Atomic Structure Calculations using GRASP2K

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Relativistic multiconfiguration methods

General Relativistic Atomic Structure Package (Grasp2K).
P. Jönsson, G. Gaigalas, J. Bieron, C. Froese Fischer, I.P. Grant
Computer Physics Communications 184, 2197 (2013).

- Conceptually easy
- Can be generally applied
- Can be used to generate massive data sets
- Allows for systematic calculations giving uncertainty estimates
- Extensive manual available

Grasp2K manual and references

- The CompAS group
  A practical guide to Grasp2K, 2015
- C. Froese-Fischer, T. Brage, P. Jönsson
  Computational Atomic Structure: An MCHF Approach
  IoP 1997
- I. Grant
  Relativistic Quantum Theory of Atoms and Molecules: Theory and Computation
  Springer 2007

What is needed

- PC running under Linux
- Grasp2K code, available as compressed tar file
- gfortran compiler
- MPI libraries (if parallel processing)

Basics: orbital

Orbital

$$\Psi(nlsjm;\mathbf{r}) = \frac{1}{r}\begin{pmatrix} P(nlj;r)\,\Omega_{lsjm}(\theta,\varphi) \\ \mathrm{i}\,Q(nlj;r)\,\Omega_{\bar{l}sjm}(\theta,\varphi) \end{pmatrix}$$

- One-electron function
- Radial functions $P(r), Q(r)$ numerically represented on a radial grid

Basics: orbital

Spectroscopic orbitals:

- same node structure as a hydrogen like orbitals
- builds CSFs in the complex or MR
- can be hard to converge, need good initial estimates

Correlation orbitals:

- no restriction on node structure
- additional orbitals to build CSFs that improves the zero order wave function
- may look quite different spectroscopic orbitals.

Basics: configuration

Number of orbitals with occupation numbers, e.g.

$$1s^2 2s^2 (2p-)^2, \quad 1s^2 2s^2 (2p-) 2p, \quad 1s^2 2s^2 2p^2,$$

Notation $1s, 2s, 2p-, 2p$ for $1s_{1/2}, 2s_{1/2}, 2p_{1/2}, 2p_{3/2}$.

In non-relativistic theory

$$1s^2 2s^2 2p^2.$$

Basics: CSF

Configuration state function (CSF)

$$\Phi(\gamma JM)$$

- Many-electron function
- Formed by angular couplings of the orbitals in a configuration
- Well defined parity and angular momentum
- Can be seen as a basis function
- γ denotes configuration and coupling

Basics: ASF

Atomic state function (ASF)

$$\Psi(\Gamma JM) = \sum_{\alpha=1}^{NCSF} c_\alpha \Phi(\gamma_\alpha JM)$$

- Many-electron function
- Approximate wave function of a state
- c_α expansion (or mixing) coefficients

SD substitutions

SD substitutions from $1s^2 2s^2 2p^2$ describing valence correlation

Reference configuration + rule + orbital set

```
1s(2,i)2s(2,*)2p(2,*)
 3s, 3p, 3d
```

- occupation (in red)
- i = inactive, no substitutions
- $*$ = no restrictions on occupation after substitutions
- substitutions to $\{1s, 2s, 3s, 2p, 3p, 3d\}$

SD substitutions

SD substitutions from $1s^2 2s^2 2p^2$ describing valence and core-valence correlation

Reference configuration + rule + orbital set

```
1s(2,1)2s(2,*)2p(2,*)
 3s, 3p, 3d
```

- occupation (in red)
- minimum occupation in blue (we allow at most S substitution)
- $*$ = no restrictions on occupation after substitutions
- substitutions to $\{1s, 2s, 3s, 2p, 3p, 3d\}$

Tasks related to atomic structure calculations

Identify the states you want to target (NIST, Chianti, other work)

- Define nuclear properties (charge, distribution, spin, etc)
- Generate CSF expansion
- Perform angular integration and set up energy expression (sum angular coefficient times radial integrals)
- Initial estimates of radial orbitals $P(a,r), Q(a,r), P(b,r), Q(b,r)$ etc on a grid
- Determine radial orbitals and expansion coefficients self-consistently (MCDHF)
- Add transverse Breit and QED and determine only expansion coefficients (RCI)
- Compute additional properties (transition rates etc)
- Generate LaTeX tables, plots etc

Important files in Grasp2K

- `isodata`: nuclear data
- `rcsf.inp`: list of CSFs arranged according to symmetry
- `rwfn.inp`: initial estimates of the radial functions
- `rwfn.out`: radial functions after a successful run
- `rmix.out`: expansion (mixing) coefficients for CSFs after a successful run

Important files in Grasp2K

After successful MCDHF run above files saved as

- `name.c`: list of CSFs
- `name.w`: radial wave functions
- `name.m`: expansion (mixing) coefficients

where the user determines the name.

These files define the wave functions and are used as input to other programs.

Program groups in Grasp2K

Generate list of CSFs (`rcsf....`)

- `rcsfexcitation`: define rules for SD substitutions, wrapper program
- `rcsfgenerate`: generates the lists of CSFs based on rules from wrapper program
- `rcsfinteract`: removes unimportant CSFs based on analysis of couplings

Program groups in Grasp2K

Estimates of radial orbitals (`rwfn....`)

- `rwfnestimate`: estimates radial orbitals, several sources can be used
- `rwfnmchfmcdf`: convert non-relativistic radial orbitals to relativistic ones

Program groups in Grasp2K

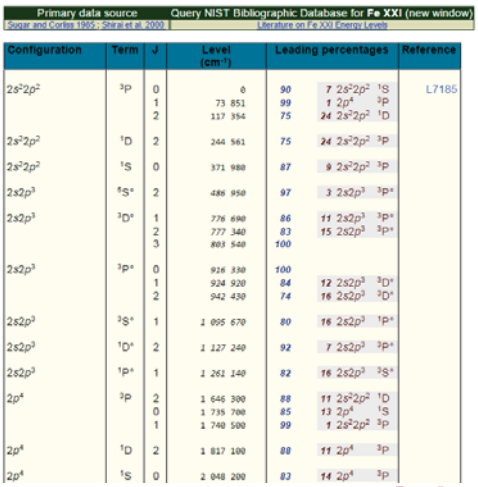
Compute and display wave functions and energies

- `rangular`: angular integration, defines energy expressions for `rmcdhf`
- `rmcdhf`: determines both radial orbitals and expansion coefficients
- `rci`: assumes radial orbitals available, determine expansion coefficients
- `jj2lsj`: transforms to LSJ-coupling
- `rlevels`: displays energies and labels

Program groups in Grasp2K

Application programs, computes transition rates, Lande factors etc from CSF file, radial wave function file, mixing coefficient file

- `rbiotransform`: transforms radial orbitals to a biortonormal basis
- `rtransition`: computes transition parameters
- `rhfs`: computes hfs and Lande factors



Primary data source: Sugar and Corliss 1985; Shirai et al. 2000

Query NIST Bibliographic Database for **Fe XXI** (new window)

Literature on Fe XXI Energy Levels

Configuration	Term	J	Level (cm⁻¹)	Leading percentages	Reference
$2s^22p^2$	^{3}P	0	0	90 $2s^22p^2$ ^{3}P	L7185
		1	73 851	99 $2p^4$ ^{3}P	
		2	117 354	75 $2s^22p^2$ ^{1}D	
$2s^22p^2$	^{1}D	2	244 561	75 $2s^22p^2$ ^{3}P	
$2s^22p^2$	^{1}S	0	371 980	87 $2s^22p^2$ ^{3}P	
$2s2p^3$	^{5}S*	2	486 950	97 $2s2p^3$ ^{3}P*	
$2s2p^3$	^{3}D*	1	776 690	86 $2s2p^3$ ^{3}P*	
		2	777 340	83 $2s2p^3$ ^{3}P*	
		3	803 540	100	
$2s2p^3$	^{3}P*	0	916 330	100	
		1	924 920	84 $2s2p^3$ ^{3}D*	
		2	942 430	74 $2s2p^3$ ^{3}D*	
$2s2p^3$	^{3}S*	1	1 095 670	80 $2s2p^3$ ^{1}P*	
$2s2p^3$	^{1}D*	2	1 127 240	92 $2s2p^3$ ^{3}P*	
$2s2p^3$	^{1}P*	1	1 261 140	82 $2s2p^3$ ^{3}S*	
$2p^4$	^{3}P	2	1 646 300	88 $2s^22p^2$ ^{1}D	
		0	1 735 700	85 $2p^4$ ^{1}S	
		1	1 740 500	99 $2s^22p^2$ ^{3}P	
$2p^4$	^{1}D	2	1 817 100	88 $2p^4$ ^{3}P	
$2p^4$	^{1}S	0	2 048 200	82 $2p^4$ ^{3}P	

Computational steps even states

- `rnucleus`: Z = 26, M = 56 (only once)
- `rcsfexcitation`, `rcsfgenerate`: CSFs belonging to $1s^22s^22p^2$, $1s^22p^4$, $J = 0, 1, 2$
- `rwfnestimate`: Thomas-Fermi
- `rangular`: angular inegration
- `rmcdhf`: optimize on $J = 0, \underbrace{1-4}_{\text{state}}, J = 1, 1-2, J = 2, 1-4,$ orbitals spectroscopic
- `rsave`: save and give name evenMR

Computational steps, even states

- `rci`: transverse, QED, mass, $J = 0, 1-4, J = 1, 1-2, J = 2, 1-4$
- `jj2lsj`: transform to LSJ coupling
- `more evenMR.lsj.lbl`: display LSJ-composition
- `rlevels`: display energies and labels, indata from `evenMR.cm`
- `rhfs`: Lande factors, indata just the name `evenMR`
- `more evenMR.ch`: display Lande factors

Computational steps, odd states

- `rcsfexcitation`, `rcsfgenerate`: CSFs belonging to $1s^22s2p^3$, $J = 0, 1, 2, 3$
- `rwfnestimate`: Thomas-Fermi
- `rangular`: angular integration
- `rmcdhf`: optimize on $J = 0, 1, J = 1, 1-4, J = 2, 1-4, J = 3, 1,$ orbitals spectroscopic
- `rsave`: save and give name oddMR

Computational steps, odd states

- `rci`: transverse, QED, mass, $J = 0, 1, J = 1, 1-4, J = 2, 1-4, J = 3, 1$
- `jj2lsj`: transform to LSJ coupling
- `more oddMR.lsj.lbl`: display LSJ-composition
- `rlevels`: display energies and labels, indata from `evenMR.cm` `oddMR.cm`
- `rhfs`: Lande factors, indata just the name `oddMR`
- `more oddMR.ch`: display Lande factors

Computational steps, transition parameters

- `rbiotransform`: transform to biorthonormal radial orbitals, indata just the names `evenMR, oddMR`
- `rtransition`: indata just the names `evenMR, oddMR`, multipoles E1, M2
- `more evenMR.oddMR.ct.lsj`

Improve wave functions, even states

- `rcsfexcitation`, `rcsfgenerate`: SD-substitutions describing valence and core-valence from $1s^2 2s^2 2p^2$, $1s^2 2p^4$ to $\{3s, 3p, 3d\}$
- `rwfnestimate`: $\{1s, 2s, 2p\}$ from old $\{3s, 3p, 3d\}$ hydrogenic
- `rangular`: angular integration
- `rmcdhf`: optimize on $J = 0, 1-4, J = 1, 1-2, J = 2, 1-4$ only new orbitals optimized, not spectroscopic
- `rsave`: save and give name even3

Improve wave functions, even states

- `rci`: transverse, QED, mass, $J = 0, 1-4, J = 1, 1-2, J = 2, 1-4$
- `jj2lsj`: transform to LSJ coupling
- `more even3.lsj.lbl`: display LSJ-composition
- `rlevels`: display energies and labels, indata from `even3.cm`
- `rhfs`: Lande factors, indata just the name `even3`
- `more even3.ch`: display Lande factors

Improve wave functions, odd states

- `rcsfexcitation`, `rcsfgenerate`: SD-substitutions describing valence and core-valence from $1s^2 2s 2p^3$ to $\{3s, 3p, 3d\}$
- `rwfnestimate`: $\{1s, 2s, 2p\}$ from old $\{3s, 3p, 3d\}$ hydrogenic
- `rangular`: angular integration
- `rmcdhf`: optimize on $J = 0, 1, J = 1, 1-4, J = 2, 1-4, , J = 3, 1$ only new orbitals optimized, not spectroscopic
- `rsave`: save and give name odd3

Improve wave functions, odd states

- `rci`: transverse, QED, mass, $J = 0, 1, J = 1, 1-4, J = 2, 1-4, J = 3, 1$
- `jj2lsj`: transform to LSJ coupling
- `more odd3.lsj.lbl`: display LSJ-composition
- `rlevels`: display energies and labels, indata from `odd3.cm`
- `rhfs`: Lande factors, indata just the name `odd3`
- `more odd3.ch`: display Lande factors

Computational steps, transition parameters

- `rbiotransform`: transform to biorthonormal radial orbitals, indata just the names `even3, odd3`
- `rtransition`: indata just the names `even3, odd3`, multipoles E1, M2
- `more even3.odd3.ct.lsj`

LaTeX tables of energies

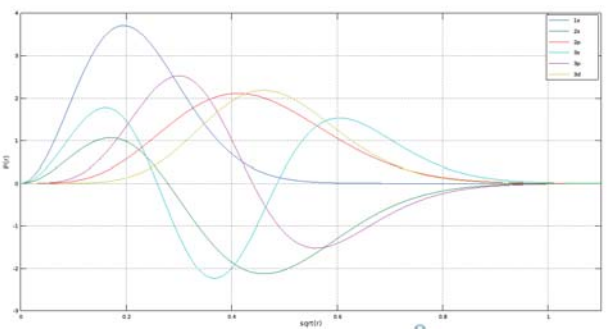
- Pipe output from `rlevels` to files
- `rtablevels`

LaTeX tables of transition rates and lifetimes

- `rtabtrans1`: input data `even3.cm odd3.cm`, output energylabel
- Edit LaTeX strings in energylabel if desirable
- `rtabtrans2`: input `even3.odd3.ct`

Produce plots

`rwfnplot`: produces and Octave m-file



Thank you for your attention