Uncertainties for Theoretical Atomic Data: Transition Energies and Probabilities

Per Jönsson, Henrik Hartman, Jörgen Ekman
Tomas Brage, Roger Hutton, Kai Wang

Group for Materials Science and Applied Mathematics
Malmö University, Sweden

21 december 2016

Outline

- The Computational Atomic Structure (COMPAS) group
- Systematic computational procedures
- Uncertainty assessment for transition energies
- Uncertainty assessment for transition rates

Computational Atomic Structure (COMPAS) Group

Aim and activities of the COMPAS group

- 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
- Educate new generation of scientists
- Collaboration to attract funding

Open source multiconfiguration codes

- ATSP2K
  multiconfiguration Hartree-Fock-Breit Pauli (MCHF-BP)
- GRASP2016
  multiconfiguration Dirac-Hartree-Fock (MCDHF)
- Bound state properties: transition energies, rates etc
- MPI for supercomputing
- Perturbative corrections, non-orthogonal orbital sets
- Open source – users can modify and add modules
- Extensive documentation to ensure correct operation

Assessing accuracy in multiconfiguration calculations

General principles

- Code is nothing – model is everything
- Accurate results – supercomputing
- Systematic enlargement of basis functions – monitor convergence of computed transition energies, rates etc

Transition rates (E1,E2 etc)

- Internal validation – consistency of rates in different gauges

Hard cases

- Complex shell structures (W with open f-shells) where basis expansions blow up – convergence difficult to attain
- Neutral systems are harder than a few times ionized systems

Systematic calculations

Basis set methods: wave function given as a basis expansion

- Many-electron basis functions constructed from one-electron orbitals
- Use a model to construct basis functions from orbitals: target different electron correlation effects
- Within a model: more orbitals give more basis functions
- Relax model: include more electron correlation effects
- Everything comes with a prize

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

OPEN ACCESS
atoms
ISSN 2218-2004
www.mdpi.com/journal/atoms

Article

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

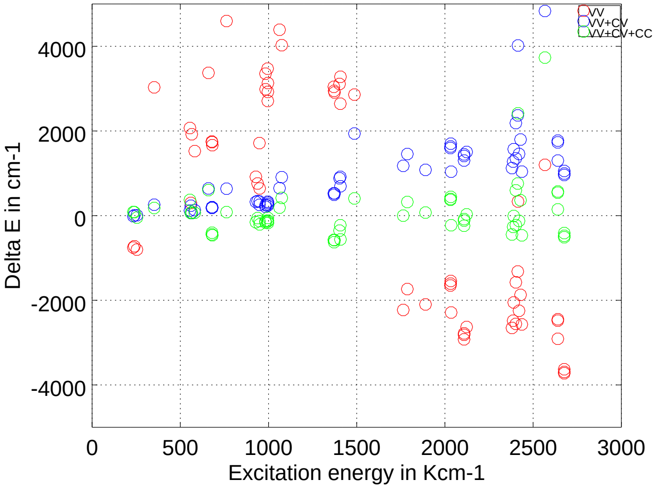
Stefan Gustafsson, [1] Per Jönsson, [1*] Charlotte Froese Fischer, [2] and Ian Grant [3]

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%

Energy uncertainties for different computational models



Complete data sets from MCDHF calculations

- Hundreds of states for a large range of ions in the Be-, B-, C-, N-, O-, F-, Ne-, Mg-, Al-, Si-, P-, S- sequences
- Accurate transition energies, uncertainties 0.01 - 0.05 %
- Validated against relativistic many-body perturbation (RMBPT) calculations for several sequences
- RMBPT calculations perform very well for more highly charged ions!
- Calculations also for W ions, e.g. $3d^k$, uncertainty degrades somewhat but predictive powers
- Calculations for line identification in W (Roger Huttons talk)

Transition energies in W

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

OPEN ACCESS
atoms
ISSN 2218-2004
www.mdpi.com/journal/atoms

Article

Core effects on transition energies for $3d^k$ configurations in Tungsten ions

Charlotte Froese Fischer [1,†], Gediminas Gaigalas [2,†] and Per Jönsson [3,†]

W^{51+} (V-like)

				GRASP1	GRASP2	Obs	GRASP$_P$	RMBPT$_g$	RMBPT$_s$
$3d^5\ ^4P^3$	5/2	$3d^5\ ^6S^5$	5/2	21.290	21.243	21.203(3)	21.317	21.185	21.492
$3d^5\ ^4P^3$	5/2	$3d^5\ ^4G^5$	7/2	17.700	17.674	17.660(3)	17.660	17.655	17.826
$3d^5\ ^4P^3$	5/2	$3d^5\ ^4D^5$	3/2	17.253	17.227	17.215(3)	17.247	17.228	17.249
$3d^5\ ^4P^3$	5/2	$3d^5\ ^4D^5$	5/2	15.368	15.350				
$3d^5\ ^4P^3$	5/2	$3d^5\ ^2F^5$	7/2	14.541	14.529	14.531(3)	14.475	14.537	14.513
$3d^5\ ^4P^3$	5/2	$3d^5\ ^2D^1$	3/2	12.136	12.122				
$3d^5\ ^4P^3$	5/2	$3d^5\ ^6S^5$	5/2	9.747	9.728				

Status transition energies

- Well establish procedures for estimating uncertainties
- Extrapolation along iso-electronic sequences
- Enough accurate experimental data to assess computational procedures and models
- Calculations provide good support for experimental identifications
- Code improvement to include more correlation
- Open f-shells still very challenging
- Code can not be used as a black box

Lifetimes

- Very few accurate lifetime measurements
- Fast-beam laser and picosecond spectroscopy, uncertainties down to 0.5 %, work not continued
- Accurate storage ring and EBIT measurements, often M1
- Many lifetimes with large error bars.
- Much inconsistent experimental lifetime data

Picosecond spectroscopy: $6p^2(^3P)7s\ ^4P_{1/2}$ in Bi

Physica Scripta. Vol. 39, 442–446, 1989.

Laser Spectroscopy Studies of Lifetimes in Neutral Atoms

Jörgen Carlsson

Department of Physics, Lund Institute of Technology, P.O. Box 118, S-221 00 Lund, Sweden

Table 2. Natural radiative lifetime of the studied bismuth state

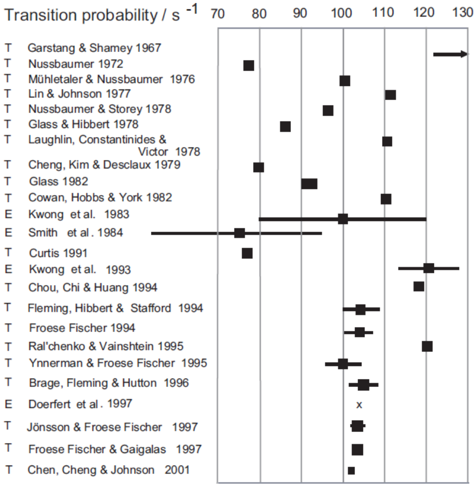
State	Wavelength/nm	Lifetime/ns				
		This study	Ref. 13	Ref. 14	Ref. 15	Ref. 16
Bi $6p^2(^3P_0)7s\ ^4P_{1/2}$	306.8	5.66 (0.03)	$5.4^{+2.3}_{-1.7}$	5.9 (0.2)	4.7 (1.0)	4.3 (0.2)

Uncertainty picosecond measurement: 0.5%
Often measurements with small error bars, non-overlapping, see Refs 14, 16:

Storage ring measurements: $2s^2\ ^1S_0 - 2s2p\ ^3P_1$ in C III

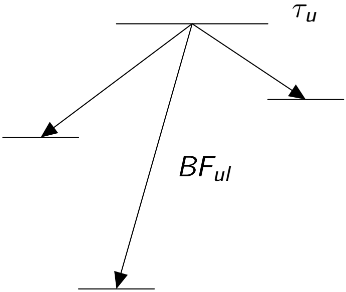
Träbert, Atoms 2014, 2(1), 15-85

E = exp., T = theory



Transition rates from LIF + BF

Lifetime with laser induced fluorescence (LIF) +
branching fraction (BF) with Fourier Transform Spectra (FTS) =
Gold standard for line list data

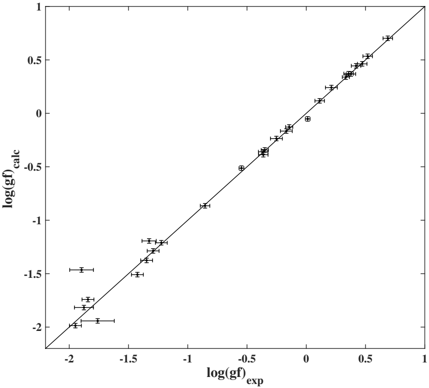


Transition rates from LIF + BF

- Restricted to neutral and singly charged ions
- Branching fractions: calibration, self absorption (radiative transfer), unobserved lines, 0-30%.
- Radiative lifetime: statistical and systematic errors, 5-15%
- Few labs, NIST, Imperial College, Lund, LIF closing down.
- Can discriminate between calculations, but difficult to assess theoretical uncertainties

LIF + BF vs calculations in Mg I

Pehlivan et al. A & A, in press 2016, two experimental outliers



Internal uncertainty assessment of transition rates A

Uncertainty δA from transition matrix elements in length and velocity gauge + transition energies

$$\delta A' = (\delta E + \delta S) A'$$

A' energy scaled transition rate and

$$\delta E = |E_{calc} - E_{obs}|/E_{obs}, \quad \delta S = |S_l - S_v|/\max(S_l, S_v)$$

where S_l and S_v line strength in length and velocity form.

(Froese Fischer, Phys. Scr. 2009, T134 014019)

Statistical validation

Atoms **2014**, *2*, 215-224; doi:10.3390/atoms2020215

OPEN ACCESS
atoms
ISSN 2218-2004
www.mdpi.com/journal/atoms

Review

Validation and Implementation of Uncertainty Estimates of Calculated Transition Rates

Jörgen Ekman [1,*], Michel R. Godefroid [2] and Henrik Hartman [1]

Assumptions statistically validated by an analysis of a large number of allowed transitions from different and highly accurate calculations (as judge by transition energies)

Uncertainties from method intercomparisons

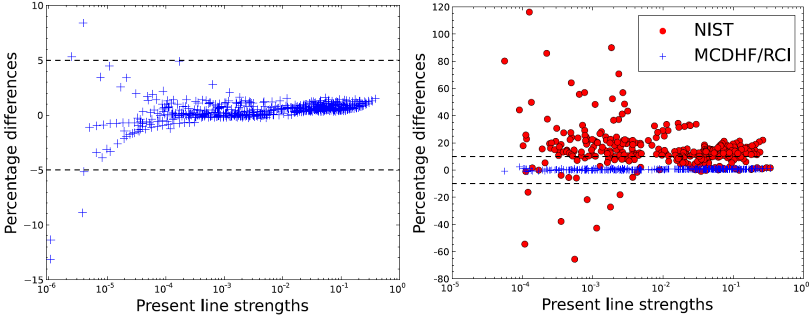
The Astrophysical Journal Supplement Series, 223:3 (33pp), 2016 March
doi:10.3847/0067-0049/223/1/3

CALCULATIONS WITH SPECTROSCOPIC ACCURACY: ENERGIES AND TRANSITION RATES IN THE NITROGEN ISOELECTRONIC SEQUENCE FROM Ar XII TO Zn XXIV

K. Wang[1,2,3], R. Si[3,4], W. Dang[1], P. Jönsson[5], X. L. Guo[3,4], S. Li[2,3,4], Z. B. Chen[6], H. Zhang[2], F. Y. Long[2], H. T. Liu[2], D. F. Li[2], R. Hutton[3,4], C. Y. Chen[3,4], and J. Yan[2,7,8]

Uncertainty assessments from method intercomparisons (RMCBPT, RMCDHF/RCI)

Uncertainties from method intercomparisons



Comparing MCDHF/RCI and NIST line strengths with RMBPT line strengths. Percental difference

Status transition rates

- Internal accuracy assessment from δE and δS can, and should, be used
- Systematic method intercomparisons to confirm uncertainty estimates
- Systematic method intercomparisons should be made also for complex systems.
- LIF + BF measurements important for assessment, but accuracy needs to be improved
- Funding is an issue for providing data

End

Thank you for your attention