Theoretical and Experimental Investigation of Atomic Radiative Lifetimes and Hyperfine Structures

Per Jönsson

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Abstract

Atomic radiative lifetimes and hyperfine structures as well as other properties, such as total energy and specific mass shift, have been studied theoretically and experimentally.

Computer programs to calculate hyperfine structure constants from non-relativistic multi-configuration Hartree-Fock (MCHF) and relativistic multi-configuration Dirac-Fock (MCDF) wavefunctions have been written. Using these programs large-scale calculations of hyperfine structures in lithium and sodium have been performed. It is shown, that the MCHF method is able to predict hyperfine structures to an accuracy of a few per mille in lithium, whereas for the more complex sodium atom an accuracy of a few per cent is obtainable. For lithium convergence of the total energy, ionization energy, specific mass shift and hyperfine parameters has been studied with the MCHF method.

Radiative lifetimes and hyperfine structures of excited states in sodium and silver have been experimentally determined using time-resolved laser spectroscopy.

By recording the fluorescence light decay curves following VUV excitation, the radiative lifetimes and hyperfine structures of the $7p \, ^2P$ states in silver were measured.

The delayed-coincidence technique has been used to make very accurate measurements of the radiative lifetimes and hyperfine structures of the lowest $P$ states in sodium and silver.
To my Parents
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List of papers

1. A program for computing magnetic dipole and electric quadrupole hyperfine constants from MCHF wavefunctions.

2. A program for computing magnetic dipole and electric quadrupole hyperfine constants from MCDF wavefunctions.

3. Large multiconfigurational Hartree-Fock calculations on the hyperfine structure constants of the $^7Li \, 2s \, ^2S$ and $2p \, ^2P$ states

4. Convergence studies of atomic properties from variational methods: total energy, ionization energy, specific mass shift, and hyperfine parameters for Li.

5. Multi-configuration Hartree-Fock calculations and time-resolved laser spectroscopy studies of hyperfine structure constants in sodium.

6. Studies on radiative lifetimes in the $4d^{10}ns \, ^2S$ and $4d^{10}nd \, ^2D$ sequences of neutral silver.


8. Time-resolved spectroscopic studies of the $7p \, ^2P$ states of neutral silver following VUV excitation.
Chapter 1

Introduction

Since the foundation of quantum mechanics in the mid twenties, atomic theory has developed rapidly. For simple systems, like helium and lithium, it is now possible to calculate non-relativistic energy levels to almost spectroscopic accuracy [1, 2]. In recent years much theoretical work has been focused on relativistic and quantum electrodynamical (QED) effects in these systems [3].

In parallel with the theoretical development new experimental techniques have emerged, making determination of atomic parameters to an astonishing precision possible.

Although the experimental values and the theoretical predictions are in excellent agreement, this does not mean that atomic physics is a closed subject, where everything basically is known. In the light of the physics history, one would expect that the development on the experimental and theoretical side will bring about new and interesting effects in atoms. One example of this is parity non-conserving effects, where a neutral vector boson $Z^0$ is exchanged between the atomic nucleus and the $s_{1/2}$ and $p_{1/2}$ electrons, causing the atomic state as a whole not to have a well-defined parity. It is therefore possible to test the electro-weak interaction in atomic physics experiments [4]. Another example is the accurate determination of ground state hyperfine splittings of trapped ions, where an accuracy of a few parts in $10^{15}$ can be obtained [5]. If the relativistic electron wavefunction is known, the distribution of the nuclear magnetic moment can be probed, giving important information about nuclear structure [6, 7]. The above effects are very small, and the atomic wavefunction has to be calculated very accurately in order to extract information about the higher-order interactions with the nucleus.

On the other extreme are the complex systems with several open shells, where it so far has been very difficult to make even rough prediction of atomic parameters. With today's supercomputers this situation is slowly hanging, and much work is done to understand these systems [8]. The demand for basic atomic data has increased since the Hubble Space Telescope was launched. The resolution of this instrument is so high that even small effects like isotope shift and hyperfine structure are observed in stellar spectra.

In this thesis much of the work has been concerned with the hyperfine structure. Hyperfine
structure is very sensitive to both electronic correlation and relativistic effects, and its study has given valuable insight into atomic theory. For the ground state of lithium the hyperfine structure has been calculated with the MCHF method to an accuracy where relativistic effects become important, and work is now in progress to make a fully relativistic calculation [9]. For the more complex systems, like sodium and magnesium, hyperfine structures have been calculated to an accuracy within a few per cent from the experimental values.
Chapter 2
Computational methods

An atomic state is described by a wavefunction, $\psi$, which is an eigenfunction to the Hamiltonian

$$H\psi = E\psi \quad (2.1)$$

Here the eigenvalue $E$ can be interpreted as the total energy of the system. For an $N$-electron system the normal starting point is the Hamiltonian, in atomic units

$$H = -\sum_{i=1}^{N}(\frac{1}{2}\nabla_i^2 + \frac{Z}{r_i}) + \sum_{i>j}\frac{1}{r_{ij}} \quad (2.2)$$

Relativistic and higher-order nuclear effects are not included at this stage, but can be treated later as perturbations.

2.1 The MCHF method

In the multi-configuration Hartree-Fock (MCHF) method the atomic state wavefunction, $\Psi$, is expanded in terms of configuration-state functions with the same LS term

$$\Psi = \sum_{i=1}^{m}c_{i}(\gamma_iLS) \quad (2.3)$$

The configuration-state functions, $\Phi(\gamma_iLS)$, are antisymmetrized eigenfunctions to $L^2, L_z, S^2, S_z$ and parity, which can be written as sums of products of spin-orbitals

$$\phi(r, \theta, \varphi, \sigma) = \frac{1}{r}P_{nl}(r)Y_{lm}(\theta, \varphi)\xi_{m,\sigma} \quad (2.4)$$

where $Y_{lm}(\theta, \varphi)$ is a spherical harmonic and $\xi_{m,\sigma}$ a spin function. By demanding the energy functional for an MCHF wavefunction, $\langle \Psi | H | \Psi \rangle$, to be stationary with respect to variations in the radial functions and expansion coefficients, a system of coupled non-linear differential equations, one for each function, together with a secular problem for the expansion coefficients is obtained. This problem is then solved by the self-consistent field (SCF) method. The MCHF method is described in some detail in [10, 11, 12].
2.2 The Breit-Pauli approximation

For light atoms relativistic effects can be treated as perturbations. In the Breit-Pauli approximation operators representing the relativistic effects are added to the non-relativistic Hamiltonian [13]

\[ H_{BP} = H_{nr} + H_{rel} \]  

(2.5)

The wavefunction is now expanded in terms of configuration-state functions with different LS terms but with the same total angular momentum \( J \).

\[ \Psi = \sum_{i=1}^{m} c_i \Phi(\gamma_i L_i S_i J) \]  

(2.6)

The expansion coefficients are determined by diagonalizing the interaction matrix

\[ \langle \Phi(\gamma_i L_i S_i J) | H_{BP} | \Phi(\gamma_j L_j S_j J) \rangle \]  

(2.7)

2.3 The MCDF method

For heavy atoms and highly charged ions the relativistic effects should not be treated as small perturbations. The atomic state must in these cases be described by an eigenfunction to the relativistic Hamiltonian [14, 15]

\[ H = \sum_{i=1}^{N} (c \vec{\alpha}_i \cdot \vec{p}_i + e^2 \beta_i - \frac{Z}{r_i}) + \sum_{i<j} \frac{1}{r_{ij}} \]  

(2.8)

Here

\[ \vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \]  

(2.9)

and

\[ \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \]  

(2.10)

where \( \vec{\sigma} \) are the Pauli spin matrices and \( I \) a two dimensional unit matrix. As in the non-relativistic case some higher-order effects are left out, but they can be treated later as perturbations.

The multi-configuration Dirac-Fock (MCDF) method is the relativistic analogue of the MCHF method. The atomic state wavefunction, \( \Psi \), is expanded in terms of configuration state functions, which are antisymmetrized eigenfunctions of \( J^2, J_z \) and parity.

\[ \Psi = \sum_{i}^{m} c_i \Phi_i(\gamma_i J) \]  

(2.11)

The configuration state functions are sums of products of single-electron Dirac orbitals

\[ \phi(r, \theta, \varphi, \sigma) = \frac{1}{r} \begin{pmatrix} P_{nm}(r) \chi_{nm}(\theta, \varphi, \sigma) \\ iQ_{nm}(r) \chi_{-nm}(\theta, \varphi, \sigma) \end{pmatrix} \]  

(2.12)
where \( n \) is the principal quantum number, and \( \kappa \) is the relativistic angular quantum number, 
\( \kappa = \pm (j + \frac{1}{2}) \) for \( l = j \pm \frac{1}{2} \), with \( l \) and \( j \) being the orbital and total angular momenta of the electron. 

\( P_{\kappa n}(r) \) and \( Q_{\kappa n}(r) \) are the large and small component radial wavefunctions and \( \chi_{\kappa m}(\theta, \varphi, \sigma) \) are the spinor spherical harmonics in the \( lsj \) coupling scheme:

\[
\chi_{\kappa m}(\theta, \varphi, \sigma) = \sum_{m_s} \langle lm - m_s | l_s^1 j m \rangle Y_{lm - m_s}(\theta, \varphi) \zeta_{m_s}(\sigma) 
\] (2.13)

The relativistic self-consistent field method is then used to solve the system of coupled non-linear differential equations together with the secular problem for the expansion coefficients, as obtained by applying the stationary condition to the relativistic energy functional.

It should be pointed out that MCDF calculations are much more time consuming than equivalent MCHF calculations. Furthermore, there are sometimes severe convergence problems. A review of relativistic calculations is given in [16].
Chapter 3

Nuclear effects

In accurate calculations effects arising from the finite nuclear size and mass and higher-order electromagnetic multipoles must be taken into account. This is normally done by treating these effects as perturbations.

3.1 Mass effect

When the finite nuclear mass is taken into account, the atomic energy levels are slightly shifted due to the nuclear motion relative to the center of mass. The motion of the nucleus modifies the non-relativistic Hamiltonian in two ways [17]. The mass of the electron should be replaced with the reduced mass

\[ \mu = \frac{mM}{m + M} \]

(3.1)

where \( m \) and \( M \) is the electron and nuclear mass, respectively. This is the so called normal mass effect. Secondly, the operator

\[ -\frac{1}{M} \sum_{i<j} \nabla_i \cdot \nabla_j \]

(3.2)

should be added as an perturbation. This is the specific mass effect. The modifications to the relativistic Hamiltonian are much more complicated and are not treated here.

3.2 Volume effect

Due to the finite volume of the nucleus the electrostatic potential inside the nuclear charge distribution deviates from the potential of a point charge \( Z \). For light atoms where non-relativistic wavefunctions can be used, the volume effect can be accounted for by adding the operator [17],

\[ \frac{2\pi Z}{3} \delta(r)(r^2) \]

(3.3)

where \( \langle r^2 \rangle \) is the mean squared radius of the nuclear charge distribution. In heavy atoms the volume effect must be treated self-consistently. This is done by introducing a potential from a
realistic nuclear charge distribution in the relativistic Hamiltonian. Often the Fermi distribution is used \[18, 19\]

\[ \rho(r) = \frac{\rho_0}{1 + e^{(r-c)/a}} \]  

(3.4)

where \( c \) is the half-density radius and \( a \) is related to the nuclear skin thickness \( t \) through

\[ \frac{t}{a} = 4 \ln 3 \]  

(3.5)

### 3.3 Hyperfine structure

The hyperfine structure of the atomic energy levels is caused by the interaction between the electrons and the electromagnetic multipole moments of the nucleus \[20\]. The contribution to the Hamiltonian can be represented by an expansion in multipoles of order \( K \),

\[ H_{\text{hf}} = \sum_{K \geq 1} T^{(K)} \cdot M^{(K)} \]  

(3.6)

where \( T^{(K)} \) and \( M^{(K)} \) are spherical tensor operators of rank \( K \) in the electronic and nuclear space, respectively. The \( K = 1 \) term represents the magnetic dipole interaction and the \( K = 2 \) term the electric quadrupole interaction. Higher-order terms are much smaller and can often be neglected.

The nuclear tensor operators \( M^{(1)} \) and \( M^{(2)} \) are related to the scalar nuclear magnetic dipole moment \( \mu_I \) and electric quadrupole moment \( Q \)

\[ \langle \gamma I I | M^{(1)}_0 | \gamma I I \rangle = \mu_I \]  

(3.7)

\[ \langle \gamma I I | M^{(2)}_0 | \gamma I I \rangle = \frac{Q}{2} \]  

(3.8)

When the hyperfine contributions are added to the Hamiltonian, the wavefunction representation for which the total Hamiltonian is diagonal is \(| \gamma I I J F M_F \rangle \), where \( F = I + J \). In this representation, perturbation theory gives the following diagonal hyperfine energy corrections to the electronic energy

\[ W_{M_1}(J) = \langle \gamma I I J F M_F | T^{(1)} \cdot M^{(1)} | \gamma I I J F M_F \rangle \]  

(3.9)

\[ W_{E 2}(J) = \langle \gamma I I J F M_F | T^{(2)} \cdot M^{(2)} | \gamma I I J F M_F \rangle \]  

(3.10)

This can, using tensor algebra, also be written as

\[ W_{M_1}(J) = (-1)^{I+J-F} W(IJ J I; F1) \langle \gamma J J | T^{(1)} | \gamma I I \rangle \langle \gamma I I | M^{(1)} | \gamma I I \rangle \]  

(3.11)

\[ W_{E 2}(J) = (-1)^{I+J-F} W(IJ J I; F2) \langle \gamma J J | T^{(2)} | \gamma I I \rangle \langle \gamma I I | M^{(2)} | \gamma I I \rangle \]  

(3.12)

where \( W(IJ J I; F1) \) and \( W(IJ J I; F2) \) are \( W \) coefficients of Racah.
The energies are usually expressed in terms of the hyperfine interaction constants ($A$ and $B$ factors)

$$ A_J = \frac{\mu I}{I} \left[ \frac{1}{(J(J+1)(2J+1))^{\frac{1}{2}}} \langle \gamma_J | T^{(1)} | \gamma_J \rangle \right] $$

$$ B_J = 2Q \left[ \frac{J(2J-1)}{(J+1)(2J+1)(2J+3)} \right]^{\frac{1}{2}} \langle \gamma_J | T^{(2)} | \gamma_J \rangle $$

The energy corrections are then given by

$$ W_{M1}(J) = \frac{1}{2} A_J C $$

$$ W_{E2}(J) = B_J \frac{3C(C+1) - I(I+1)J(J+1)}{2I(2I-1)J(2J-1)} $$

where $C = F(F+1) - J(J+1) - I(I+1)$. For an $N$-electron atom the non-relativistic electronic tensor operators are, in atomic units,

$$ T^{(1)} = \frac{\alpha^2}{2} \sum_{i=1}^{N} [2g_{\ell} l^{(1)}(i) r_i^{-3} - g_s \sqrt{10}[C^{(2)}(i) \times s^{(1)}(i)] r_i^{-3} + g_s \frac{8}{3} \delta(r_i) s^{(1)}(i)] $$

$$ T^{(2)} = - \sum_{i=1}^{N} C^{(2)}(i) r_i^{-3} $$

where $g_{\ell} = (1 - m_{\ell}/M_{\text{nucleus}})$ and $g_s = 2.0023193$ are the orbital and electron spin g-factors. $\delta(r)$ is the three-dimensional delta function and $C^{(k)}_q = \sqrt{4\pi/(2k+1)}Y_{k\ell}$, with $Y_{k\ell}$ being a normalized spherical harmonic. The operators have the following classical interpretation. The first term of the dipole operator represents the field caused by orbital motion of the electrons and is called the orbital term. The second term represents the dipole field due to the spin motions of the electron and is called the spin-dipole term. The last term represents the contact interaction between the nucleus and the electron spin and contributes only for s-electrons. The electric quadrupole operator represents the electric field gradient at the site of the nucleus.

The relativistic tensor operators have a simpler form

$$ T^{(1)} = -ia \sum_{i=1}^{N} [\mathbf{\bar{a}}(i) \cdot \mathbf{l}(i) C^{(1)}(i)] r_i^{-2} $$

$$ T^{(2)} = - \sum_{i=1}^{N} C^{(2)}(i) r_i^{-3} $$

where $\alpha$ is the fine-structure constant and $\mathbf{\bar{a}}$ is the Dirac matrix.
Chapter 4

Radiative transitions

An atom in an excited state can relax to a lower state by emitting a photon. Our knowledge about atoms has largely been based on a careful analysis (spectral analysis) of the photon flow from excited atoms. The spectral analysis is also the basis of astronomy. From stellar spectra the astronomers can determine not only what atoms and molecules are present in the stellar atmosphere, but also other parameters such as temperature, magnetic fields and atmospheric velocities.

4.1 Multipole radiation

Classically the radiation field of a system of charges can be represented as a superposition of electric and magnetic multipole fields [21]. Each multipole field is characterised by parity and by the angular momentum it transfers. When a multipole field of order \((l, m)\) is coupled to a quantum system through a transition from an initial state \(|\gamma'J'M'\rangle\) to a final state \(|\gamma J M\rangle\), preservation of angular momentum gives the following selection rules \(|J - J'| \leq 1 \leq J + J'\) and \(M = m + M'\). The probability per unit of time, \(A_{\gamma'J'M',\gamma JM}\), for such a transition is proportional to

\[
(E_{\gamma'J'} - E_{\gamma J})^{2l+1}/\langle \gamma'J'M' | O_m^{(l)} | \gamma J M \rangle^2
\]  

(4.1)

where the transition operator \(O_m^{(l)}\) for electric and magnetic transitions, respectively, has the form [22]

\[
E_m^{(l)} = \sum_{i=1}^{N} r_i^{(l)} C_m^{(l)(i)}
\]  

(4.2)

and

\[
M_m^{(l)} = \sum_{i=1}^{N} \nabla[r_i^{(l)} C_m^{(l)(i)}] \cdot \left[\frac{1}{l+1} \mathbf{l}(i) + \frac{1}{2} g_s(i)\right]
\]  

(4.3)

The total probability per unit of time for a radiative transition to a lower state is given by

\[
A_{\gamma'J'M'} = \sum_{\gamma J M} A_{\gamma'J'M',\gamma JM}
\]  

(4.4)
The mean lifetime of the initial state is the inverse of the total transition probability

$$\tau = \frac{1}{A_{\gamma J'M'}}$$  \hspace{1cm} (4.5)

When allowed, the electric dipole transition is the dominating transition channel, compared with which the other multipole transitions often can be neglected. Frequently, the probability for a transition is given in terms of the unitless absorption oscillator strength, $f(\gamma J; \gamma' J')$, which for an electric dipole transition is defined as

$$f(\gamma J; \gamma' J') = \frac{2(E_{\gamma'J'} - E_{\gamma J})}{3(2J + 1)} |\langle \gamma' J' || \sum_{i=1}^{N} r_i C^{(1)}(i) || \gamma J \rangle|^2$$  \hspace{1cm} (4.6)

In the LS coupling approximation, the appropriate oscillator strength is that for the multiplet, that is, a weighted sum of oscillator strength over all lines in the multiplet. The multiplet oscillator strength is defined as

$$f(\gamma LS; \gamma' LS') = \frac{2(E_{\gamma'LS'} - E_{\gamma LS})}{3(2L + 1)} |\langle \gamma' LS' || \sum_{i=1}^{N} r_i C^{(1)}(i) || \gamma LS \rangle|^2$$  \hspace{1cm} (4.7)

The multiplet oscillator strength is non-zero only when $S' = S$ since the transition operator has rank 0 in spin space.

4.2 Comparison with experiment

The resonance transition in lithium has been studied extensively due to the rather large discrepancy between experiment and theory. Two accurate experimental values of the oscillator strength exist, $f(2S; 2P) = 0.7416 \pm 0.0012$ and $f(2S; 2P) = 0.7435 \pm 0.0055$, measured with the fast-beam laser [23] and delayed-coincidence technique [24], respectively. The experimental values are typically 1% to 5% smaller than the theoretical values. The fact that almost all ab initio calculations, based on different approaches, agree, indicates that the experimental errorbars, at least for the fast-beam laser measurement, are underestimated. It is interesting to note, however, that the semiempirical calculation of reference 31 is in agreement with experiment. One should also note the recent quantum Monte Carlo calculation of reference 32, which gives a low $f$-value. The statistical errorbars of the calculation are rather large, and so the interpretation of the result is difficult. In Table I experimental and theoretical $f$-values for the resonance transition are presented.
Table I. Oscillator strength for the $2s - 2p$ transition in lithium

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Length</th>
<th>Velocity</th>
<th>$f$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>fast-beam laser</td>
<td></td>
<td></td>
<td>$0.7416 \pm 0.0012$</td>
<td>[23]</td>
</tr>
<tr>
<td>delayed-coincidence</td>
<td></td>
<td></td>
<td>$0.7435 \pm 0.0055$</td>
<td>[24]</td>
</tr>
<tr>
<td>Theory</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sims et al. (CI-Hyll.)</td>
<td>$0.7476$</td>
<td></td>
<td>$0.7476$</td>
<td>[25]</td>
</tr>
<tr>
<td>Johnson et al. (MBPT)</td>
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<td>$0.7495$</td>
<td>[26]</td>
</tr>
<tr>
<td>Blundell et al. (MBPT)</td>
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<td></td>
<td>$0.7471$</td>
<td>[27]</td>
</tr>
<tr>
<td>Weiss (CI)</td>
<td>$0.7478$</td>
<td>$0.7498$</td>
<td>$0.7478$</td>
<td>[28]</td>
</tr>
<tr>
<td>Ynnerman (CCSD)</td>
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<td></td>
<td>$0.7471$</td>
<td>[29]</td>
</tr>
<tr>
<td>Pipin and Bishop (CI-Hyll.)</td>
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<td></td>
<td>$0.7470$</td>
<td>[2]</td>
</tr>
<tr>
<td>Chung (CI)</td>
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<td>[30]</td>
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<tr>
<td>Theodosius et al. (semiempirical)</td>
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<td></td>
<td>$0.7415$</td>
<td>[31]</td>
</tr>
<tr>
<td>Barnett et al. (quantum Monte Carlo)</td>
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<td></td>
<td>$0.7419(69)$</td>
<td>[32]</td>
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<tr>
<td>Olsen (finite element MCHF)</td>
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<tr>
<td>Paper 4 (MCHF)</td>
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<td>$0.7470$</td>
<td>$0.7472$</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 5

Large-scale atomic calculations

Today’s workstations with a fast CPU and large internal memory allow MCHF and MCDF calculations where the wavefunction expansion contains thousands of configuration state functions (CSFs). In this thesis convergence of different atomic parameters towards relativistic and non-relativistic limits has been studied as the wavefunction expansion was systematically enlarged. This method gives an indication of the accuracy with which the parameters have been calculated, which, of course, is of importance when no measurements are at hand.

5.1 The active space approach

An effective way of choosing the wavefunction expansion is by using an active set of radial orbitals. In this approach all possible CSFs of a particular parity and symmetry (in non-relativistic formalism the CSFs should have the same $LS$ values and in the relativistic the same $J$ value) are generated from the active set of orbitals by excitations from a reference set of configurations. The active set of orbitals is then increased stepwise by adding orbitals with the same principal quantum number, $n$, but with different orbital quantum number, $l$. By imposing different restrictions on the way excitations can be done, orbitals can be targeted to describe different electron correlation effects. A few examples will illustrate this approach.

5.2 The $1s^22s\,^2S$ state in $^7Li$

Here the reference set consists of only one configuration $1s^22s\,^2S$. All one-, two- and three-particle excitations from the reference configuration have been included for orbitals with $n \leq 5$, whereas for orbitals with $n > 5$ only one- and two-particle excitations were allowed. In Table II the convergence of the Fermi contact term and the total energy is shown as the active set of orbitals is increased.
Table II. The Fermi contact term and the energy (in a.u.) of the $2s\,^{2}S$ term (From Paper 3)

<table>
<thead>
<tr>
<th>active set</th>
<th>$a_c$</th>
<th>Energy</th>
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<tbody>
<tr>
<td>$2sp$</td>
<td>2.0731</td>
<td>-7.454565</td>
</tr>
<tr>
<td>$3spd$</td>
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<td>-7.477512</td>
</tr>
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<td>$13sp$</td>
<td>2.9048</td>
<td>-7.477726</td>
</tr>
<tr>
<td>Non-relativistic limit</td>
<td>2.90502$^a$</td>
<td>-7.4780596$^b$</td>
</tr>
</tbody>
</table>

$^a$ Estimated from the experimental value $a_c = 2.90602$ where relativistic, finite nuclear size and finite nuclear mass corrections from Ref. 34 has been subtracted.

$^b$ From Paper 4

5.3 The $3s3p\,^1P$ and $3s3d\,^1D$ states in $^{25}Mg$

For the $3s3p\,^1P$ term the reference set consists of only one configuration, $3s3p\,^1P$. The $3s3d\,^1D$ term interacts strongly with $3p^2\,^1D$, and the latter term must also be included in the reference set for the $3s3d\,^1D$ term. From the reference set one- and two-particle excitations have been allowed. Contributions to the hyperfine structure from the 1s sub-shell showed to be small, and no excitations from this sub-shell were allowed. Orbitals optimized on these CSF expansions tend to describe core-core correlation effects and deep core-valence effects, that is, the orbitals have small radial expectation values. In addition to these orbitals, a set of core-valence and valence correlating orbitals is needed. By not allowing any excitations from the 1s and 2s sub-shells and only one-particle excitations from the 2p sub-shell, orbitals can be targeted to describe core-valence and valence correlation. In Tables III and IV the convergence of hyperfine structure constants for the $3s3p\,^1P$ and $3s3d\,^1D$ states is shown. The orbitals targeted to describe core-valence and valence correlation are marked with a slash.
Table III. The hyperfine structure constants (in MHz) of the $3s^3p \, ^1P$ state in $^{25}Mg$

<table>
<thead>
<tr>
<th>reference set</th>
<th>active set</th>
<th>$A_1$</th>
<th>$B_1/Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3s3p , ^1D$</td>
<td>HF</td>
<td>-4.046</td>
<td>11.649</td>
</tr>
<tr>
<td></td>
<td>$3spd$</td>
<td>-4.126</td>
<td>11.781</td>
</tr>
<tr>
<td></td>
<td>$4spdf$</td>
<td>-7.368</td>
<td>23.833</td>
</tr>
<tr>
<td></td>
<td>$5spdfg$</td>
<td>-7.170</td>
<td>22.300</td>
</tr>
<tr>
<td></td>
<td>$6spdf$</td>
<td>-7.485</td>
<td>25.073</td>
</tr>
<tr>
<td></td>
<td>$6spdf/7spdf$</td>
<td>-7.750</td>
<td>25.505</td>
</tr>
<tr>
<td></td>
<td>$6spdf/7spdf - 8spdf$</td>
<td>-7.797</td>
<td>25.779</td>
</tr>
<tr>
<td>Experiment</td>
<td></td>
<td>-7.7(5)$^a$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Ref. 35

Table IV. The hyperfine structure constants (in MHz) of the $3s3d \, ^1D$ state in $^{25}Mg$

<table>
<thead>
<tr>
<th>reference set</th>
<th>active set</th>
<th>$A_2$</th>
<th>$B_2/Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3s3d , ^1D$</td>
<td>HF</td>
<td>-0.079</td>
<td>0.325</td>
</tr>
<tr>
<td>${3s3d, 3p^2} , ^1D$</td>
<td>$3spd$</td>
<td>-5.181</td>
<td>30.102</td>
</tr>
<tr>
<td></td>
<td>$4spdf$</td>
<td>-5.656</td>
<td>37.661</td>
</tr>
<tr>
<td></td>
<td>$5spdfg$</td>
<td>-5.493</td>
<td>35.724</td>
</tr>
<tr>
<td></td>
<td>$5spdfg/6spdf$</td>
<td>-5.220</td>
<td>35.084</td>
</tr>
<tr>
<td></td>
<td>$5spdfg/6spdf - 7spdf$</td>
<td>-5.201</td>
<td>34.055</td>
</tr>
<tr>
<td>Experiment</td>
<td></td>
<td>-5.14$^a$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Ref. 36

In Table V the radial expectation values, $\langle r \rangle_m$, of the orbitals optimized on the $3s3d \, ^1D$ term, are shown. Orbitals targeted to describe core-valence and valence correlation have expectation values in the core-valence region, that is between 2$p$ and 3$s$, or in the valence region, between 3$s$ and 3$d$.

Table V. Radial expectation value $\langle r \rangle_m$ (in a.u.) of the normal and valence correlating orbitals

<table>
<thead>
<tr>
<th>normal orbitals</th>
<th>valence correlating orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1s$</td>
<td>$6s$</td>
</tr>
<tr>
<td>$2s$</td>
<td>$6p$</td>
</tr>
<tr>
<td>$2p$</td>
<td>$6d$</td>
</tr>
<tr>
<td>$3s$</td>
<td>$6f$</td>
</tr>
<tr>
<td>$3p$</td>
<td>$7s$</td>
</tr>
<tr>
<td>$3d$</td>
<td>$7p$</td>
</tr>
<tr>
<td>$4s$</td>
<td>$7d$</td>
</tr>
<tr>
<td>$4p$</td>
<td>$7f$</td>
</tr>
</tbody>
</table>
Chapter 6

Experiments on atoms

6.1 Time-resolved laser spectroscopy

All theory must be founded on comparison with experimental data. Time-resolved laser spectroscopy [37] has supplied theoreticians with radiative lifetimes of many excited atomic states. Also, by studying quantum beats, fine and hyperfine structures have been determined.

6.2 Direct observation of fluorescent light decay

The most direct method for measuring lifetimes of excited states is by observing the fluorescent light decay following short-pulse excitation. The decay of the fluorescence light is detected with a fast photo-multiplier tube and a transient digitizer, and from the decay curve the mean lifetime can be derived directly. By using tunable lasers, selective excitations can be obtained, excluding problems from cascade population.

The wavelengths needed for the excitation are often in the UV or VUV spectral region, outside the wavelength region of normal lasers. Then non-linear optical processes have to be used in order to generate the desired radiation. A number of such techniques are now available, where the radiation from pulsed lasers is mixed in non-linear crystals, such as β-Barium Borate and Lithium Tri-Borate. The radiation obtained from the mixing process can then be Raman shifted to even shorter wavelength [38].

Free atoms can be produced in a number of different ways. For the experiments in this thesis an atomic beam, produced by evaporating atoms in an electrically heated oven, has been used.

In order to get accurate lifetime data a number of experimental parameters must be controlled. The atomic density in the beam must be kept low to avoid multiple photon scattering and atomic collisions. Further, non-linearities in the detection system must be avoided.
6.3 Delayed-coincidence technique

In the delayed-coincidence technique [39] the intensity of the fluorescence light is kept so low that the detection probability is below one photon per excitation pulse. With the single photon counting technique the time between the laser pulse and the fluorescence photon is measured. The distribution of this time interval will be a decay curve, which gives the lifetime of the excited state. In order to get good statistics the laser must have a high pulse repetition rate, typically 1 MHz. The advantage of the delayed-coincidence technique to ordinary pulsed techniques is that no direct, time-resolved recording of the transient is made. Thus, no problems with detector non-linearities are present.

Figure 1: Experimental set-up for a delayed-coincidence measurement.
6.4 Quantum beats

When closely spaced atomic levels are simultaneously excited by a short laser pulse, the time-resolved fluorescence intensity may show a modulated exponential decay [40]. The modulation pattern, known as quantum beats, is due to interference between fluorescence amplitudes emitted from the coherently excited levels and is a pure quantum mechanical phenomenon. Quantum beats can be used to determine the level structure since the modulation frequencies are proportional to the energy splittings. This method has been used to determine hyperfine structures in excited states of sodium and silver.

Figure 2: Quantum beats revealing the fine structure of the $1s^23d\,^2D$ term in lithium. The number of photons is shown on a logarithmic scale.
Chapter 7

Concluding remarks

7.1 Comments on the papers

This thesis is divided into three parts: a computational, a theoretical and an experimental part. Papers 1 and 2 are descriptions of a non-relativistic and a relativistic hyperfine structure program, being parts of the MCHF atomic structure package of Froese Fischer and of GRASP2 (General-Purpose Relativistic Atomic Structure Program) of Parpia, Grant and Froese Fischer, respectively. Paper 3 contains a theoretical study of the hyperfine structures in the lowest $S$ and $P$ states of lithium. In Paper 4 results from a convergence study of different atomic properties in lithium, using an $nl$-expansion in configuration space, are reported. Paper 5 consists of two parts: an MCHF study of the hyperfine structure constants in the $3s^2 S_{1/2}$ and $3p^2 P_{1/2,3/2}$ states in sodium and an accurate experimental determination of the hyperfine structure constant in the $3p^2 P_{1/2}$ state using quantum beat spectroscopy. The last three papers are experimental. Paper 6 reports results from lifetime measurements on the $S$ and $D$ sequences of neutral silver using direct observation of the decay. In Paper 7 results from accurate lifetime and hyperfine structure measurements of the $5p^2 P_{1/2,3/2}$ states in silver, using the delayed-coincidence technique, are discussed. Paper 8 contains a report from lifetime and hyperfine structure measurements of the $7p^2 P_{1/2,3/2}$ and $7p^2 P_{3/2}$ states in silver, respectively, using direct observation of the decay.

7.2 Acknowledgements

During the work at the Division of Atomic Physics I have received support and help from a number of persons, whom I would like to thank. First of all I would like to thank my supervisor, Professor Sune Svanberg, for his enthusiasm and for letting me do atomic theory in an experimental group. During two periods I have had the great pleasure to work in Professor Charlotte Froese Fischer's group at Vanderbilt University, which has been very stimulating and rewarding. I would like to thank Professor Froese Fischer for all her advice and for her kind interest in my work. I also would like to thank Dr Tomas Brage and his wife Barbara for taking care of me in Nashville and for being
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Bibliography


