Psi\Psi'} = \langle \Psi | \hat{F} | \Psi' \rangle. \tag{A.10}$$

where \hat{F} is either a sum of one electron or two electron operators. Considering first the case where \hat{F} is a sum of one electron operators. In that case the following results are obtained

a. $F_{\Psi\Psi'} = 0$, if Ψ and Ψ' differ in two or more spin orbitals. b. $F_{\Psi\Psi'} = \langle \psi_k | \hat{f} | \psi'_k \rangle$, if Ψ and Ψ' differ in only the k'th spin orbitals. c. $F_{\Psi\Psi'} = \sum_k \langle \psi_k | \hat{f} | \psi_k \rangle$, if $\Psi = \Psi'$, i.e. they do not differ in any spin-orbitals. (A.11) In the case where \hat{F} is a sum of two electron operators the following results are obtained

a.
$$F_{\Psi\Psi'} = 0$$
, if Ψ and Ψ' differ in three or more spin orbitals.
b. $F_{\Psi\Psi'} = \langle \psi_k \psi_l | \hat{f} | \psi'_k \psi'_l \rangle - \langle \psi_k \psi_l | \hat{f} | \psi'_l \psi'_k \rangle$, if Ψ and Ψ' differ in exactly two spin orbitals.
c. $F_{\Psi\Psi'} = \sum_{k \neq l} \left[\langle \psi_k \psi_l | \hat{f} | \psi'_k \psi_l \rangle - \langle \psi_k \psi_l | \hat{f} | \psi_l \psi'_k \rangle \right]$, if Ψ and Ψ' differ in exactly one spin orbital.
d. $F_{\Psi\Psi'} = \frac{1}{2} \sum_{k=1}^{N} \sum_{l=1}^{N} \left[\langle \psi_k \psi_l | \hat{f} | \psi_k \psi_l \rangle - \langle \psi_k \psi_l | \hat{f} | \psi_l \psi_k \rangle \right]$, if $\Psi = \Psi'$, i.e. they do not differ in any spin-orbitals. (A.12)

The notation $\langle \psi_k \psi_l | \hat{f} | \psi'_k \psi'_l \rangle$ is meant to indicate that ψ_k is a function of x_1 and ψ_l is a function of x_2 so that the two terms in square brackets in case d. are not equal.

These results can be used to evaluate the matrix element $\langle \Psi | \hat{H} | \Psi \rangle$ with \hat{H} given by

$$\hat{H} = \sum_{i=1}^{N} \hat{h}_i + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{r_{ij}}$$
(A.13)

$$\hat{h}_i = -\frac{1}{2}\boldsymbol{\nabla}_i^2 - \frac{Z}{r_i} \tag{A.14}$$

where Z is the charge of the nucleus, r_i is the distance from the i'th electron to the nucleus and r_{ij} is the distance between the i'th and j'th electron. The first term in Eqn. A.13 is a sum of one electron operators and the second term is a sum of two electron operators. Thus, by using the results in Eqn. A.11 and Eqn. A.12, the expectation value of the Hamiltonian can be written as

$$\langle \Psi | \hat{H} | \Psi \rangle = \sum_{i=1}^{N} h'_i + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left(J'_{ij} - K'_{ij} \right)$$
(A.15)

where

$$h_{i}^{\prime} = \langle \psi_{i} | \, \hat{h}_{i} \, | \psi_{i} \rangle \,, \tag{A.16}$$

$$J_{ij}' = \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_i \psi_j \rangle, \qquad (A.17)$$

$$K'_{ij} = \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_j \psi_i \rangle, \qquad (A.18)$$

and the prime indicates that the spin integrations have not yet been made. J_{ij} is called the Coulomb integral because it represents the Coulomb interaction between electron *i* and electron *j*. K_{ij} is called the exchange integral and it represents the exchange interaction between

electron i and electron j. As opposed to the Coulomb interaction, the exchange interaction does not have a classical analog. From the expression for K_{ij} it can be seen that if electron i and electron j have different spin K_{ij} vanish. Therefore parallel spins are favoured in accordance with Hund's rules because this will tend to lower the energy. Since the integration variables x_1 and x_2 in the Coulomb and exchange integrals are just dummy variables the Coulomb and exchange matrix elements obey the following symmetry relations

$$J_{ij} = J_{ji}, \qquad K_{ij} = K_{ji}, \qquad J_{ii} = K_{ii}.$$
 (A.19)

Thus, even though the expression Eqn. A.15 seems to include the Coulomb and exchange interaction of one electron with itself, this contribution is zero because $J_{ij} = K_{ij}$.

Appendix B

Atomic Term Symbols

B.1 Determining a Set of Good Quantum Numbers

This section describes the idea of atomic term symbols, it has been written using [6] [7]. The motivation behind atomic term symbols is to determine a set of commuting operators which also commute with the Hamiltonian of the system. In hydrogen the operators \hat{l}^2 , \hat{l}_z , \hat{s}^2 and \hat{s}_z all commute with the Hamiltonian which for hydrogen has the form

$$\hat{H} = -\frac{1}{2}\boldsymbol{\nabla}^2 - \frac{Z}{r} \tag{B.1}$$

The eigenvalues of these operators are said to be good quantum numbers, because they commute with the Hamiltonian. The purpose of the determination of atomic term symbols is to determine another set of good quantum numbers, because the operators listed above will in general not commute with the Hamiltonian of more complex systems. In multielectron atoms the Hamiltonian has the form

$$\hat{H} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \frac{Z}{r_i} + \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{r_{ij}}$$
(B.2)

where r_{ij} is the interelectron distance and the extra term represents the interelectron interaction. This term is the cause of problems. Since the Hamiltonian is independent of spin, the operators \hat{s}_i^2 and \hat{s}_{iz} will still commute with the Hamiltonian. But due to the interelectron term \hat{l}_i^2 and \hat{l}_{iz} will no longer commute with the Hamiltonian (the extra index refers to different electrons). This will now be shown for \hat{l}_{iz} . The angular momentum operator is given by

$$\hat{l}_{iz} = (\boldsymbol{r}_i \times \hat{\boldsymbol{p}}_i)_z = \frac{\hbar}{i} \left(x_i \frac{\partial}{\partial y_i} - y_i \frac{\partial}{\partial x_i} \right)$$
(B.3)

The commutator between \hat{l}_{iz} and $\frac{1}{r_{ii}}$ is

$$[\hat{l}_{iz}, \ \frac{1}{r_{ij}}] = \hat{l}_{iz} \frac{1}{r_{ij}} + \frac{1}{r_{ij}} \hat{l}_{iz} - \frac{1}{r_{ij}} \hat{l}_{iz} = \hat{l}_{iz} \frac{1}{r_{ij}}$$
(B.4)

where the middle term stems from the fact that \hat{l}_{iz} is a differential operator and the commutator also has to operate on whatever stands right of it $(\hat{l}_{iz}(\frac{1}{r_{ij}}\psi) = \hat{l}_{iz}(\frac{1}{r_{ij}})\psi + \frac{1}{r_{ij}}\hat{l}_{iz}(\psi))$. The following results can be easily derived

$$\frac{\partial}{\partial x_i} \frac{1}{r_{ij}} = -\frac{x_i - x_j}{r_{ij}^{3/2}} \quad \text{and} \quad \frac{\partial}{\partial x_j} \frac{1}{r_{ij}} = -\frac{\partial}{\partial x_i} \frac{1}{r_{ij}} \tag{B.5}$$

with similar results for y and z. Using these results the commutator becomes

$$\frac{i}{\hbar} [\hat{l}_{iz}, \frac{1}{r_{ij}}] = \frac{x_i y_i}{r_{ij}^{3/2}} - \frac{x_j y_i}{r_{ij}^{3/2}}$$
(B.6)

Thus, \hat{l}_{iz} does not commute with the Hamiltonian and its eigenvalues do not serve as good quantum numbers. Consider instead the total angular momentum operator.

$$\hat{L}_z = \sum_{i=1}^N \hat{l}_{iz} \tag{B.7}$$

Its commutator with $\frac{1}{r_{ij}}$ is then

$$[\hat{L}_z, \ \frac{1}{r_{ij}}] = \sum_{k=1}^{N} [\hat{l}_{kz}, \ \frac{1}{r_{ij}}]$$
(B.8)

 \hat{l}_{kz} will of course commute with $\frac{1}{r_{ij}}$ when $k \neq i, j$ since the two then refers to different degrees of freedom. Therefore only two terms are left in the sum and these two terms cancel out due to the second of the relations Eqn. B.5. Therefore

$$[\hat{L}_z, \frac{1}{r_{ii}}] = 0$$
 (B.9)

and the eigenvalue of \hat{L}_z is a good quantum number. A similar argument can be made for \hat{L}^2 . Since the Hamiltonian is independent of spin \hat{s}^2 and \hat{s}_z remain good quantum numbers even for multielectron systems. But because the total wavefunction has to be antisymmetric only the total spin comes into play

$$\hat{S} = \sum_{i=1}^{N} \hat{s}_i \tag{B.10}$$

An atomic term symbol is the specification of a state by its total angular momentum, its total spin angular momentum and the projection of the two and it is denoted by

$$|LM_L SM_S\rangle =^{2S+1} L \tag{B.11}$$

B.2 Energy of Atomic Terms

When calculating the energy of atomic terms one have to evaluate matrix elements of the form

$$\langle LM_L SM_S; \lambda | \hat{H} | LM_L SM_S, \lambda' \rangle = H_{LM_L SM_S}$$
(B.12)

where

$$|LM_LSM_S;\lambda\rangle = \sum_{\alpha} c_{\alpha\lambda} |m_{l1}m_{s1},...,m_{lN}m_{sN};\alpha\rangle$$
(B.13)

and λ and λ' indicates two different electron configurations (Slater determinants) of the same L, M_L, S and M_S . The sum over α represents a sum over all the different determinants with the same M_L and M_S . This could for example be $|\stackrel{++}{10}|$ and $2\stackrel{++}{21}|$, where the horizontal bar under 1 means that this m_l is negative ($m_l = -m_l$). The c's are the coefficients which transform from the uncoupled to the coupled representation. For two electrons they are the Clebsch-Gordan coefficients. Since $|LM_LSM_S; \lambda\rangle$ is a sum of determinants it becomes necessary to evaluate the matrix element of \hat{H} between two different Slater determinants. In the following it is assumed that all shells are full except for one and this one shell contains N electrons. From Eqn. B.12 and Eqn. B.13 the matrix elements become

$$\langle LM_LSM_S; \lambda | \hat{H} | LM_LSM_S, \lambda' \rangle = \sum_{\alpha} \sum_{\beta} c^*_{\alpha\lambda} c_{\beta\lambda'} \langle m_{l1}m_{s1}, ..., m_{lN}m_{sN}; \alpha | \hat{H} | m_{l1}m_{s1}, ..., m_{lN}m_{sN}; \beta \rangle \quad (B.14)$$

The Hamiltonian contains two parts. A one electron part, \hat{h} , representing the electron-nucleus interaction and the kinetic energy of the electrons, and a two electron part, $\frac{1}{r_{ij}}$, representing the electron-electron interaction. Considering first the one electron part. According to Eqn. A.11 the matrix element vanishes if the two determinants differ in more than one orbital. If the determinants differ in exactly one orbital the matrix element is $\langle \psi_i | \hat{h} | \psi'_i \rangle$ but since ψ'_i is an eigenfunction of \hat{h} this contribution also vanishes. The only contribution left from the one electron part is the one arising from matrix elements between identical determinants ($\alpha = \beta$) so that

$$\langle LM_LSM_S; \lambda | \hat{h} | LM_LSM_S, \lambda' \rangle = \sum_{\alpha} c^*_{\alpha\lambda} c_{\alpha\lambda'} \langle m_{l1}m_{s1}, ..., m_{lN}m_{sN}; \alpha | \hat{h} | m_{l1}m_{s1}, ..., m_{lN}m_{sN}; \alpha \rangle \quad (B.15)$$

and by using the last of the relations Eqn. A.11 one finds that

$$\langle LM_L SM_S; \lambda | \hat{h} | LM_L SM_S, \lambda' \rangle = \delta_{\lambda\lambda'} \sum_i \langle \psi_i | \hat{h} | \psi_i \rangle$$
(B.16)

where the Kronecker delta follows from the fact that the transformation matrix is unitary and the columns (or rows) of a unitary matrix are orthonormal. The sum can be split into two, one sum over the orbitals of the complete shells and a sum over the orbitals of the incomplete shells

$$\sum_{i} \langle \psi_{i} | \hat{h} | \psi_{i} \rangle = \sum_{\substack{i \\ \text{complete}}} \langle \psi_{i} | \hat{h} | \psi_{i} \rangle + \sum_{\substack{i \\ \text{incomplete}}} \langle \psi_{i} | \hat{h} | \psi_{i} \rangle$$
(B.17)

The first term on the right hand side is the same for all determinants since the determinants only differ in the incomplete shell. The last term on the right hand side is independent of m_l and m_s since \hat{h} is and therefore each term in the last sum contributes the same and the sum can be replaced with a multiplication by N. Therefore

$$\langle LM_L SM_S; \lambda | \hat{h} | LM_L SM_S, \lambda' \rangle = \delta_{\lambda\lambda'} \left(\sum_{\substack{i \\ \text{complete}}} \langle \psi_i | \hat{h} | \psi_i \rangle + N \langle \psi | \hat{h} | \psi \rangle \right).$$
(B.18)

In the term multiplying N the ψ can be any ψ from the incomplete shell, it does not matter which one since \hat{h} is independent of m_l and m_s . This shows that the one electron part of the Hamiltonian is independent of the configuration of the incomplete shell. If one calculates only energy differences between terms the contribution from \hat{h} can be ignored because it is the same for all terms.

For the two electron operator $\frac{1}{r_{12}}$ the expression to be evaluated is

$$\langle LM_L SM_S; \lambda | \frac{1}{r_{12}} | LM_L SM_S, \lambda' \rangle = \sum_{\alpha} \sum_{\beta} c^*_{\alpha\lambda} c_{\beta\lambda'} \langle m_{l1} m_{s1}, ..., m_{lN} m_{sN}; \alpha | \frac{1}{r_{12}} | m_{l1} m_{s1}, ..., m_{lN} m_{sN}; \beta \rangle$$
 (B.19)

By using the relations Eqn. A.12 this expression can be split into contributions arising from (1) two orbitals different between the two determinants, (2) one orbital different between the two determinants and (3) all orbitals the same. It can be shown that case two is zero and thus give no contribution. Case three can be divided into contributions from complete-complete (C-C), incomplete-incomplete (I-I) and complete-incomplete (C-I) electron integrals where for example complete-incomplete means that one electron is in a complete shell and the other is in an incomplete shell. C-C integrals are obviously the same for all determinants since the determinants differ only in the configuration of the incomplete shell. C-I can be shown to be the same for each orbital in the incomplete shell and are thus also independent of the configuration of the incomplete shell. Thus, when calculating energy differences contributions from C-C and

C-I can be ignored. Incomplete-incomplete is not independent of configuration and needs to be considered even when calculating energy differences. Lastly, case one needs consideration. This contribution can be expressed by again using Eqn. A.12. No simplifications can be made but one should note that both orbitals involved in the two electron integrals lie in the incomplete shell (since the two determinants differ only in the incomplete shell).

From all these qualitative considerations and the expression Eqn. B.18 the following expression for the matrix element Eqn. B.12 is obtained

$$\langle LM_L SM_S; \lambda | \hat{H} | LM_L SM_S, \lambda' \rangle = \\ \delta_{\lambda\lambda'} \left(\sum_{\substack{i \mid j \\ \text{complete}}} \langle \psi_i | \hat{h} | \psi_i \rangle + \frac{1}{2} \sum_{\substack{i,j \\ \text{complete}}} \left[\langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_j \psi_i \rangle \right] + \\ N \langle \psi_i | \hat{h} | \psi_i \rangle + N \sum_{\substack{j \\ \text{complete}}} \left[\langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_j \psi_i \rangle \right] \right) + \\ \frac{1}{2} \sum_{\alpha} c^*_{\alpha\lambda} c_{\alpha\lambda'} \sum_{\substack{i,j \\ \text{incomplete}}} \left[\langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_j \psi_i \rangle \right] + \\ \sum_{\alpha,\beta} c^*_{\alpha\lambda} c_{\beta\lambda'} \left[\langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_j \psi_i \rangle \right]$$
(B.20)

The quantity in the parentheses is independent of m_l and m_s and can be ignored when calculating energy differences. The last term arises when the two determinants differ by exactly two determinants. Therefore the sum over α and β is restricted to those determinants which differ in exactly two orbitals.

Appendix C

Mathematica Code - Matrix Elements

This appendix contains the Mathematica code used to calculate the matrix elements used in the Hartree-Fock calculations. S, J and K are overlap, Coulomb and exchange matrix elements respectively. In the code 1 represents angular momenta, ml represents projections of angular momenta, Z is the atomic charge and bi and bj are entries in the Gaussian basis. In the J and K matrix elements q and p are sums of entries into the Gaussian basis (see Eqn. 2.40 and Eqn. 2.41). q and p are used because only the sum of two basis entries is involved in the matrix elements. J and K matrix elements are calculated using the spherical average method to determine a spherically symmetric potential. Only matrix elements up to $l_1 = l_2 = 2$ are shown. They are found in brackets after the Table operation.

A number of assumptions are made in order to obtain simpler expressions for the matrix elements. These assumptions can be seen in the Assuming list in the code. The assumptions are not approximations and by using the Gaussian basis from [12] they will not be violated.

H0 - Matrix Elements

 $\begin{aligned} &\ln[75]:= \operatorname{Clear}[1, g, h, f]; \\ &f[r_{-}] := r^{1} \operatorname{Exp}[-bjr^{2}]; \\ &g[r_{-}] := D[f[r], r]; \\ &h[r_{-}] := D[g[r], r]; \\ &Table[Simplify[\\ & \operatorname{Assuming}[\operatorname{Re}[bi+bj] > 0 \&\& \operatorname{Re}[11] \ge 0 \&\& \operatorname{Re}[12] \ge 0, \operatorname{Integrate}[r^{(1+2)} \operatorname{Exp}[-bir^{2}] \\ &(-h[r]/2 - 2/rg[r]/2 + 1 (1 + 1)/r^{2}/2 f[r] - 2/rf[r]), \{r, 0, \infty\}]]], \{1, 0, 2\}] \end{aligned}$ $\operatorname{Out}[79]= \left\{ \frac{3 \operatorname{bi} bj \sqrt{\pi}}{4 (\operatorname{bi} + \operatorname{bj})^{5/2}} - \frac{Z}{2 (\operatorname{bi} + \operatorname{bj})}, \frac{15 \operatorname{bi} bj \sqrt{\pi}}{8 (\operatorname{bi} + \operatorname{bj})^{7/2}} - \frac{Z}{2 (\operatorname{bi} + \operatorname{bj})^{2}}, \frac{105 \operatorname{bi} bj \sqrt{\pi}}{16 (\operatorname{bi} + \operatorname{bj})^{9/2}} - \frac{\operatorname{bi} Z}{(\operatorname{bi} + \operatorname{bj})^{4}} - \frac{\operatorname{bj} Z}{(\operatorname{bi} + \operatorname{bj})^{4}} \right\} \end{aligned}$

S - Matrix Elements

 $In[74]:= Table[Assuming[Re[bi + bj] > 0 &\& Re[1] \ge 0,$ $Integrate[r^{(21+2)} Exp[-bir^{2}] Exp[-bjr^{2}], \{r, 0, \infty\}]], \{1, 0, 2\}]$ $Out[74]= \left\{ \frac{\sqrt{\pi}}{4 (bi + bj)^{3/2}}, \frac{3\sqrt{\pi}}{8 (bi + bj)^{5/2}}, \frac{15\sqrt{\pi}}{16 (bi + bj)^{7/2}} \right\}$

J - Matrix Elements

$$\begin{split} &\ln[55]= JF = \lambda ssuming \Big[Re[q] > 0 & \& & Re[p] > 0 & \& & Re[1] \ge 0 & \& & Re[11] \ge 0 & \& & Re[12] \ge 0, & Integrate \Big[\\ &r1^{(211+2)} Exp[-pr1^{2}] & \Big[Integrate \Big[r2^{(212+2)} Exp[-qr2^{2}] & \frac{r2^{1}}{r1^{(1+1)}}, & \{r2, 0, r1\} \Big] + \\ &Integrate \Big[r2^{(212+2)} Exp[-qr2^{2}] & \frac{r1^{1}}{r2^{(1+1)}}, & \{r2, r1, \infty\} \Big] \Big), & \{r1, 0, \infty\} \Big] \Big]; \\ &\ln[56]= JG := Integrate \Big[Integrate [SphericalHarmonicY[11, m1, t, p]^{*} SphericalHarmonicY[1, 0, t, p] \\ &SphericalHarmonicY[11, m1, t, p] &Sin[t], & (t, 0, Pi] \Big], & (p, 0, 2Pi] \Big]; \\ &JH := Integrate \Big[Integrate [SphericalHarmonicY[12, m2, t, p]^{*} SphericalHarmonicY[1, 0, t, p] \\ &SphericalHarmonicY[12, m2, t, p] &Sin[t], & (t, 0, Pi] \Big], & (p, 0, 2Pi) \Big]; \\ &\ln[70]= m2 = 0; \\ &Table \Big[Table \Big[Simplify \Big[Sum \Big[Sum \Big[\frac{1}{211+1} & \frac{4Pi}{21+1} & JF * JG * JH, & (1, 0, Max[11, 12]) \Big], & (m1, -11, 11) \Big], \\ &Assumptions \rightarrow Re[p] > 0 & \& Re[q] > 0 & \& Im[q] = 0 & \& Im[p] = 0 \Big], & (11, 0, 2) \Big], & (12, 0, 2) \Big] \\ Out[71]= & \Big\{ \Big\{ \frac{\sqrt{\pi}}{8pq\sqrt{p+q}}, & \frac{\sqrt{\pi} & (3p+2q)}{16p^2q(p+q)^{3/2}}, & \frac{\sqrt{\pi} & (15p^2+20pq+8q^2)}{32p^3q(p+q)^{5/2}} \Big\}, \\ & \Big\{ \frac{\sqrt{\pi} & (8p^2+3q)}{16pq^2(p+q)^{3/2}}, & \frac{3\sqrt{\pi} & (2p^2+5pq+2q^2)}{32p^2q^2(p+q)^{5/2}}, & \frac{3\sqrt{\pi} & (10p^3+35p^2q+28pq^2+8q^3)}{64p^3q^2(p+q)^{7/2}} \Big\}, \\ & \Big\{ \frac{\sqrt{\pi} & (8p^2+20pq+15q^2)}{32pq^2(p+q)^{5/2}}, & \frac{3\sqrt{\pi} & (8p^3+28p^2q+35pq^2+10q^3)}{64p^2q^2(p+q)^{7/2}}, \\ & \Big\{ \frac{\sqrt{\pi} & (8p^4+36p^3q+63p^2q^2+36pq^3+8q^4)}{128p^3q^3(p+q)^{9/2}} \Big\} \Big\} \\ \end{split}$$

K - Matrix Elements

$$\begin{split} \ln[49] = & \text{KF} = \text{Assuming} \left[\text{Re}[q] > 0 & \text{&\& Re}[p] > 0 & \text{&\& Re}[1] \ge 0 & \text{&\& Re}[11] \ge 0 & \text{&\& Re}[12] \ge 0 , \\ & \text{Integrate} \left[r1^{\wedge} (11 + 12 + 2) & \text{Exp}[-q r2^{\wedge} 2] & \frac{r2^{\wedge} 1}{r1^{\wedge} (1 + 1)}, \ \{r2, 0, r1\} \right] + \\ & \text{Integrate} \left[r2^{\wedge} (11 + 12 + 2) & \text{Exp}[-q r2^{\wedge} 2] & \frac{r1^{\wedge} 1}{r2^{\wedge} (1 + 1)}, \ \{r2, r1, \varpi\} \right] \right), \ \{r1, 0, \varpi\} \right] \right]; \\ \ln[50] = & \text{KG} := \text{Integrate} \left[r2^{\wedge} (11 + 12 + 2) & \text{Exp}[-q r2^{\wedge} 2] & \frac{r1^{\wedge} 1}{r2^{\wedge} (1 + 1)}, \ \{r2, r1, \varpi\} \right] \right), \ \{r1, 0, \varpi\} \right] \right]; \\ \ln[50] = & \text{KG} := \text{Integrate} \left[\text{Integrate} \left[\text{SphericalHarmonicY}[11, m1, t, p]^{*} & \text{SphericalHarmonicY}[1, m2 - m1, t, p]^{*} \\ & \text{SphericalHarmonicY}[12, m2, t, p] & \text{Sin}[1], \ \{t, 0, Pi\} \right], \ \{p, 0, 2Pi\} \right]; \\ \ln[72] = & \text{m2} = 0; \\ & \text{Table} \left[\text{Table} \left[\text{Table} \left[\text{Sum} \left[\text{Sum} \left[\frac{1}{211 + 1} & \frac{4Pi}{21 + 1} * \text{KF} * \text{KG} * \text{KG}^{*}, \ \{1, \text{Abs}[11 - 12], 11 + 12\} \right], \ \{m1, -11, 11\} \right], \\ & \text{Assumptions} \rightarrow \text{Re}[p] > 0 & \text{\&\& Re}[q] > 0 & \text{\&\& Im}[q] = 0 & \text{\&\& Im}[p] = 0 \right], \ \{11, 0, 2\} \right], \ \{12, 0, 2\} \right] \\ Out[73] = & \left\{ \left\{ \frac{\sqrt{\pi}}{8 \, p \, q \, \sqrt{p + q}}, \frac{\sqrt{\pi}}{16 \, p \, q \, (p + q)^{3/2}}, \frac{3 \, \sqrt{\pi}}{32 \, p \, q \, (p + q)^{5/2}} \right\}, \\ & \left\{ \frac{3 \, \sqrt{\pi}}{16 \, p \, q \, (p + q)^{3/2}}, \frac{\sqrt{\pi} \left(4 \, p^2 + 23 \, p \, q + 4 \, q^2\right)}{32 \, p^2 \, q^2 \, (p + q)^{5/2}}, \frac{3 \, \sqrt{\pi} \left(8 \, p^4 + 40 \, p^3 \, q + 99 \, p^2 \, q^2 + 40 \, p \, q^3 + 8 \, q^4} \right)}{128 \, p^3 \, q^3 \, (n + q)^{9/2}} \right\} \right\} \end{split}$$

$$\left\{\frac{3\sqrt{\pi}}{32 p q (p+q)^{5/2}}, \frac{\sqrt{\pi} (4 p^2 + 23 p q + 4 q^2)}{64 p^2 q^2 (p+q)^{7/2}}, \frac{3\sqrt{\pi} (8 p^4 + 40 p^3 q + 99 p^2 q^2 + 40 p q^3 + 128 p^3 q^3 (p+q)^{9/2})}{128 p^3 q^3 (p+q)^{9/2}}\right\}$$

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