Multiconfiguration calculations of hyperfine structures and isotope shifts

Per Jönsson, Michel Godefroid, Gediminas Gaigalas, Charlotte Froese Fischer

Material Science and Applied Mathematics, Malmö University, Sweden

25 Augusti 2015
Contributions from:

- Jacek Bieroń (Krakow)
- Jörgen Ekman (Malmö)
- Ian Grant (father of GRASP code, Oxford)
- Tomas Brage (Lund)
- Jiguang Li (Beijing)
- Jon Grumer (Lund)
- Simon Verdebout (Brussels)
- Cedric Nazé (Brussels)
- Pavel Rynkun (Vilnius)
Outline

- COMPutational Atomic Structure Group (COMPAS)
- What data can we provide
- Available computer codes
- How to improve our description of many-electron systems to match current needs

Per Jönsson, Michel Godefroid, Gediminas Gaigalas, Charlotte Froese Fischer
Welcome

To meet the demands for atomic data the Computational Atomic Structure (CompAS) group has been formed. The group is involved in developing state of the art computer codes for atomic calculations in the non-relativistic scheme with relativistic corrections in the Breit-Pauli approximation ATSP2K [1] as well as in the fully relativistic scheme GRASP2K [2]. The codes rely on multiconfiguration methods and the wave function for an atomic state is expanded in configuration state functions (CSFs).

Moreover, the RATIP [3] program supports the calculation of atomic properties for open-shell atoms with one electron in the continuum, including transition probabilities, Auger parameters as well as a variety of excitation, ionization and recombination amplitudes and cross sections.

In addition to the code development itself, the group includes members with expertise in the methods and is constantly developing computational techniques for the evaluation of atomic properties of the highest quality.

Some of the group’s research are highlighted in this “Lab Talk” article in Journal of Physics B.
Contributions from the COMPAS group

- Multiconfiguration codes: source codes freely available.
- Methods for computing atomic parameters for general systems: mass shift parameters, hfs parameters, Landé $g_J$-factors, EDM etc (Jacek Bieroń, Jiguang Li).
- Methods for the detailed interaction between the nuclear and electron charge distributions (Jörgen Ekman).
- Methods for computing interaction with external magnetic fields and magnetically- and hfs induced transitions.
- New methods for treating electron correlation in many-electron systems: Pair-Correlation Function Interaction (PCFI).
Atomic systems and accuracy

- Hfs and lifetimes of thousands of atomic levels in a range of charge states, limited accuracy.
- Mass shift parameters, hfs parameters for few-electron systems with different charge states. Accuracy at the percent level.
- Mass shift parameters, hfs parameters and EDM for many-electron near neutral systems. Accuracy depends very much of the system.
- Multiconfiguration methods DO NOT provide high precision in the sense of Hylleraas or explicitly correlated Gaussian methods

Per Jönsson, Michel Godefroid, Gediminas Gaigalas, Charlotte Froese Fischer
Materials Science and Applied Mathematics, Malmö University, Sweden
An MCHF atomic-structure package for large-scale calculations

Charlotte Froese Fischer, Georgio Tachiev, Gediminas Gaigalas, Michel R. Godefroid

- Non-relativistic multiconfiguration code with Breit-Pauli
- Runs in parallel under MPI
- Programs for hyperfine structure and isotope shift
- Source codes freely downloadable
New version: GRASP2K relativistic atomic structure package

P. Jönsson, G. Gaigalas, J. Bieron, C. Froese Fischer, I.P. Grant

- Relativistic multiconfiguration code
- Runs in parallel under MPI
- Programs for hyperfine structure, isotope shift, EDM, interaction with external magnetic fields etc
rIS3: A program for relativistic isotope shift calculations

C. Nazé, E. Gaidamauskas, G. Gaigalas, M. Godefroid, P. Jönsson

- Nuclear recoil (mass shift) operators in the Breit approximation
- New formulation of field-shift implemented (in preparation Jörgen Ekman)
- Source code and extensive manual freely downloadable
Applications: thousands of levels

A priori calculations of hyperfine interactions in highly ionized atoms: g-factor measurements on aligned pico-second states populated in nuclear reactions

N. J. Stone · J. R. Stone · P. Jonsson

Calibration of Recoil-In-Vacuum attenuations from first principles: comparison with recent experimental data on Fe isotopes

Nicholas James Stone · Jirina Rikovska Stone · Andrew E. Stuchbery · Per Jonsson
HYPERFINE INDUCED TRANSITIONS AS DIAGNOSTICS OF ISOTOPIC COMPOSITION AND DENSITIES OF LOW-DENSITY PLASMAS

TOMAS BRAGE, PHILIP G. JUDGE, ABBELLATIF ABOUSSAÏD, MICHEL R. GODEFROID, P. JÖNSSON, ANDERS YNNERMAN, CHARLOTTE FROÈSE FISCHER, AND DAVID S. LECKRONE

$M_F$-dependent hyperfine induced transition rates in an external magnetic field for Be-like $^{47}$Ti$^{18+}$

Jiguang Li, Chenzhong Dong, Per Jönsson, Gediminas Gaigalas

Multiconfiguration calculations of hyperfine structures and isotope shifts

© 1998. The American Astronomical Society. All rights reserved. Printed in U.S.A.
Applications: hfs and isotope shift in few-electron systems

Isotope shifts in beryllium-, boron-, carbon-, and nitrogen-like ions from relativistic configuration interaction calculations

Hyperfine structures and Landé $g_f$-factors for $n = 2$ states in beryllium-, boron-, carbon-, and nitrogen-like ions from relativistic configuration interaction calculations
Applications: hfs in many-electron neutral systems

PHYSICAL REVIEW A 71, 012502 (2005)

Nuclear quadrupole moment of $^{201}$Hg

Jacek Bieron,$^1$ Pekka Pyykkö,$^2$ and Per Jönsson$^3$
Multiconfiguration methods for many-electron systems and how to improve these methods
Hartree Fock (HF) wave function = one configuration state function.

A configuration state function (CSF)

\[ \Phi((nl)_i \nu_i LS) \]

is antisymmetrized one-electron product functions coupled to correct \( LS \) symmetry. \((nl) = (n_1 l_1, n_2 l_2, \ldots, n_N l_N)\) defines the orbitals (spin-orbitals)
\( \nu \) is a label that specifies the coupling.

Example \( \Phi(1s^2 2s^2 S), \Phi(1s^2 2s^2 2p^6 3s3p^3 P) \)
Property of the HF wave function

Two electron system with spin-up and spin-down. Introduce relative coordinates

\[ \mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2), \quad \mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1 \]

Shape of HF and exact wave function and as functions of \( r \)
Describing electron correlation = correcting for the difference between HF and the exact wave function
Approximate multiconfiguration Hartree Fock (MCHF) wave functions expansions over CSFs

\[ \Psi((nl)\nu LS) = \sum_{i=1}^{M} c_i \Phi((nl)_i\nu_i LS) \]

- Equations for the expansion coefficients and the radial functions building the CSFs obtained by applying the variational principle on an energy functional
- Equations solved iteratively until converged.
Shape of HF, MCHF and exact wave function and as functions of $r$.
Building a SD-MR-MCHF wave function

- Start with multireference (MR) expansion to account for orbital degeneracies
- Generate CSFs by SD substitutions of orbitals in the CSFs in the MR with orbitals in an active set
- These CSFs build the Correlation Function (CF) space
- Wave function $\Psi$ is an expansion over CSFs in the MR and CF spaces
SD-MR-MCHF approximation for $1s^22s^2 \, ^1S$

Multireference \{\Phi(1s^22s^2 \, ^1S), \Phi(1s^22p^2 \, ^1S)\}

\[
\Phi(1s^22s^2 \, ^1S) \rightarrow \Phi(1s^2nln'l' \, ^1S) \quad \text{valence correlation}
\]

\[
\Phi(1s^22s^2 \, ^1S) \rightarrow \Phi(1s2snln'l' \, ^1S) \quad \text{core-valence correlation}
\]

\[
\Phi(1s^22p^2 \, ^1S) \rightarrow \Phi(1s2pnln'l' \, ^1S)
\]

\[
\Phi(1s^22s^2 \, ^1S) \rightarrow \Phi(2s^2nln'l' \, ^1S)
\]

\[
\Phi1s^22p^2 \, ^1S) \rightarrow \Phi(2p^2nln'l' \, ^1S) \quad \text{core-core correlation}
\]

\[
nl, n'l' \in \{1s, 2s, 2p, 3s, 3p, 3d, \ldots, \}
\]

active set
Strengths and weaknesses

- Generally applicable
- Good at capturing close degeneracies and valence correlation
- Conceptually easy
- Difficult to capture core-core correlation effects (large expansions and slow convergence)
- Need to understand the interplay between CSF expansion and orbital set
Non-relativistic variational calculations of atomic properties in Li-like ions: Li I to O VI

M Godefroid, C Froese Fischer and P Jönsson

CAS expansion $\Phi(1s^22s^22S) \rightarrow \Phi(nln'l'n''l'' 2S)$
$\Phi(1s^22p^22S) \rightarrow \Phi(nln'l'n''l'' 2P)$

Orbitals increased up to $\{1s, 2s, 2p, \ldots, 11k\}$

Parameters compared with data from Hylleraas
Convergence of the $S_{sms}$ parameter of $1s^22s\,^2S$ in Li I

Multiconfiguration calculations of hyperfine structures and isotope...
Convergence of the $a_c$ parameter of $1s^22p \, ^2P$ in Li I
Convergence of the $b_q$ parameter of $1s^22p^2 \, ^2P$ in Li I

$b(q)$ for $1s(2)p \, ^2P$ in Li

$n$

$b(q)$ in a.u.
### $1s^22s\ ^2S,\ 1s^22p\ ^2P$ in $^7\text{Li}$

<table>
<thead>
<tr>
<th>$S_{SMS}$</th>
<th>$A_{1/2}\ (\text{MHz})$</th>
<th>MCHF</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30203039</td>
<td>401.81</td>
<td>MCHF</td>
</tr>
<tr>
<td>0.30184280</td>
<td>401.714</td>
<td>Hylleraas</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$S_{SMS}$</th>
<th>$A_{1/2}\ (\text{MHz})$</th>
<th>$A_{3/2}\ (\text{MHz})$</th>
<th>MCHF</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.24694843</td>
<td>45.974</td>
<td>−3.052</td>
<td>MCHF</td>
</tr>
<tr>
<td>0.24673781</td>
<td>45.9392</td>
<td>−3.0550</td>
<td>Hylleraas</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\Delta S_{SMS}$</th>
<th>$gf_l$</th>
<th>$gf_v$</th>
<th>MCHF</th>
</tr>
</thead>
<tbody>
<tr>
<td>−0.055082</td>
<td>1.49391</td>
<td>1.49374</td>
<td>MCHF</td>
</tr>
<tr>
<td>−0.055105</td>
<td>1.49391</td>
<td>1.49391</td>
<td>Hylleraas</td>
</tr>
</tbody>
</table>

Yan and Drake PRA 52 R4317 1995
Puchalski et al. PRA 79, 032510 2009
Due to restrictions in tensor algebra used to build the energy functional, orbitals should be orthonormal.

All CSFs must be built from the same orthonormal orbital set.

Orthonormal orbital set inefficient for larger systems with many shells.
## Example orthogonality problems

Ground state $1s^22s^22p^63s^23p^64s^2$ $^1S$ in Ca I

Mean radii in a.u. of the sub shells

<table>
<thead>
<tr>
<th></th>
<th>1s</th>
<th>2s</th>
<th>2p</th>
<th>3s</th>
<th>3p</th>
<th>4s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.077</td>
<td>0.363</td>
<td>0.327</td>
<td>1.159</td>
<td>1.2745</td>
<td>4.218</td>
</tr>
</tbody>
</table>
Ground state $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 \,^1S$ in Ca I

- Correlation in the $1s$ shell: tailor orbital set where some orbitals have a large overlap with the $1s$ orbital
- Correlation in the $2s$ shell: needs to be described in terms of the previous orbitals, tailored for describing correlation in the $1s$ shell, as well as some new orbitals that are overlapping with the $2s$ orbital etc.
To capture the correlation between electrons in all the different shells, the orbital basis needs to be extended to a large number of orbitals for each symmetry.

- large orbital sets lead to massive CSF expansions
- performance of MCHF calculations degrades with the number of shells in the atom
- scaling-wall (millions and millions of CSFs)
Handle non-orthogonalities

Transition probability calculations for atoms using nonorthogonal orbitals

Jeppe Olsen, Michel R. Godefroid, Per Jönsson, Per Åke Malmqvist, and Charlotte Froese Fischer

- fast transformation techniques allows the computation of transition matrix elements between $\Psi$ and $\Psi'$ built on separate orbital sets
- same transformation can be used to evaluate any, including two-particle, matrix element
Normal SD-MR-MCHF method

\[ \Psi = \Psi^{MR} + \Lambda \]

- \( \Psi^{MR} \) is the multireference CSF expansion
- \( \Lambda \) is a CSF expansion built from the CF space
- \( \Lambda \) is optimized in one VERY LARGE calculation
- Generated orbital basis may be unsuited for describing correlation effects that are not strongly coupled to energy (spin-polarization)
A partitioned correlation function interaction approach for describing electron correlation in atoms

S Verdebout\textsuperscript{1}, P Rynkun\textsuperscript{2}, P Jönsson\textsuperscript{3}, G Gaigalas\textsuperscript{4}, C Froese Fischer\textsuperscript{5} and M Godefroid\textsuperscript{1}
Partitioned correlation function interaction (PCFI)

- Partition the CF space \( \Lambda \) into subspaces and perform separate MCHF calculations

\[
\Psi_i = \Psi^{MR} + \sum_{i=1}^{\Lambda_i \text{ CSF exp.}} \psi_i, \quad i = 1, \ldots, n
\]

where \( \Lambda_i \) partitioned correlation functions (PCFs).

- Normalize \( \Lambda_i \rightarrow \bar{\Lambda}_i \)

- Expand total wave function

\[
\Psi = \Psi^{MR} + \sum_i \alpha_i \bar{\Lambda}_i
\]

- Obtain expansion coefficient by constructing the Hamiltonian and overlap matrices and solving a generalized eigenvalue problem
PCFI method

Advantages

▶ Relies on a divide-and-conquer strategy: many small MCHF calculations
▶ Partition of CF space can be done in many ways to capture different effects, spin-polarization can be described with very high accuracy
▶ The orbital set for each PCF optimally located
▶ The final expansion is a low-dimensional problem
▶ Allows you to analyze the importance of different correlation effects (we can learn something)
Drawbacks

- Construction of matrix elements between PCFs based on a biorthogonal transformation
- The expansion coefficients of the CSFs in each PCFs are locked (constraint effect)

Constraint effects can now be handled efficiently through a matrix formulation
Exploring biorthonormal transformations of pair-correlation functions in atomic structure variational calculations

S Verdebout\textsuperscript{1}, P Jönsson\textsuperscript{2}, G Gaigalas\textsuperscript{3}, M Godefroid\textsuperscript{1} and C Froese Fischer\textsuperscript{4}
PCFI method for $1s^2 2s^2 \, {}^1S$ in Be I

$1s^2 2s^2 \, {}^1S$ in Be I.

- Start from MR \( \{1s^22s^2, 1s^22p^2, 1s^23s^2, 1s^23p^2, 1s^23d^2\} \)
- Generate the CF space \( \Lambda \) by SD-excitations from the MR to active sets of orbitals
- Partition the CF in the following subspaces:
  - valence-valence \( \Lambda_{vv} \) CSFs from valence shell subst.
  - core-valence \( \Lambda_{cv} \) CSFs from valence and core shell subst.
  - core-core \( \Lambda_{cc} \) CSFs from core shell subst.
PCFI method for $1s^22s^2 \, ^1S$ in Be I

Perform three separate MCHF calculations for:

$$
\psi_{vv} = \psi^{MR} + \Lambda_{vv}
$$

$$
\psi_{cv} = \psi^{MR} + \Lambda_{cv}
$$

$$
\psi_{cc} = \psi^{MR} + \Lambda_{cc}
$$

Expand the final wave function

$$
\psi = \psi^{MR} + \alpha_{vv} \Lambda_{vv} + \alpha_{cv} \Lambda_{cv} + \alpha_{cc} \Lambda_{cc}
$$

5 CSFs normalized corr. func.

Determine expansion coefficients by solving an $8 \times 8$ eigenvalue problem
Radial orbitals for the different PCFs

Valence correlation

Core–Valence correlation

Core correlation
Results for $1s^22s^2\,^1S$ in Be

Tabell: Results for the PCFI method. The energies are compared with CAS-MCHF results based on a single orthonormal orbital set.

<table>
<thead>
<tr>
<th>$n \leq$</th>
<th>$E_{PCFI}$</th>
<th>$E_{CAS-MCHF}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>$-14.660,679,48$</td>
<td>$-14.661,403,17$</td>
</tr>
<tr>
<td>5</td>
<td>$-14.665,553,46$</td>
<td>$-14.664,839,93$</td>
</tr>
<tr>
<td>6</td>
<td>$-14.666,582,83$</td>
<td>$-14.666,067,32$</td>
</tr>
<tr>
<td>7</td>
<td>$-14.666,905,87$</td>
<td>$-14.666,541,14$</td>
</tr>
<tr>
<td>8</td>
<td>$-14.667,047,86$</td>
<td>$-14.666,857,41$</td>
</tr>
<tr>
<td>9</td>
<td>$-14.667,122,76$</td>
<td>$-14.667,012,75$</td>
</tr>
<tr>
<td>10</td>
<td>$-14.667,168,08$</td>
<td>$-14.667,114,20$</td>
</tr>
</tbody>
</table>

- CAS-MCHF 650 000 CSFs, days on a super computer cluster
- PCFI method, a few hours on an ordinary computer.
The term position of $1s^22s^22p^2 \, 4P$ is not known.

Two different positions available from extrapolation

Edlen 28867.15 cm$^{-1}$, Kramida 28644.27 cm$^{-1}$
Doublet-quartet energy separation in boron: A partitioned-correlation-function-interaction method

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Gediminas Gaigalas
5Institute of Theoretical Physics and Astronomy, Vilnius University, LT-01108 Vilnius, Lithuania

(Received 8 October 2013; published 6 December 2013)
PCFI method

- MR: $1s^2\{2s, 2p, 3s, 3p, 3d\}^3 \ 2P^o, \ 1s^2\{2s, 2p, 3s, 3p, 3d\}^3 \ 4P$
- Divide the CF space into valence-valence, core-valence, core-core subspaces
- Run separate MCHF calculations
- Expand final wave function in the MR and PCFs
- Add relativistic shift correction
Results for B I

Results include relativistic and mass shift correction

<table>
<thead>
<tr>
<th>$n_{\text{max}}$</th>
<th>Energy $^2P^o$</th>
<th>Energy $^4P$</th>
<th>$\Delta E$</th>
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<tbody>
<tr>
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<td>$-24.525847143$</td>
<td>$28810.52$</td>
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<tr>
<td>6</td>
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<tr>
<td>7</td>
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<td>9</td>
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<td>10</td>
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<td>$-24.527912772$</td>
<td>$28944.32$</td>
</tr>
<tr>
<td>$\infty$</td>
<td>$-24.659910$</td>
<td>$-24.527993$</td>
<td>$28952.52$</td>
</tr>
</tbody>
</table>

Edlén et al. [1] \hspace{1cm} $28866 \pm 15$
Kramida and Ryabtsev [2] \hspace{1cm} $28643.1 \pm 1.8$
Tachiev and Froese Fischer [3] \hspace{1cm} $29021$
Results include relativistic and mass shift correction.
Look at the accuracy: $\Delta E = 4 \text{ cm}^{-1}$!

<table>
<thead>
<tr>
<th>$n_{max}$</th>
<th>Energy $^2P^o$</th>
<th>Energy $^4P$</th>
<th>$\Delta E$</th>
</tr>
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<tbody>
<tr>
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<td>$\infty$</td>
<td>$-37.444878$</td>
<td>$-37.249003$</td>
<td>42989.59</td>
</tr>
</tbody>
</table>

**ASD [4]**

42993.5

**Young et al. [13]**

42993.34 $\pm$ 0.87
Theory nightmare, mass shift

The $1s^2 2s^2 2p^6 3s^2 S - 1s^2 2s^2 2p^6 3p^2 P$ transition energy and isotope shift in Na I.

- Separate PCFI calculations for the two states
- CF space for active set $n = 8$ partitioned into the following PCFs: $1s1s, 1s2s, 1s2p, 1sv, 2s2s, 2s2p, 2sv, 2p2p, 2pv$
  - 9 separate calculations
- Look at accumulated contributions from each PCF to understand effect of correlation
- Look at the contributions for the states versus the contributions for the differences. We have much to learn from analysis of this kind.

Per Jönsson, Michel Godefroid, Gediminas Gaigalas, Charlott Multiconfiguration calculations of hyperfine structures and isotope shift
## Accumulated contributions to energy $E$ (a.u.)

<table>
<thead>
<tr>
<th>$PCF$</th>
<th>$E(2S)$</th>
<th>$E(2P)$</th>
<th>$\Delta E$</th>
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</thead>
<tbody>
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<td>$HF$</td>
<td>$-161.858580$</td>
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<td>$0.072293$</td>
</tr>
<tr>
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<tr>
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<td>$-162.122580$</td>
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</tr>
<tr>
<td>$1s1s$</td>
<td>$-162.238215$</td>
<td>$-162.161813$</td>
<td>$0.076402$</td>
</tr>
</tbody>
</table>
Accumulated contributions to the specific mass shift $S$.

<table>
<thead>
<tr>
<th>$PCF$</th>
<th>$S(,^2S)$</th>
<th>$S(,^2P)$</th>
<th>$\Delta S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$HF$</td>
<td>20.81090</td>
<td>20.81222</td>
<td>0.00131</td>
</tr>
<tr>
<td>$2pv$</td>
<td>20.77740</td>
<td>20.80179</td>
<td>0.02438</td>
</tr>
<tr>
<td>$2p2p$</td>
<td>18.31926</td>
<td>18.33383</td>
<td>0.01457</td>
</tr>
<tr>
<td>$2sv$</td>
<td>18.31464</td>
<td>18.33454</td>
<td>0.01989</td>
</tr>
<tr>
<td>$2s2p$</td>
<td>18.28679</td>
<td>18.30240</td>
<td>0.01560</td>
</tr>
<tr>
<td>$2s2s$</td>
<td>18.27115</td>
<td>18.28663</td>
<td>0.01548</td>
</tr>
<tr>
<td>$1sv$</td>
<td>18.27017</td>
<td>18.28552</td>
<td>0.01535</td>
</tr>
<tr>
<td>$1s2p$</td>
<td>17.49344</td>
<td>17.50950</td>
<td>0.01605</td>
</tr>
<tr>
<td>$1s2s$</td>
<td>17.45370</td>
<td>17.46972</td>
<td>0.01602</td>
</tr>
<tr>
<td>$1s1s$</td>
<td>16.40403</td>
<td>16.41976</td>
<td>0.01573</td>
</tr>
</tbody>
</table>

Additional SDTQ effects
Properties weakly coupled to energy

Hfs very difficult to compute due to important effects from spin- and orbitals polarization

These effects are only weakly connected to the energy

Energy optimized orbitals will give oscillatory behavior

No general solution to the problem

Large-scale MCHF calculations of hyperfine structures in nitrogen and oxygen

M.R. Godefroid, G. Van Meulebeke, P. Jönsson, C. Froese Fischer

- Hfs very difficult to compute due to important effects from spin- and orbitals polarization
- These effects are only weakly connected to the energy
- Energy optimized orbitals will give oscillatory behavior
- No general solution to the problem
Spin-polarization: spin dependent part of the electron coulomb interaction

Changes the electron spin density at the nucleus

Important for hfs
Weak connections to energy

- Spin- and orbital polarization are energetically unimportant long range rearrangements in electron spin- and charge densities
- Variational calculations may not properly account for these effects
- Energy optimized orbitals will give oscillatory behavior for hfs
The electric quadrupole term $b_q$ is oscillating as a function of the energy optimized orbital set $n$. 

![Graph of $b(q)$ for $1s(2)p^2 2P$ in Li](image-url)
Targeted PCFs

General technique that applies to all computed properties

- Use perturbation theory to analyze which CSFs are important for a specific property e.g. spin- or orbital polarization
- Build and optimize a PCF to account for the important interactions
- Optimize additional PCFs to account for additional electron correlation
- Put everything together in a total wave function
The electric quadrupole term in $1s^2 2p \, ^2P$ in Li

Convergence when including targeted PCF
Conclusions

- The COMPAS group offers codes and methods for supplying atomic data for current experiments
- Computation hfs and isotope shift for neutral many-electron systems remain a challenge
- Divide and conquer strategies offers one way forward for multiconfiguration methods
- Work in progress to provide fast and reliable codes implementing PCFI
Thank you for your attention
Perturbative improvements of ordinary MCHF/MCDHF or RCI calculations

- Partition of the CSF space
- Limited interactions in the Hamiltonian matrix
- Compute integrals on the fly
Perform RSCF calculations up to some limit

Optimize additional layers of orbitals by partition the CSFs in a zero- and first order space

The zero order space may consist of the CSFs in the MR

Include interactions:
  in the zero-order space
  between the zero- and first order spaces
  on the diagonal
Matrix sparse, calculations very fast
Use the additional orbital layers from RSCF to perturbatively improve RCI results

- Partition the CSFs in three spaces
- Include part of the interactions
RCI calculations

Calculation to be improved
Calibration of the observed attenuations has been achieved in favourable cases through comparison with measurements on states having previously known $g$-factors and lifetimes. The general lack of suitable states with known $g$-factors has limited application of the RIV method. This paper concerns the present status of efforts to describe the states of excited ions recoiling into vacuum in detail so that the average interaction can be estimated with useful precision from a-priori theory. The calculations use the GRASP2K package (Froese-Fischer et al. 1997 and Jonsson, Comp. Phys. Comm., 177, 597, 2007 184, 2197, 2013) to obtain, for each recoiling ion change state, the individual possible electronic states, their configurations, lifetimes and hyperfine interactions.
Perturbative corrections need only small changes to the GRASP2K code.

When using large orbital sets the number of Breit integrals will become very large.

The Breit integrals needed to compute the additional interaction matrix elements (not very many) should be computed on the fly and not stored in any array.

Perturbative code soon finished.