Atomic Structure Calculations New developments in relativistic multiconfiguration methods

Per Jönsson

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21 december 2019

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Malmö group for Atomic Astrophysics

- Henrik Hartman
- Jörgen Ekman
- Stefan Gustafsson
- Hampus Nilsson
- Wenxian Li (Post-Doc)
- Kai Wang (former Post-Doc)
- Betul Atalay (former Post-Doc)
- Madeleine Burheim (PhD student)
- Asimina Papoulia (PhD student)
- Sacha Schiffmann (PhD student)





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Computational Atomic Structure Group (COMPAS).



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COMPAS - people

- Charlotte Froese Fischer
- Ian Grant
- Michel Godefroid
- Gediminas Gaigalas
- Tomas Brage
- Jacek Bieron
- Jon Grumer (former PhD)
- Many more

- Provide open source multiconfiguration codes for atomic bound state properties
- Improve computational methodologies to meet the requirements in different applications
- Collect and exchange knowledge in atomic structure calculations
- Lab astrophysics part knowledge exchange
- Educate new generation of scientists
- Collaboration to attract funding

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- Michel, a hommage
- Multiconfiguration methods and codes
- Atomic structure calculations science goals
- What have we done and what did we learn?
- New developments: PCFI calculations

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Working with Michel since 1993 - a great pleasure



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Working with Michel - first paper Code development: F-dependent CI program

PHYSICAL REVIEW A

VOLUME 51, NUMBER 3

MARCH 1995

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Multiconfigurational Hartree-Fock calculations of hyperfine-induced transitions in heliumlike ions

A. Aboussaïd and M. R. Godefroid

Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, Code Postal 160/09, 50 avenue F. Roosevelt, B-1050, Brussels, Belgium

> P. Jönsson Department of Physics, Lund Institute of Technology, P.O. Box 118, S-22100 Lund, Sweden

C. Froese Fischer Department of Computer Science, Vanderbilt University, Nashville, Tennessee 37235 (Received 8 July 1994)

Working with Michel - science should be fun!



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Michel Honorary Doctor at Malmö University



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Michel as a code developer - Seven programs with Michel as an author in Computer Physics Communications



Computer Physics Communications

Volume 51, Issue 3, November 1988, Pages 285-293



Non-orthogonal orbitals in MCHF or configuration interaction wave functions

A. Hibbert *, C. Froese Fischer +, M.R. Godefroid **



Computer Physics Communications Volume 64, Issue 3, June 1991, Pages 486-500



A program for performing angular integrations for transition operators

Charlotte Froese Fischer, Michel R. Godefroid, Alan Hibbert

'A limited amount of non-orthogonality is allowed between orbitals of the initial and final state'



Computer Physics Communications Volume 176, Issue 8, 15 April 2007, Pages 559-579



An MCHF atomic-structure package for large-scale calculations \bigstar

Charlotte Froese Fischer ^a ≈ ∞, Georgio Tachiev ^a, Gediminas Gaigalas ^b, Michel R. Godefroid ^c

'For transition probabilities the orbitals of the initial and final state need not be orthogonal. A bi-orthogonal transformation is used for the evaluation of matrix elements in such cases.'



Computer Physics Communications Volume 235, February 2019, Pages 433-446



RIS 4: A program for relativistic isotope shift calculations ★

J. Ekman ^a 😤 🖾, P. Jönsson ^a, M. Godefroid ^b, C. Nazé ^b, G. Gaigalas ^c, J. Bieroń ^d

Includes an accurate and general formalism for the electron-nucleus interaction (J. Ekman)

- ► State in *N*-electron atom described by a wave function $\Psi(\mathbf{q}_1, \dots, \mathbf{q}_N)$
- Wave function solution to the wave equation

$$\mathcal{H}\Psi(\mathbf{q}_1,\ldots,\mathbf{q}_N)=E\Psi(\mathbf{q}_1,\ldots,\mathbf{q}_N)$$

► Differential operator \mathcal{H} depends on the underlying quantum mechanical formalism. *E* total energy of the system.

(4月) (4日) (4日)

- Non-relativistic
- Breit-Pauli terms added as perturbations
- Fully relativistic
- Transverse Breit interaction and QED effects added as perturbations.

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Dimensionality: 30 electrons, represent the wave function on a grid with 10 points per dimension, total 10⁹⁰ grid points!

Product representation needed

Singularities

$$\sum_{i < j}^{N} rac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Wave function has cusps (nightmare)

QED is not fully developed

Variational multiconfiguration methods

Multiconfiguration Hartree-Fock + Breit Pauli (MCHF-BP) Multiconfiguration Dirac-Hartree-Fock (MCDHF)

• Expand in many-electron basis functions (CSFs) $\Phi(\gamma_i JM_J)$

$$\Psi(\gamma JM_J) = \sum_i c_i \Phi(\gamma_i JM_J)$$

- CSFs symmetry adapted, anti-symmetrized products of one-electron orbitals. Radial part represented on a grid.
- Radial orbitals fulfill the orthogonality condition

$$\int_0^\infty P(nl;r)P(n'l;r)\,dr=\delta(n,n')$$

- Energy functional: radial integrals × angular coefficients × weighted product of expansion coefficients of CSFs for targeted states + terms for orthonormality
- Apply variational principle
- Eigenvalue problem for coefficients

$$\mathbf{Hc} = E\mathbf{c}$$

where $H_{ij} = \langle \Phi(\gamma_i J M_J) | \mathcal{H} | \Phi(\gamma_j J M_J) \rangle$

- Coupled integro differential equations for the radial orbitals
- Eigenvalue problem and differential equations solved iteratively until convergence

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Transition rates, HFS, IS parametes etc.

- Transformations of wave functions to bi-orthonormal orbital basis
- Radial integrals × angular coefficients × product of expansion coefficients of CSFs

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ATSP2K (Fischer, Tachiev, Gaigalas, Godefroid) Multiconfiguration Hartree-Fock-Breit Pauli (MCHF-BP)

GRASP2018 (Fischer, Gaigalas, Jönsson, Bieron) Multiconfiguration Dirac-Hartree-Fock (MCDHF)

- Bound state properties: transition energies, rates etc
- ▶ Broadening: HFS, IS, Landé-g_J, external fields
- MPI for supercomputing
- Perturbative corrections, non-orthogonal orbital sets
- Open source users can modify and add modules
- Extensive documentation to ensure correct operation

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- Use a model to construct basis functions from orbitals: target different electron correlation effects; VV, CV CC.
- Within a model: more orbitals give more basis functions
- Relax model: include more electron correlation effects
- Everything comes with a prize large expansions
- Accurate results supercomputing

(4月) イヨト イヨト

Shortcuts - Brillouin-Wigner perturbation theory

Construct only part of the matrix $\{\underbrace{\Phi(\gamma_1 J), \dots, \Phi(\gamma_M J)}_{\text{zero-order, dim } M}, \underbrace{\Phi(\gamma_{M+1} J), \dots, \Phi(\gamma_{M+N} J)}_{\text{first-order, dim } N}\}$

M N



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Science Part

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'Lab spectroscopy has long lagged behind telescope observations, but it is striking just how wide the gap has now grown'

Editorial, Nature, 503, 437 (2013)

Oscillator strengths are extremely difficult to measure

Gold standard for oscillator strengths gf includes two steps:

- Lifetimes with time-resolved laser spectroscopy (LIF)
- Branching fractions (BF) with spectrometer (FTS)

Setup in Lund, Sweden (courtesy Hans Lundberg)



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Lifetime of upper state together with branching fractions from FTS give the oscillator strengths of individual transitions



- Limitations on the ions and the transitions for LIF
- Uncertainties in lifetimes due to plasma effects
- Uncertainties in BF due to calibration of spectrometer
- Uncertainties of oscillator strengths at best 5 10 %
- Very few labs left that perform LIF measurements!
- Future: calculated lifetimes and experimental BF
- Good compromise.

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Accurate oscillator strengths in Si I and Si II

Astronomy & Astrophysics manuscript no. PehlivanRhodin April 26, 2018

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Accurate and experimentally validated transition data for Si1 and Si1

A. Pehlivan Rhodin^{1,2}, H. Hartman^{1,2}, H. Nilsson², and P. Jönsson¹

- LIF and BF measurements (e.g. Hartman's talk)
- Calculations;
 - Si I, 20 $\times 10^{6}$ CSFs Si II. 12 $\times 10^{6}$ CSFs

Si I comparison experiment and theory



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Lower	Upper	λ	Athis calc.	A^a_{exp}	A^b_{theo}	A^{c}_{theo}	
Level	Level	(nm)	(s^{-1})	(s^{-1})	(s^{-1})	(s^{-1})	
$3s^2 3p {}^2P^o_{1/2}$	3s ² 3d ² D _{3/2}	126.042	2.48E+09	-	2.60E+09	2.01E+09	9
$3s^2 3p {}^2P_{3/2}^{o'}$	3s ² 3d ² D _{5/2}	126.474	2.92E+09	-	3.04E+09	2.31E+09	9
$3s^2 3p {}^2P_{3/2}^{o'}$	3s ² 3d ² D _{3/2}	126.500	4.55E+08	-	4.63E+08	5.23E+08	8
$3s^2 3p {}^2P_{1/2}^{o'2}$	3s3p ² ² S _{1/2}	130.437	3.74E+08	-	3.64E+08	3.60E+08	8
$3s^2 3p {}^2P_{3/2}^{o}$	$3s3p^2 {}^2S_{1/2}$	130.928	6.33E+08	-	6.23E+08	6.60E+08	8
$3s^2 3p {}^2P_{1/2}^{o'2}$	$3s^24s {}^2S_{1/2}$	152.671	3.65E+08	-	3.81E+08	3.90E+08	8
$3s^2 3p {}^2P_{3/2}^{o}$	$3s^24s {}^2S_{1/2}$	153.343	7.20E+08	-	7.52E+08	7.90E+08	8
$3s^2 3p {}^2P_{1/2}^{o'2}$	3s3p ² ² D _{3/2}	180.801	2.00E+06	-	2.54E+06	1.00E+0.00	5
$3s^2 3p {}^2P_{3/2}^{o}$	3s3p ² ² D _{5/2}	181.693	1.99E+06	-	2.65E+06	2.00E+05	5
$3s^2 3p {}^2P_{3/2}^{o}$	3s3p ² ² D _{3/2}	181.745	2.29E+05	-	3.23E+05	5.30E+04	4
$3s^2 3p {}^2P_{1/2}^{o'2}$	3s3p ² ⁴ P _{3/2}	232.852	36	10 ± 5	23.5	11.1	
$3s^2 3p {}^2P_{1/2}^{0}$	$3s3p^2 {}^4P_{1/2}$	233.441	5280	5200 ± 988	5510	2296	
$3s^2 3p {}^2P_{3/2}^{0}$	$3s3p^2 {}^4P_{5/2}$	233.461	2205	2460 ± 197	2440	397	
$3s^2 3p {}^2P_{3/2}^{o}$	$3s3p^2 {}^4P_{3/2}$	234.420	1119	1220 ± 122	1310	157	
$3s^2 3p {}^2P_{3/2}^{o'2}$	$3s3p^2 {}^4P_{1/2}$	235.017	4882	4410 ± 926	4700	3078	

^(a) Calamai et al. (1993); ^(b) Nahar (1998); ^(c) Aggarwal & Keenan (2014)

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Work by:

Asli Pehlivan, Asimina Papoulia, Madeleine Burheim, Betul Atalay

- ► Measurements/calculations done for Mg I, AI I-II, Si I-IV
- Very good agreement between theory and experiment
- Hfs also measured and analyzed
- Valuable validation!

(4月) イヨト イヨト

Hinode, X-ray telescope



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Hinode, science goals

- Understand how energy generated by magnetic-field changes in the lower solar atmosphere (photosphere) is transmitted to the upper solar atmosphere (corona),
- Understand how that energy influences the dynamics and structure of that upper atmosphere, and
- Determine how the energy transfer and atmospheric dynamics affects the interplanetary-space environment.
- Atomic data for magnetic field determination, Zeeman induced transitions (compare Tomas Brage)
- Atomic data for plasma modeling
- Atomic data for line identification

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- MCDHF/RCI do very well for highly ionized systems
- Be- to Cl-like ions of Cr, Fe, Ni etc
- Hundreds of states for each ion
- Computed λ with uncertainties 1 mÅ for line identification
- MCDHF/RCI data validated against RMBPT (Kai Wang)
- New concept 'calculations with spectroscopic accuracy'
Systematic MCDHF calculations for Mg-like Fe

Atoms 2016, xx, 1-x; doi:10.3390/-----



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 Grant ³

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

Tabell : Number of basis functions 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%	
				4.3

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Energy uncertainties for different computational models - detection of miss assignments



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Atomic Data and Nuclear Data Tables 120 (2018) 152-262



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}

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

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Calculations for Fe XIV

NØ.	Level	LS-composition	E _{RCI}	E _{NIST}	ΔE
1	3s ² 3p ² P ^o _{1/2}	97	0	0	0
2	$3s^2 3p P_{3/2}^{\circ}$	97	18855	18853	2
3	$3s^2S 3p^2({}^3_2P) {}^4P_{1/2}$	98	225086	225114	-28
4	$3s^2S 3p^2(\frac{3}{2}P) {}^4P_{3/2}$	99	232777	232789	-12
5	$3s^2S 3p^2(\frac{3}{2}P) ^4P_{5/2}$	97	242372	242387	-15
6	$3s^2S 3p^2(\frac{1}{2}D)^2D_{3/2}$	86+11 3s ² 3d ² D	299402	299242	160
7	$3s^2S 3p^2(\frac{1}{2}D)^2D_{5/2}$	$85+11 3s^2 3d^2D+2 3s^2S 3p^2({}_2^3P)^4P$	301627	301469	158
8	$3s^2S 3p^2(\frac{1}{0}S)^2S_{1/2}$	$75+21 \ 3s^{2}S \ 3p^{2}(^{3}_{2}P)^{2}P$	364945	364693	252
9	$3s^2S 3p^2({}^3_2P)^2P_{1/2}$	$75+22 3s^2 S 3p^2 ({}_0^1 S)^2 S$	388711	388510	201
10	$3s^2S 3p^2(\frac{3}{2}P)^2P_{3/2}$	$95+2 \ 3p^2 (\frac{1}{2}D) \ ^1D \ ^3d \ ^2P$	396687	396512	175
11	3s ² 3d ² D _{3/2}	$86+11 3s^{2}S 3p^{2}(^{1}_{2}D)^{2}D+2 3p^{2}(^{1}_{0}S)^{1}S 3d^{2}D$	473231	473223	8
12	$3s^2 3d^2 D_{5/2}$	$86+11 3s^{2}S 3p^{2}({}^{1}_{2}D)^{2}D+2 3p^{2}({}^{1}_{0}S)^{1}S 3d^{2}D$	475215	475202	13
13	$3p^{3}(^{2}_{3}D)^{2}D^{\circ}_{3/2}$	64+27 3s ² S 3p ³ P 3d ² D°+4 3p ³ (² P) ² P°	576599	576383	216
14	$3p^{3}(^{2}_{3}D)^{2}D^{\circ}_{5/2}$	69+29 3s ² S 3p ³ P 3d ² D°	580450	580233	217
15	$3p^{3}(_{3}^{4}S) {}^{4}S_{3/2}^{\circ}$	$92+3 3p^{3}({}^{2}_{3}D) {}^{2}D^{\circ}+2 3p^{3}({}^{2}_{1}P) {}^{2}P^{\circ}$	589023	589002	21
16	$3s^2S^2p^3P^3d^4F_{3/2}^{\circ}$	96	641955		
17	$3p^{3}(^{2}_{1}P)^{2}P^{\circ}_{1/2}$	80+13 3s ² S 3p ³ P 3d ² P°+5 3s ² S 3p ¹ P 3d ² P°	642591	642310	281
18	3s ² S 3p ³ P 3d ⁴ F ₅ / ₂	98	646042	645988	54
19	$3p^{3}({}^{2}P)^{2}P^{\circ}_{2/2}$	$71+13$ 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	$3s^2S 3p^3P 3d^4F_{2/2}^{\circ}$	98	651972	651946	26
21	$3s^{2}S 3p^{3}P 3d^{4}F_{0}^{0}$	100	660304	660263	41
22	$3s^2S 3p^3P 3d^4P_{0}^{\circ}$	$65+28$ 3s ${}^{2}S$ 3p ${}^{3}P$ 3d ${}^{4}D^{\circ}+2$ 3s ${}^{2}S$ 3p ${}^{3}P$ 3d ${}^{2}D^{\circ}$	690311	690304	7

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Calculations for Fe XIV, miss identifications and tentative assignments

No.	Configuration LS.	J	Р	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)

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Review

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

Per Jönsson ¹,*, Gediminas Gaigalas ², Pavel Rynkun ², Laima Radžiūtė 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 CI-like
- Spectroscopic accuracy a number of miss identifications found, tentative identifications confirmed
- Much work by Kai Wang

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Gaia ESO survey



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science goals

www.gaia-eso.eu/sites/default/files/messenger-no147-25-31.pdf

- Abundance determination for 10 million stars
- Abundances accurate down to 1%
- ▶ Na, Mg, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Sr, Zr, Ba
- Chemical similarities
- Atomic transition data and broadening data
- Atomic data for Rydberg states for 3D non-LTE modeling

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- Measurements and calculations planned for Ca, Ti II (Wenxian Li)
- Accurate calculations for many of the remaining elements extremely challenging.
- Semi-empirical tuning necessary, orthogonal operators?

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Combine computed electronic quantities with of measured HFS and IS for isotopic chains (ISOLDE) to extract nuclear parameters Our financing: Swedish Science Council

- Heavy and superheavy neutral elements
- ► IS cancellation effects: very accurate wave functions needed
- ► HFS oscillations in computed A and B constants as a function of the increasing orbital set
- Correlation deep down in the atomic core

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- Proper relativistic IS operators (RIS4)
- Refined treatment of electron-nucleus interaction, general nuclear models, deformations etc (RIS4)
- Hyperfine anomalies, variety of nuclear magnetization models
- Natural orbitals transformation
- ▶ Small system, we do really well (+)
- Large system, challenging but possible, Q for many ions
- Orbital set needs to be further extended to obtain well converged electronic quantities (-)
- Size of CSF expansion grows too fast to include core-core correlation effects deep down (-)

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Science Part - what have we learnt?

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MCDHF/RCI limitations and bottle necks

- Hard to extend Hamiltonian matrix size much more than a few million CSFs per symmetry block (CPU requirement and memory)
- Computed properties sometimes not fully converged with respect to the orbital basis
- Computational models can often not be extended to include CC correlation
- Sometimes oscillatory behavior with respect to the increasing orbital basis
- Energy shifts in strongly interacting systems due to unbalances
- No way to a priori condense a CSF list

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- Complex shell structures (open *f*-shells), basis expansions blow up as a function of the orbital set
- Dense level structures problematic in general
- Neutral systems are harder than a few times ionized systems

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Ways forward?

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Non-orthonormal orbital sets

PHYSICAL REVIEW E

VOLUME 52, NUMBER 4

OCTOBER 1995

Transition probability calculations for atoms using nonorthogonal orbitals

Jeppe Olsen,¹ Michel R. Godefroid,² Per Jönsson,³ Per Åke Malmqvist,¹ and Charlotte Froese Fischer⁴



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Test case for the paper

$$1s^22s^22p\ ^2P^o - 1s^22s^2p^2\ ^2D$$
 in B I

- ▶ 2s, and 2p orbitals of the two configurations are very different
- ▶ We want to perform separate calculations for the two states.
- Problem: how to compute the transition rates? Racha algebra requires one orthonormal orbital set.
- Solution: transform wave functions so that the orbital basis becomes biorthonormal

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I and r built from different orbital sets

$$\Psi_l = \sum_{i=1}^{N_l} c_i^l \Phi_i^l$$
 and $\Psi_r = \sum_{i=1}^{N_r} c_i^r \Phi_i^r$

Transform I and r orbital sets to become biorthonormal, counter transform expansion weights (representation change)

$$\Psi_{l} \equiv \sum_{i=1}^{N_{l}} \widetilde{c}_{i}^{\, \prime} \widetilde{\Phi}_{i}^{\prime} \quad \text{and} \quad \Psi_{r} \equiv \sum_{i=1}^{N_{r}} \widetilde{c}_{i}^{\, \prime} \widetilde{\Phi}_{i}^{r}.$$

Counter transformation distributes weights of one CSF onto other CSFs (small subset) according to Malmqvists algorithm

Racah algebra can be used for new representation.

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Partitioned Correlation Function Interaction (PCFI) Michel is taking the picture.



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Partitioned Correlation Function Interaction (PCFI)

- Based on the transformation we have tools to construct any matrix element, including Hamiltonian, between individual CSFs or groups of CSFs built on different orbital basis.
- Much faster than other methods (Löwdins co-factor method)

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Partitioned correlation function interaction (PCFI)

IOP PUBLISHING

JOURNAL OF PHYSICS B: ATOMIC, MOLECULAF

J. Phys. B: At. Mol. Opt. Phys. 46 (2013) 085003 (18pp)

doi:10.1088/095

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)

- Main CSFs 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 it's 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.

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Partitioned correlation function interaction (PCFI)

- ► Full MCHF-BP PCFI program available, with manual
- Racah algebra can not be used for matrix elements (-)
- Biorthonormal transformation needed for matrix elements (-)
- Original MCHF-BP implementation very slow (-)
- Now tools to make the transformation very efficient and fast

Optimally localized orbital sets in $1s^22s^{2-1}S$ in Be



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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

$n \leq$	$E_{5 \times 5}$	E _{CAS-MCHF}		
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		

CAS-MCHF 650 000 CSFs, days on a super computer cluster

Optimally localized orbital sets, a few hours on a PC.

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- ▶ Basis is quite small (+)
- PCFs with optimally localized orbitals efficient in capturing correlation effects (compact representation) (+)
- Small basis, little time needed for biorthonormal transformation (+)
- Loosing the variational freedom that comes with the expansion coefficients of the basis; constraining effect (-)
- We can deconstrain

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PHYSICAL REVIEW A 88, 062506 (2013)

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

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Excitation energies

Excitation energies for $2s^22p \ ^2P^0_{3/2} - 2s2p^2 \ ^4P_{5/2}$ in C II

n	$E(^2P^o)$	$E(^4P)$	ΔE	$\Delta E(\mathbf{D})$
4	-37.434 442 461	-37.241 016 132	42 452.17	42 454.33
5	-37.441 661 608	-37.246648961	42 800.32	42 804.62
6	-37.443 459 176	-37.247 990 596	42 900.39	42 905.57
7	-37.444132978	-37.248 491 723	42 938.29	42 944.35
8	-37.444453444	-37.248717425	42 959.09	
9	-37.444620358	-37.248830141	42 970.98	
10	-37.444 721 702	-37.248898421	42978.24	
∞	-37.444878	-37.249003	42 989.59	
Dee	constraint		7.05	
Fin	ite mass		-10.22	_
Exc	citation energy		42 986.42	
You	ung <i>et al</i> . [20]		42993.0 ± 0.9	
AS	D [3]		42 993.5	

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Complete-active-space multiconfiguration Dirac-Hartree-Fock calculations of hyperfine-structure constants of the gold atom

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Oscillations, one orbital set



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One orbital set (inefficient)

- MR (spectroscopic orbitals)
- If VV+CV or VV+CV+CC; large oscillations with respect to increasing orbital set

Many non-orthonormal orbital sets (good)

- MR (spectroscopic orbitals)
- ▶ VV, CV, CC, SP, OP, separated, with different orbital sets
- Calculations for VV, CV, CC, SP, OP decoupled
- ► Oscillations with respect to increasing orbital set damped out → allows for basis extrapolation

(4月) イヨト イヨト



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In progress.

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Thank you for your attention

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