

Atomic Structure Calculations using the General (Purpose) Relativistic Atomic Structure Package (GRASP) – coding efforts under way for accurate atomic data

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Thanks to the organizers

Extend my thanks to the organizers
Anders, Paul, and Jon for inviting me.

I am very honored to be here and everything is great so far!

Main collaborators in current efforts

Coding and methodology development

- ▶ Gediminas Gaigalas (Vilnius)
- ▶ Michel Godefroid (Brussels)
- ▶ Chongyang Chen (Shanghai)

Collaborators



Left: with Charlotte Froese Fischer. Right: with Michel Godefroid and Gediminas Gaigalas.

People to honor: father and mother of GRASP and ATSP



Ian Grant and Charlotte Froese Fischer after a visit to Tycho Brahe's observatory at the island Hven.

In 1573, Brahe published a book *De nova stella*, thereby coining the term nova for a "new" star (we now classify this star as a supernova and know that it is 7,500 light-years from Earth)

- ▶ CompAS
- ▶ Basics of computational atomic structure (background for talks by Patric Palmeri and Ricardo da Silva)
- ▶ GRASP atomic structure package
- ▶ What we can compute very accurately and why
- ▶ What we can't compute very accurately and why
- ▶ Improving codes and methodology
- ▶ Conclusions

Combined experimental and computational atomic spectroscopy group. A multidisciplinary environment is a great benefit (necessary) for progress. Will be covered by Henrik Hartman

What is CompAS?

- ▶ **CompAS** is a network for Atomic Structure Theory, based on Multiconfiguration Methods, initiated 2012.
- ▶ Core of CompAS : groups that are **users** and **developers** of the **MC(D)HF** methods in the form of the **ATSP** and **GRASP** packages and successors,
- ▶ The CompAS **network** consists of different groups and individuals that are interested in the work of the CompAS core groups.
- ▶ More information (including the codes repositories) can be found on github <https://compas.github.io/>

The CompAS international collaboration

CompAS is led by a **board** with at least one representative from each core group. The current composition of the board is

Jacek Bieroń, Krakow

Charlotte Froese Fischer, NIST

Michel Godefroid, Brussels

Jon Grumer, Uppsala

Per Jönsson/Jörgen Ekman, Malmö

Chongyang Chen/Ran Si, Fudan

Wenxian Li, Beijing

Tomas Brage, Lund

Gediminas Gaigalas, Vilnius

Ian Grant, Oxford

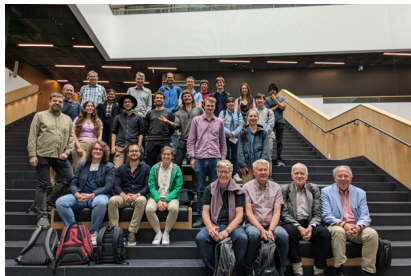
Alan Hibbert, Belfast

Jose Marques, Lisbon

Pawel Syty/Jozef Sienkiewicz, Gdansk

The CompAS international collaboration

A **CompAS meeting** has been set up **every year** to report on further computational and methodological developments for more efficient atomic structure calculations. Next meeting in **Lisbon June or July 2024, join!**



Computational atomic structure

Start with a wave equation $H\Psi = E\Psi$ where

$$H = \sum_{i=1}^N (c\alpha_i \cdot \mathbf{p}_i + (\beta_i - 1)c^2 + V(r_i)) + \sum_{i<j}^N + \frac{1}{r_{ij}} \quad (+H_{\text{Breit}} + \text{QED}).$$

- ▶ Solve the equation approximately for the targeted states (up to thousands of states).
- ▶ **Measurable quantities** such as energy separations, oscillator strengths, hyperfine structures, isotope shifts etc. obtained as integrals (**expectation values**) involving the wave functions and an operator

Fundamental difficulties

- ▶ Dimensionality: 60 electrons (Nd), represent the wave function on a grid with 10 points per dimension, total 10^{180} grid points!

Product representation needed

- ▶ Singularities

$$\sum_{i < j}^N \frac{1}{r_{ij}} \equiv \sum_{i < j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Wave function has cusps (nightmare)

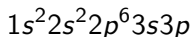
- ▶ QED is not fully developed

Way forward: central-field approximation

Assuming that the electrons move in a central field, the **wave function** separates into a **product of one-electron Dirac orbitals**

$$\phi(\mathbf{r}, \sigma) = \frac{1}{r} \begin{pmatrix} P_{n\kappa}(r)\chi_{\kappa m}(\theta, \vartheta) \\ iQ_{n\kappa}(r)\chi_{-\kappa m}(\theta, \vartheta) \end{pmatrix}$$

The configuration notation defines what product of one-electron orbitals to form



All **expectation values** can be written as **sums over one- and two electron radial integrals** (angular part computed analytically).

Anti-symmetry and angular coupling

Wave functions for electronic states are **anti-symmetric** with well-defined **angular symmetries**. Start from products of one-electron orbitals:

- ▶ **anti-symmetrize** (form Slater determinants)
- ▶ **couple to final symmetries**. *jj*- (relativistic formalism) or *LSJ* (non-relativistic formalism) coupling to final JM_J

The result is a many-electron function called a **configuration state function (CSF)**

$$\Phi(\gamma P J M_J)$$

where γ gives the orbital occupancy and the couplings.

Expectation values - angular integration

- ▶ Antisymmetrization and coupling increases the complexity dramatically.
- ▶ All expectation values still sums over one- and two electron radial integrals.
- ▶ The resolution of expectation values into sums of one- and two electron radial integrals is called angular integration
- ▶ Angular integration complex and at the heart of all computer codes (Gediminas Gaigalas, Vilnius, leading expert)

Multiconfiguration Wave functions

In multiconfiguration methods, wave functions of the targeted electronic states are expanded in CSFs

$$\Psi(\gamma P(LS)JM_J) = \sum_{i=1}^M c_i \underbrace{\Phi(\gamma_i PL_i S_i JM_J)}_{\text{CSF}} \quad (\text{non-relativistic})$$

$$\Psi(\gamma PJM_J) = \sum_{i=1}^M c_i \underbrace{\Phi(\gamma_i PJM_J)}_{\text{CSF}} \quad (\text{relativistic})$$

Labeling of states with dominating CSF

- ▶ Non-relativistic formalism: states often well described by a single LSJ -coupled CSF. Provides a label ☺.

$$\Psi('2s2p\ ^3P'_1) = -0.99999978|2s2p\ ^3P_1\rangle + 0.00066201|2s2p\ ^1P_1\rangle$$

- ▶ Relativistic formalism: each state needs to be described by several jj -coupled CSF. No label ☹.

$$\Psi('2s2p\ ^3P'_1) = 0.81687864|(2s_{1/2}2p_{1/2})_1\rangle - 0.57680957|(2s_{1/2}2p_{3/2})_1\rangle$$

- ▶ Label by a transformation from jj - to LSJ coupling (Gediminas Gaigalas)

Spectroscopic and correlation orbitals

- ▶ **Spectroscopic orbitals**: orbitals building the main CSFs of the targeted electronic states.
- ▶ **Correlation orbitals**: orbitals used for building the corrective CSFs.



Computer Physics Communications

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CPC 50th anniversary article

GRASP2018—A Fortran 95 version of the General Relativistic Atomic Structure Package



[C. Froese Fischer](#)^a  , [G. Gaigalas](#)^b  , [P. Jönsson](#)^c  , [J. Bierof](#)^d  

- ▶ Wave functions expanded in CSFs

$$\Psi(\gamma P J M_J) = \sum_{i=1}^M c_i \underbrace{\Phi(\gamma_i P J M_J)}_{\text{CSF}} \quad (\text{relativistic})$$

- ▶ Radial parts $\{P_{n\kappa}(r), Q_{n\kappa}(r)\}$ of the one-electron orbitals are numerically defined on a radial grid
- ▶ Orbitals are required to be orthonormal (technical requirement)

- ▶ Hamiltonian matrix

$$H = \begin{pmatrix} H_{11} & H_{12} & \dots & H_{1M} \\ H_{21} & H_{22} & \dots & H_{2M} \\ & & \vdots & \\ H_{M1} & H_{M2} & \dots & H_{MM} \end{pmatrix}$$

$H_{jk} = \langle \Phi(\gamma_j P J M_J) | H | \Phi(\gamma_k P J M_J) \rangle =$ angular coefficients \times radial integrals (needs to be computed really fast)

- ▶ Mixing coefficients for CSFs obtained by diagonalizing Hamiltonian matrix
- ▶ Radial parts of the orbitals obtained by solving a set of differential equations

- ▶ Configuration interaction (CI) - radial functions are known only diagonalization
- ▶ Typical number of orbitals: 90 – 120
- ▶ Typical number of CSFs: 5 000 000 – 50 000 0000
- ▶ Measurable quantities obtained as expectation values

$$Q = \sum_{j=1}^M \sum_{k=1}^M c_j c_k \langle \Phi(\gamma_j P J M_J) | O | \Phi(\gamma_k P J M_J) \rangle$$

$\langle \Phi(\gamma_j P J M_J) | O | \Phi(\gamma_k P J M_J) \rangle =$ angular coefficients \times radial integrals (needs to be computed really fast)



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Some concepts - multireference

Multireference (MR) - limited set of important CSFs

- ▶ MR is the zero-order approximation of the wave functions
- ▶ MR gives an approximate correct charge distributions

Example: $1s^2 2s^2 2p^6 3s^2 \ ^1S_0$

MR consists of CSFs formed from

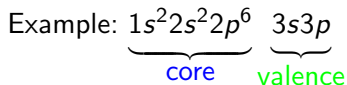
$\{1s^2 2s^2 2p^6 3s^2, 1s^2 2s^2 2p^6 3p^2, 1s^2 2s^2 2p^6 3d^2\}$

Corrective CSFs

- ▶ Account for the correlation between individual electrons (when electrons are made aware of each other, they try to avoid each other).
- ▶ Lowers the total energy of the state, changes expectation values.
- ▶ Brings energy separations and expectation values into agreement with experimental values.

Some concepts - core and valence

- ▶ **Core**, often thought of as electrons in closed subshells.
- ▶ **Valence** are electrons in open shells outside the core
- ▶ Ideally, there should be a clear energy separation between core orbitals and valence orbitals.
- ▶ For lanthanides, often no obvious separation between core and valence.



Some concepts - valence-valence correlation

Valence-valence (VV) correlation

- ▶ The valence electrons are made aware of each other.
- ▶ Effect on the total energy not large.
- ▶ Huge effect on energy separations (differential effect).
- ▶ Computationally inexpensive.

Example: CSFs formed from $1s^2 2s^2 2p^6 n l n' l'$
 $n l, n' l'$ correlation orbitals overlapping the valence region.

Some concepts - core-valence correlation

Core-valence (CV) correlation

- ▶ Valence electrons are made aware of the core electrons.
- ▶ Effect on the total energy larger than for the VV.
- ▶ Rather large effects on energy separations.
- ▶ Contraction effects for charge distributions affecting the transition rates.
- ▶ Computationally expensive.

Example: CSFs formed from

$1s^2 2s^2 2p^5 n l 3s n' l'$, $1s^2 2s^2 2p^5 n l 3p n' l'$, $1s^2 2s^2 2p^5 n l 3d n' l'$

$n l, n' l'$ correlation orbitals in between the valence and core regions.

Core-core (CC) correlation

- ▶ The core electrons are made aware of each other
- ▶ Effect on the total energy very large.
- ▶ Effects cancels and effect of the energy separations relatively small.
- ▶ Screening effects of the outer electron, small effects on transition rates
- ▶ Computationally (very) expensive.

Example: CSFs formed from

$$1s^2 2s^2 2p^4 n l n' l' 3s^2, 1s^2 2s^2 2p^4 n l n' l' 3p^2, 1s^2 2s^2 2p^4 n l n' l' 3d^2$$

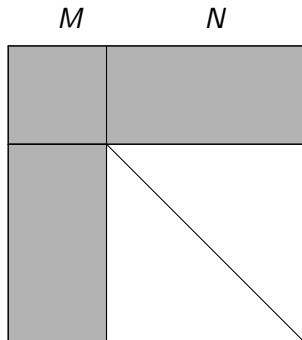
Systematic calculations

- ▶ Rules for forming the corrective CSFs from the radial orbitals
- ▶ SD-MR with some restrictions
- ▶ Increase the set of radial orbitals and monitor the convergence of computed properties
- ▶ Increase the MR and relax the rules and monitor the convergence of computed properties

Shortcuts - Brillouin-Wigner perturbation theory

Construct only part of the matrix

$$\underbrace{\{\Phi(\gamma_1 PJ), \dots, \Phi(\gamma_M PJ)\}}_{\text{zero-order, dim } M}, \underbrace{\{\Phi(\gamma_{M+1} PJ), \dots, \Phi(\gamma_{M+N} PJ)\}}_{\text{first-order, dim } N}$$



Medium-heavy ionized systems 😊

- ▶ Nuclear potential dominates, central-field approximation a good approximation
- ▶ States appear more by configuration, couplings does not affect so much
- ▶ Correlation effects can be saturated with respect to the increasing orbital set
- ▶ Brillouin-Wigner perturbation theory applicable
- ▶ Computations perform very well



Review

Multiconfiguration Dirac-Hartree-Fock Calculations with Spectroscopic Accuracy: Applications to Astrophysics

Per Jönsson ^{1,*}, Gediminas Gaigalas ², Pavel Rynkun ², Laima Radziūtė ², Jörgen Ekman ¹,
Stefan Gustafsson ¹, Henrik Hartman ¹, Kai Wang ¹, Michel Godefroid ³,
Charlotte Froese Fischer ⁴, Ian Grant ^{5,6}, Tomas Brage ⁷ and Giulio Del Zanna ⁶

- ▶ Ion coverage Be-like to Cl-like, thousands of states
- ▶ Spectroscopic accuracy - a number of miss identifications found, tentative identifications confirmed

Article

Combining multiconfiguration and perturbation methods: perturbative estimates of core-core electron correlation contributions to excitation energies in Mg-like iron

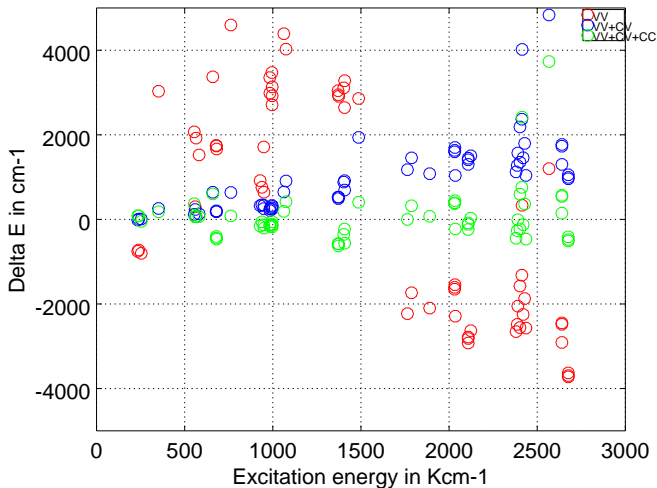
Stefan Gustafsson,¹ Per Jönsson,^{1*} Charlotte Froese Fischer,² and Ian Grant³

Excitation energies from 158 lowest states in Fe-like Mg.

Tabell: Number of CSFs and accuracy for different models

	VV	VV+CV	VV+CV+CC
even states	2 738	644 342	5 624 158
odd states	2 728	630 502	6 214 393
uncertainty	0.217%	0.051%	0.023%

Energy uncertainties for different computational models





Contents lists available at [ScienceDirect](#)

Atomic Data and Nuclear Data Tables

journal homepage: www.elsevier.com/locate/adt

Large-scale calculations of atomic level and transition properties in the aluminum isoelectronic sequence from Ti X through Kr XXIV, Xe XLII, and W LXII

J. Ekman^{a,*}, P. Jönsson^a, L. Radžiūtė^b, G. Gaigalas^b, G. Del Zanna^c, I.P. Grant^{c,d}

Calculations for Fe XIV

- ▶ 360 states for each ion, 5 000 000 CSFs
- ▶ Uncertainties in excitation energies 0.02% and 0.05%
- ▶ Nail miss identifications and confirm tentative identifications
- ▶ Internally validated transition rates

Calculations for Fe XIV

No.	Level	LS-composition	E_{RCI}	E_{NIST}	ΔE
1	$3s^2 3p^2 P_{1/2}^{\circ}$	97	0	0	0
2	$3s^2 3p^2 P_{3/2}^{\circ}$	97	18855	18853	2
3	$3s^2 S 3p^2 ({}^3P) 4P_{1/2}$	98	225086	225114	-28
4	$3s^2 S 3p^2 ({}^3P) 4P_{3/2}$	99	232777	232789	-12
5	$3s^2 S 3p^2 ({}^3P) 4P_{5/2}$	97	242372	242387	-15
6	$3s^2 S 3p^2 ({}^1D) 2D_{3/2}$	$86+11 3s^2 3d^2 D$	299402	299242	160
7	$3s^2 S 3p^2 ({}^1D) 2D_{5/2}$	$85+11 3s^2 3d^2 D+2 3s^2 S 3p^2 ({}^3P) 4P$	301627	301469	158
8	$3s^2 S 3p^2 ({}^1S) 2S_{1/2}$	$75+21 3s^2 S 3p^2 ({}^3P) 2P$	364945	364693	252
9	$3s^2 S 3p^2 ({}^3P) 2P_{1/2}$	$75+22 3s^2 S 3p^2 ({}^1S) 2S$	388711	388510	201
10	$3s^2 S 3p^2 ({}^3P) 2P_{3/2}$	$95+2 3p^2 ({}^1D) 1D 3d^2 P$	396687	396512	175
11	$3s^2 3d^2 D_{3/2}$	$86+11 3s^2 S 3p^2 ({}^1D) 2D+2 3p^2 ({}^1S) 1S 3d^2 D$	473231	473223	8
12	$3s^2 3d^2 D_{5/2}$	$86+11 3s^2 S 3p^2 ({}^1D) 2D+2 3p^2 ({}^1S) 1S 3d^2 D$	475215	475202	13
13	$3p^3 ({}^3D) 2D_{3/2}^{\circ}$	$64+27 3s^2 S 3p^3 P 3d^2 D^{\circ}+4 3p^3 ({}^2P) 2P^{\circ}$	576599	576383	216
14	$3p^3 ({}^3D) 2D_{5/2}^{\circ}$	$69+29 3s^2 S 3p^3 P 3d^2 D^{\circ}$	580450	580233	217
15	$3p^3 ({}^4S) 4S_{3/2}^{\circ}$	$92+3 3p^3 ({}^3D) 2D^{\circ}+2 3p^3 ({}^2P) 2P^{\circ}$	589023	589002	21
16	$3s^2 S 3p^3 P 3d^4 F_{3/2}^{\circ}$	96	641955		
17	$3p^3 ({}^2P) 2P_{1/2}^{\circ}$	$80+13 3s^2 S 3p^3 P 3d^2 P^{\circ}+5 3s^2 S 3p^1 P 3d^2 P^{\circ}$	642591	642310	281
18	$3s^2 S 3p^3 P 3d^4 F_{5/2}^{\circ}$	98	646042	645988	54
19	$3p^3 ({}^2P) 2P_{3/2}^{\circ}$	$71+13 3s^2 S 3p^3 P 3d^2 P^{\circ}+4 3s^2 S 3p^1 P 3d^2 P^{\circ}$	646119	645409	710
20	$3s^2 S 3p^3 P 3d^4 F_{7/2}^{\circ}$	98	651972	651946	26
21	$3s^2 S 3p^3 P 3d^4 F_{9/2}^{\circ}$	100	660304	660263	41
22	$3s^2 S 3p^3 P 3d^4 P_{5/2}^{\circ}$	$65+28 3s^2 S 3p^3 P 3d^4 D^{\circ}+2 3s^2 S 3p^3 P 3d^2 D^{\circ}$	690311	690304	7

Calculations for Fe XIV, miss identifications and tentative assignments

No.	Configuration <i>LS</i> .	<i>J</i>	<i>P</i>	E_{RCI}	E_{NIST} (%)	E_{obs} (%)
101	$3s^2 4s^2 S$	1/2	+	1427550	1435020 (0.5206)	1426965 (0.0004) T
125	$3s^2 4p^2 P$	1/2	-	1541937	1568840 (1.715)	1541394 (0.0003)
128	$3s^2 4p^2 P$	3/2	-	1548618	1574010 (1.613)	1548258 (0.0002)
136	$3s^2 S 3p^3 P 4s^2 P$	1/2	-	1690299	-	1689695 (0.0004)
150	$3s^2 S 3p^3 P 4p^4 P$	3/2	+	1795164	-	1795032 (0.00007) T
152	$3s^2 S 3p^3 P 4p^4 P$	5/2	+	1802686	-	1802292 (0.0002) T
181	$3s^2 S 3p^3 P 4d^4 D$	5/2	-	1930871	-	1933758 (0.0015)
184	$3s^2 S 3p^3 P 4d^4 D$	7/2	-	1935340	-	1938452 (0.0016)

Heavy near-neutral systems ☹️☹️

- ▶ Central-field approximation not a good approximation
- ▶ Couplings affect radial orbitals a lot
- ▶ States by different configuration occur mixed
- ▶ Brillouin-Wigner perturbation does not work so well
- ▶ The number of CSFs increases tremendously fast with respect to the included correlation orbitals.

Sad (or fun) fact of life: we have to address all these issues



Reducing the computational load – atomic multiconfiguration calculations based on configuration state function generators [☆]

Yan Ting Li ^{a,b}, Kai Wang ^c, Ran Si ^a, Michel Godefroid ^d, Gediminas Gaigalas ^e,
Chong Yang Chen ^a, Per Jönsson ^{b,*}

Reported speedups of factors up to 60 and reduction of number of CSFs with up to a factor of 2.

Speeding up the calculations, selecting important CSFs

The CSFs obtained from 'generators' that act as angular templates,

- ▶ angular resolutions for all matrix elements between CSFs in two groups obtained from a few generator cases.
- ▶ the importance of generators can be ranked from small calculations. Remove unimportant generators (CSFs) from the larger calculations (a priori condensations)

orbital set	CI based on CSFs			CI based on CSFGs			CPU ratio		
	CSF	CPU(DC)	CPU(DCB)	CSFG	CPU(DC)	CPU(DCB)	CSF/CSFG	DC	DCB
{5spdfg}	271 588	3m59s	7m10s	115 340	1m19s	3m22s	2.4	3.0	2.1
{6spdfgh}	682 291	23m3s	42m1s	153 583	3m24s	8m52s	4.3	7.1	4.8
{7spdfgh}	1 287 898	86m13s	150m33s	158 527	6m52s	17m50s	8.1	12.2	8.4
{8spdfgh}	2 088 409	233m6s	445m52s	158 527	14m24s	35m28s	13.2	16.6	12.6
{9spdfgh}	3 083 824	376m6s	950m36s	158 527	19m25s	66m45s	19.4	19.8	14.4
{10spdfgh}	4 274 143	1074m38	2008m57s	158 527	44m13s	110m48s	26.9	24.0	18.2

Partitioned Correlation Function Interaction (PCFI)

Michel Godefroid is taking the picture.



Partitioned Correlation Function Interaction (PCFI)

- ▶ Based on a biorthonormal transformation method, we have tools to construct any matrix element, including Hamiltonian, between individual CSFs or groups of CSFs built on different orbital basis.
- ▶ We can get away from the restriction to use orthogonal orbitals.

A partitioned correlation function interaction approach for describing electron correlation in atoms

S Verdebout¹, P Rynkun², P Jönsson³, G Gaigalas⁴, C Froese Fischer⁵
and M Godefroid¹

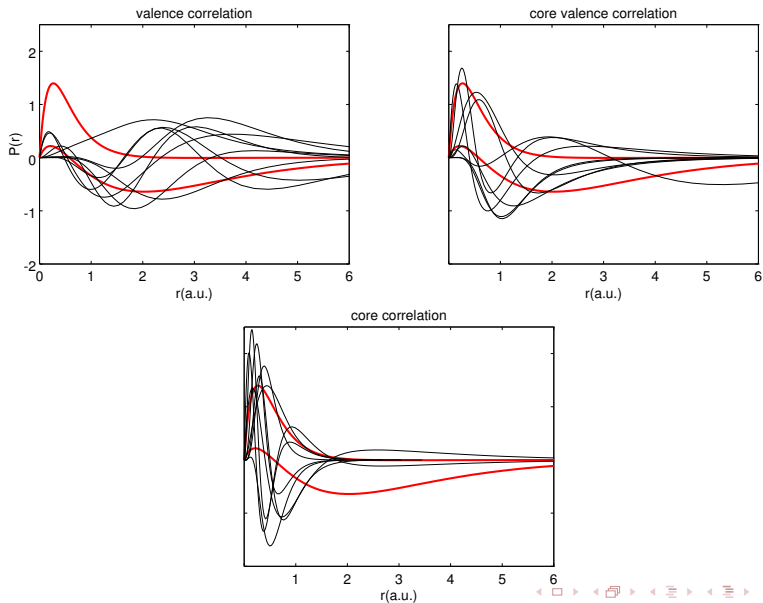
Partitioned correlation function interaction (PCFI)

- ▶ The CSFs in the MR build the zero-order wave function.
- ▶ Remaining CSFs describe corrections; divide CSFs into groups each describing different corrections, e.g., VV, CV, CC
- ▶ Each group has its own orbital sets and is optimized independently (divide and conquer)
- ▶ We can expand the wave function in all the CSFs, but with the difference that CSFs have different orbital sets depending on the group. Full size CI problem.
- ▶ We can merge the CSFs in a group to form a so called PCFs (super CSFs), leading to a low dimensional CI problem.

Partitioned correlation function interaction (PCFI)

- ▶ Full MCHF-BP PCFI program available, with manual
- ▶ Biorthonormal transformation used for computing the matrix elements
- ▶ 2013: Original MCHF-BP implementation inefficient ☹
- ▶ 2023: The use of generators makes this a fast block diagonal problem ☺

Optimally localized orbital sets in $1s^2 2s^2 \ ^1S$ in Be



One orbital set vs many orbital sets

One orbital set (inefficient)

- ▶ MR (spectroscopic orbitals)
- ▶ Correlation must be built outside in
- ▶ VV, most important differential effect
- ▶ VV+CV, second most important effect
- ▶ VV+CV+CC, last

Many non-orthogonal orbital sets (good)

- ▶ MR (spectroscopic orbitals)
- ▶ VV, CV, CC separated, with different orbital sets
- ▶ Calculations for VV, CV, CC decoupled

Results for $1s^2 2s^2 \ ^1S$ in Be

$$|1s^2 2s^2 \ ^1S\rangle, |1s^2 2p^2 \ ^1S\rangle, \underbrace{|\bar{\Lambda}_{VV}\rangle}_{200 \text{ CSFs}}, \underbrace{|\bar{\Lambda}_{CV}\rangle}_{900 \text{ CSFs}}, \underbrace{|\bar{\Lambda}_{CC}\rangle}_{1000 \text{ CSFs}}$$

Compared to 650 000 CSFs built on a single orbital set.

$n \leq$	$E_{5 \times 5}$	$E_{650k \times 650k}$
4	-14.660 679 48	-14.661 403 17
5	-14.665 553 46	-14.664 839 93
6	-14.666 582 83	-14.666 067 32
7	-14.666 905 87	-14.666 541 14
8	-14.667 047 86	-14.666 857 41
9	-14.667 122 76	-14.667 012 75
10	-14.667 168 08	-14.667 114 20

- ▶ 5 basis elements, optimally localized orbital sets.
- ▶ 650 000 CSFs, one orbital set.

Advantages and disadvantages

- ▶ Basis is quite small 😊
- ▶ PCFs with optimally localized orbitals efficient in capturing correlation effects (compact representation) 😊
- ▶ Small basis, little time needed for biorthonormal transformation 😊
- ▶ Losing the variational freedom that comes with the expansion coefficients of the basis; constraining effect 😊
- ▶ We can deconstrain (freely go between a small basis with PCFS to the full CSF basis) 😊

PHYSICAL REVIEW A **88**, 062506 (2013)

Doublet-quartet energy separation in boron: A partitioned-correlation-function-interaction method

Charlotte Froese Fischer*

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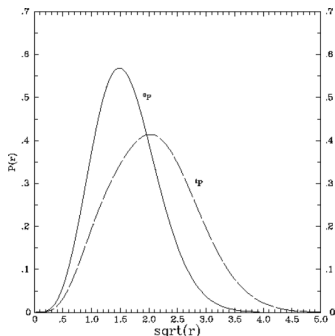
Excitation energies

Excitation energies for $2s^2 2p \ ^2P_{3/2}^0 - 2s 2p^2 \ ^4P_{5/2}$ in C II

n	$E(^2P^o)$	$E(^4P)$	ΔE	$\Delta E(D)$
4	-37.434 442 461	-37.241 016 132	42 452.17	42 454.33
5	-37.441 661 608	-37.246 648 961	42 800.32	42 804.62
6	-37.443 459 176	-37.247 990 596	42 900.39	42 905.57
7	-37.444 132 978	-37.248 491 723	42 938.29	42 944.35
8	-37.444 453 444	-37.248 717 425	42 959.09	
9	-37.444 620 358	-37.248 830 141	42 970.98	
10	-37.444 721 702	-37.248 898 421	42 978.24	
∞	-37.444 878	-37.249 003	42 989.59	
Deconstraint			7.05	
Finite mass			-10.22	
Excitation energy			42 986.42	
Young <i>et al.</i> [20]			42 993.0 \pm 0.9	
ASD [3]			42 993.5	

Accounting for angular dependencies of correlation orbitals

$2p$ Hartree-Fock radial orbitals for $2s2p$ $^1,^3P$ of Be.



Previously, common $2p$ radial orbital for both terms. Now we can have $2s2p$ 1P and $2s2p'$ 1P where $2p$ and $2p'$ non-orthogonal.

Accounting for configuration dependencies of correlation orbitals (Au I)

Configuration	Term	J	Level (cm ⁻¹)	Uncertainty (cm ⁻¹)	Landé-g	Reference
$5d^{10}6s$	2S	$1/2$	0.000		1.997	L1336
$5d^9 6s^2$	2D	$5/2$	9 161.177		1.192	L1336
		$3/2$	21 435.191		0.804	L1336
$5d^{10}6p$	$^2P^\circ$	$1/2$	37 358.991		0.661	L1336
		$3/2$	41 174.613		1.334	L1336
$5d^9 5/2 6s_{1/2} 6p_{1/2}$	$^4P^\circ$	$5/2$	42 163.530		1.532	L1336
$5d^9 5/2 6s_{1/2} 6p_{1/2}$	$^4F^\circ$	$7/2$	45 537.195		1.258	L1336
		$5/2$	46 174.979		1.011	L1336

A proper starting point would be $5d^{10}6p$ and $5d^9 6s 6p'$



Article

Fine-Tuning of Atomic Energies in Relativistic Multiconfiguration Calculations

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Atoms **2023**, *11*(4), 70; <https://doi.org/10.3390/atoms11040070>

- ▶ Transformation of Hamiltonian from jj - to LJS coupling
- ▶ Shift diagonal elements of Hamiltonian
- ▶ Reverse transformation of shifted Hamiltonian
- ▶ Think of CIV3 - and Alan Hibbert

Fine-tuning: semi-empirical corrections

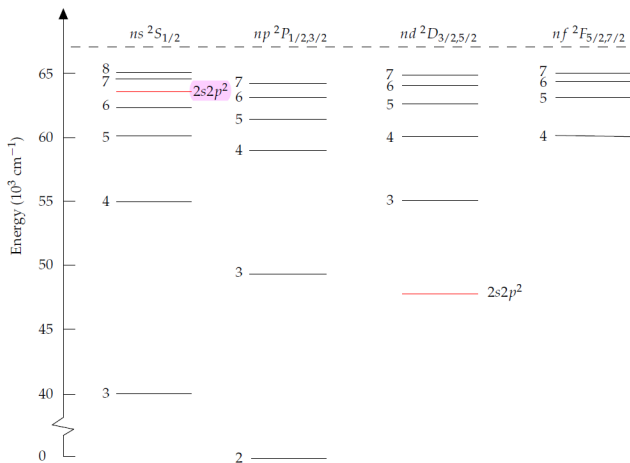


Figure 1. Energy-level diagram for neutral boron. The $2s2p^2\ ^2S_{1/2}$ perturber is embedded in the $ns^2S_{1/2}$ Rydberg series, with high impact on the lifetimes of the nearby states.

Fine-tuning: semi-empirical corrections

Table 5. Lifetimes (in ns) for the $2s^2ns\ ^2S_{1/2}$ Rydberg sequence in neutral boron from ab initio and fine-tuned CI calculations compared with experimental lifetimes and lifetimes from other theory.

State	Ab Initio	Fine-Tuned	Experiment	MCHF
$2s^23s\ ^2S_{1/2}$	4.11	3.99	4.0 (2) ^a	3.97 ^b
$2s^24s\ ^2S_{1/2}$ ⓘ	9.86	8.67	8.7 (4) ^a	8.59 ^b
$2s^25s\ ^2S_{1/2}$	17.6	12.2	11.0 (6) ^b	11.3 ^b
$2s^26s\ ^2S_{1/2}$	25.1	8.40	7.7 (4) ^b	7.65 ^b
$2s2p^2\ ^2S_{1/2}$	3.24	3.29	3.3 (2) ^b	3.65 ^b
$2s^27s\ ^2S_{1/2}$	23.6	11.1	3.6 (3) ^c	8.01 ^b
			8.3 (4) ^b	

^a Reference [30], laser-induced fluorescence. ^b Reference [8]; experiment selective laser excitation and theory fine-tuned MCHF calculations. ^c Reference [31], beam-foil.

Conclusions

- ▶ Heavy neutral systems challenge atomic theory
- ▶ A number of areas for improvements have been identified
- ▶ Working codes to deal with some of the challenges
- ▶ Fast implementation of the PCFI method in GRASP is ongoing
- ▶ Codes must be validated and put to test
- ▶ A collaborative effort (also with experiment) is necessary for progress

Come join the CompAS crowd. Thank you!