Calculations of forbidden transition probabilities in lanthanides and of hyperfine structure constants in neutron-capture elements using the GRASP package

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UMONS

fnrs

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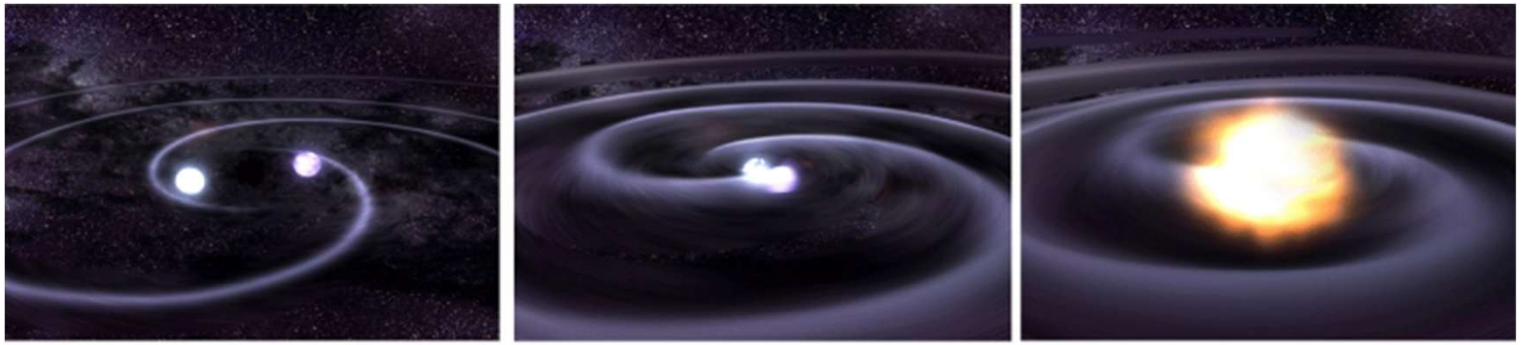
Outlines

- Forbidden lines in lanthanides: astrophysical context
- Forbidden lines in lanthanides: computation strategies
- Forbidden lines in lanthanides: results
- HFS in neutron-capture elements: astrophysical context
- HFS in neutron-capture elements: computation strategies
- HFS in neutron-capture elements: results
- Conclusion & Prospects

Forbidden lines: astrophysical context

GW170817 event:
- Detection of gravitational waves from neutron star merger for the first time on August 17, 2007 (Abbott+, 2017)

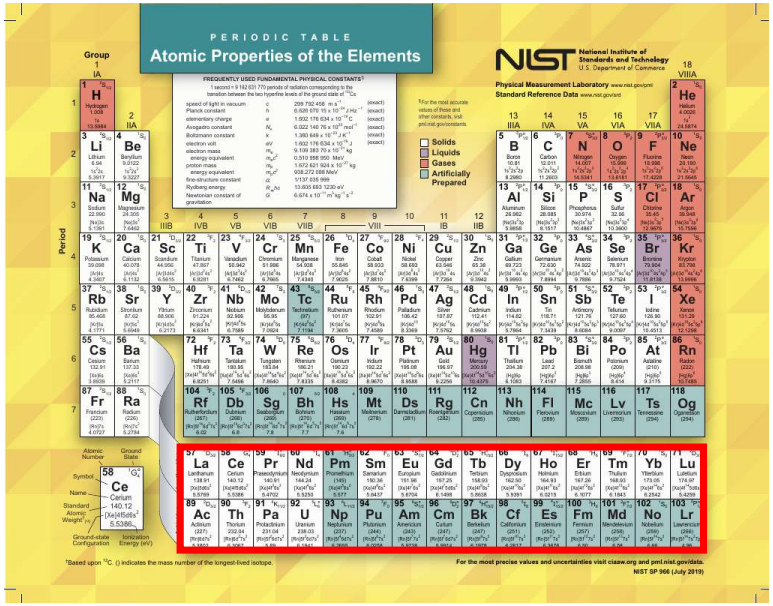


Evolving neutron star binary system (NASA/CXC/GSFC/T. Strohmayer)

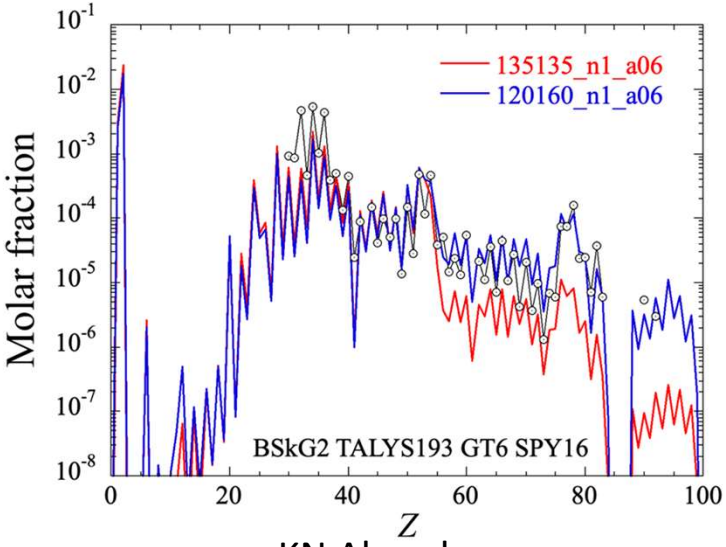
- Also produces electromagnetic signal powered by the ejection of hot and radioactive matter: kilonova (KN)

Forbidden lines: astrophysical context

- Heavy r-processed elements (Z>26) are abundant in KN.
- Lanthanides & actinides dominate the KN opacity due to their large spectral density (open f-subshell) and abundances.



Periodic Table (NIST)



KN Abundances

(Goriely & Just, private communication)

Forbidden lines: astrophysical context

Nebular phase from ~1 week after NS merger (NLTE)

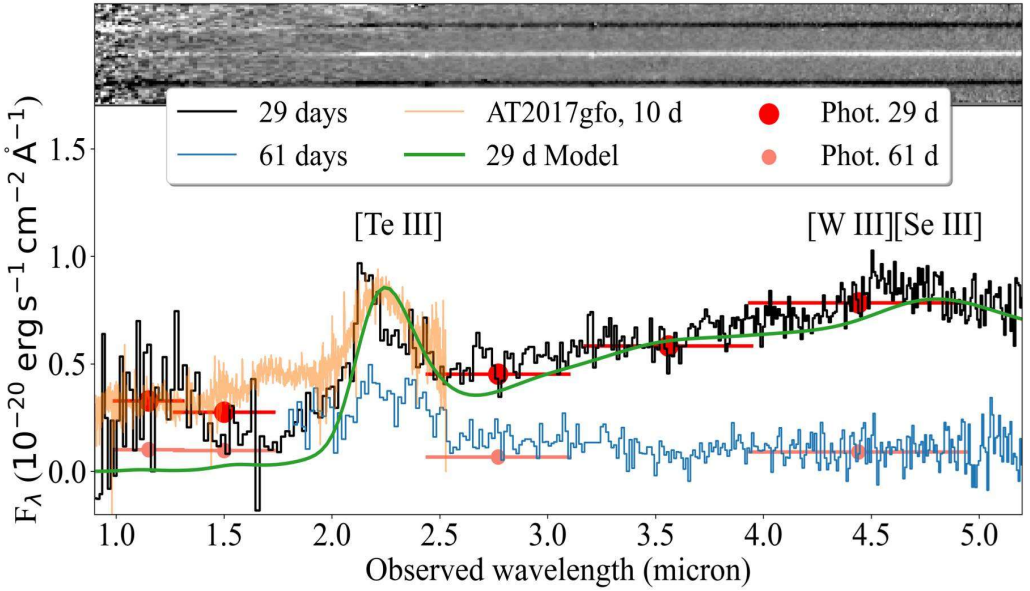
$\rho < 10^{-17}$ (g cm^{-3})

T < 1000 K

Only charge states I - III

Forbidden lines in emission

[Te III] ≡ $5s^2 5p^2\ ^3P_1$ - $5s^2 5p^2\ ^3P_0$



JWST/NIRSpec AT2023vfi (GRB230307A) KN spectra (Levan+, 2023)

Forbidden lines: astrophysical context

Other possible forbidden transition falling near ~2.1 µm & ~4.4 µm emission features

Species	λ_{vac} (Å)	Level energies (eV)		Lower level			Upper level			Relative level population
		Lower	Upper	Configuration	Term	J	Configuration	Term	J	
$\sim 2.1\,\mu$m (or ~ 2.05 and $2.28\,\mu$m) feature										
[^{47}Ag III]	21696	0.000	0.571	$4d^9$	^2D	5/2	$4d^9$	^2D	3/2	1.0
[^{50}Sn II]	23521	0.000	0.527	$5s^25p$	$^2P^o$	1/2	$5s^25p$	$^2P^o$	3/2	1.0
[^{52}Te I]	21049	0.000	0.589	$5p^4$	^3P	2	$5p^4$	^3P	1	1.0
[^{52}Te I]	21247	0.000	0.584	$5p^4$	^3P	2	$5p^4$	^3P	0	0.36
[^{52}Te III]	21050	0.000	0.589	$5s^25p^2$	^3P	0	$5s^25p^2$	^3P	1	1.0
[^{56}Ba I]	19944	2.239	2.861	6s6p	$^1P^o$	1	5d6p	$^1D^o$	2	1.0
[^{56}Ba II]	20518	0.000	0.604	6s	^2S	1/2	5d	^2D	3/2	1.0
[^{68}Er I]	19860	0.000	0.624	$4f^{12}6s^2$	^3H	6	$4f^{12}6s^2$	^3F	4	1.0
[^{68}Er II]	21312	0.055	0.636	–	–	11/2	–	–	9/2	1.0
[^{68}Er II]	19483	0.000	0.636	–	–	13/2	–	–	9/2	1.0
[^{68}Er II]	20148	0.055	0.670	–	–	11/2	–	–	7/2	0.54
[^{68}Er III]	19678	0.000	0.630	$4f^{12}$	^3H	6	$4f^{12}$	^3F	4	1.0
[^{72}Hf I]	21893	0.000	0.566	$5d^26s^2$	^3F	2	$5d^26s^2$	^3F	4	0.053
[^{74}W III]	22416	0.000	0.553	$5d^4$	^5D	0	$5d^4$	^5D	2	0.070
[^{77}Ir II]	20886	0.000	0.594	$5d^7(^4F)6s$	^5F	5	$5d^7(^4F)6s$	^5F	4	1.0
[^{78}Pt II]	21883	0.593	1.160	$5d^86s$	^4F	9/2	$5d^86s$	^4F	7/2	1.0
$\sim 4.4\,\mu$m feature										
[^{49}In I]	45196	0.000	0.274	$5s^25p$	$^2P^o$	1/2	$5s^25p$	$^2P^o$	3/2	1.0
[^{52}Te II]	45466	1.267	1.540	$5s^25p^3$	$^2D^o$	3/2	$5s^25p^3$	$^2D^o$	5/2	1.0
[^{56}Ba I]	44847	2.635	2.911	$5d^2$	^3F	3	$5d^2$	^3P	1	0.33
[^{56}Ba I]	43570	2.681	2.966	$5d^2$	^3F	4	$5d^2$	^3P	2	0.30
[^{56}Ba I]	43956	2.595	2.878	$5d^2$	^3F	2	$5d^2$	^3P	0	0.16
[^{60}Nd I]	42255	0.000	0.293	$4f^46s^2$	^5I	4	$4f^46s^2$	^5I	6	1.0
[^{60}Nd III]	41884	0.000	0.296	$4f^4$	^5I	4	$4f^4$	^5I	6	1.0
[^{72}Hf I]	42433	0.000	0.292	$5d^26s^2$	^3F	2	$5d^26s^2$	^3F	3	1.0
[^{72}Hf I]	45229	0.292	0.566	$5d^26s^2$	^3F	3	$5d^26s^2$	^3F	4	0.053
[^{74}W III]	44322	0.000	0.280	$5d^4$	^5D	0	$5d^4$	^5D	1	1.0
[^{74}W III]	45352	0.280	0.553	$5d^4$	^5D	1	$5d^4$	^5D	2	0.070
[^{89}Ac I]	44814	0.000	0.277	$6d7s^2$	^2D	3/2	$6d7s^2$	^2D	5/2	1.0

(Gillanders+, 2023)

This list is incomplete due to the lack of data notably in the lanthanides !

-> Compute rates for M1 and E2 transitions in all these elements!

Forbidden lines: computational strategy

- Start from a Single Reference (SR) or a Multi Reference (MR) + optimization of the spectroscopic orbitals

- Add + optimize the correlation orbitals by considering VV correlations with SD substitutions of valence spectroscopic orbitals. One layer at a time until convergence of level energies

- RCI step to include core correlation contributions

- Fine-tuning procedure (Li+, 2023) -> semi-empirical improvements of E and A-values

Forbidden lines: results

Forbidden lanthanide lines: example of [Pr III] calculations

Model	<ΔE/E>
SR	0.260
VV1 {5s,5p,5f,5f,5g}	0.146
VV2 {6s,6p,6d,6f,6g}	0.132
VV3 {7s,7p,7d,7f,6g}	0.131
VV4 {8s,8p,8d,8f,6g}	0.130
RCI VV4+CV(5p,5s)	0.083
RCI VV4+CV+Fine-Tuning	0.014
HFR	0.005

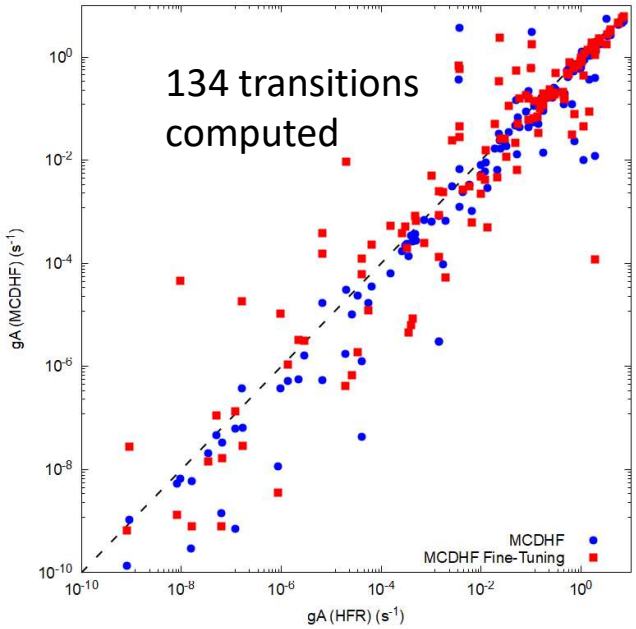
22 experimental levels with E < 20 000 cm^{-1} belonging to $4f^3$ (NIST)

MCDHF: 4 correlation layers; CV correlation with SrD from 4f,5p,5s with at most one hole in 5p or 5s core subshells
→Best model: fine-tuning

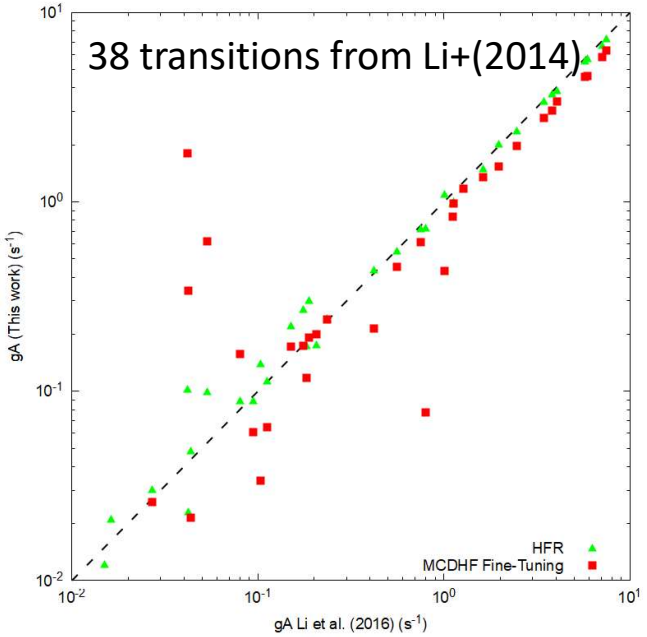
HFR: $4f^3+4f^26p+4f5d^2+4f5d6s+4f^25f+4f^27p+4f^26f+4f6s^2+4f5d7s+4f5d6d+4f5d7d+4f6d^2+4f6s7s+4f7s^2+4f6p^2+4f6p7p+5d6s6p+5d^26p+6s^26p+6p^3$ + least-squares fit

Forbidden lines: results

Example of [Pr III] calculations



Average relative deviation with HFR for the strongest transition: 0.45±0.83 without fine-tuning; 0.19±1.13 with fine-tuning



Li+(2014) agree better with HFR

Forbidden lines: results

Example of [Pr II]

- MCDHF with **GRASPG (Si+, 2025)**:
  - MR : $4f^3 6s$ and $4f^3 5d$
  - Four VV correlation layers were added for the orbital optimisation

		active set	$\overline{\left\|\frac{\Delta E}{E}\right\|}$ *Pr* II
VV	1VV	$6s, 5p, 5d, 5f, 5g$	8.17%
	2VV	$6s, 6p, 6d, 6f, 6g$	7.35%
	3VV	$7s, 7p, 7d, 7f, 6g$	7.70%
	4VV	$8s, 8p, 8d, 7f, 6g$	7.81%

		# CSFs *Pr* II
VV	1VV	8973
	2VV	43 523
	3VV	81 626
	4VV	110 496

  - RCI strategies :
    - Best model includes VV and CV+CC correlations up to 5p core subshell

      Too many CSFs for *rtransition* (high memory consumption)
    - Reduced model : CC correlations generated with the second active set, and VV and CV correlations extended to the last active set

		$\overline{\left\|\frac{\Delta E}{E}\right\|}$ *Pr* II
CV	4CV5p	11.87%
	4CV5s	17.94%
CC	4CC5p	4.26%
	4CC5p(2as)	4.53%
Références		9.59% (Radžiūtė et al., 2020)

		# CSFs *Pr* II
CV	4CV5p	3 008 621
	4CV5s	3 989 453
CC	4CC5p	11 819 347
	4CC5p(2as)	4 540 050

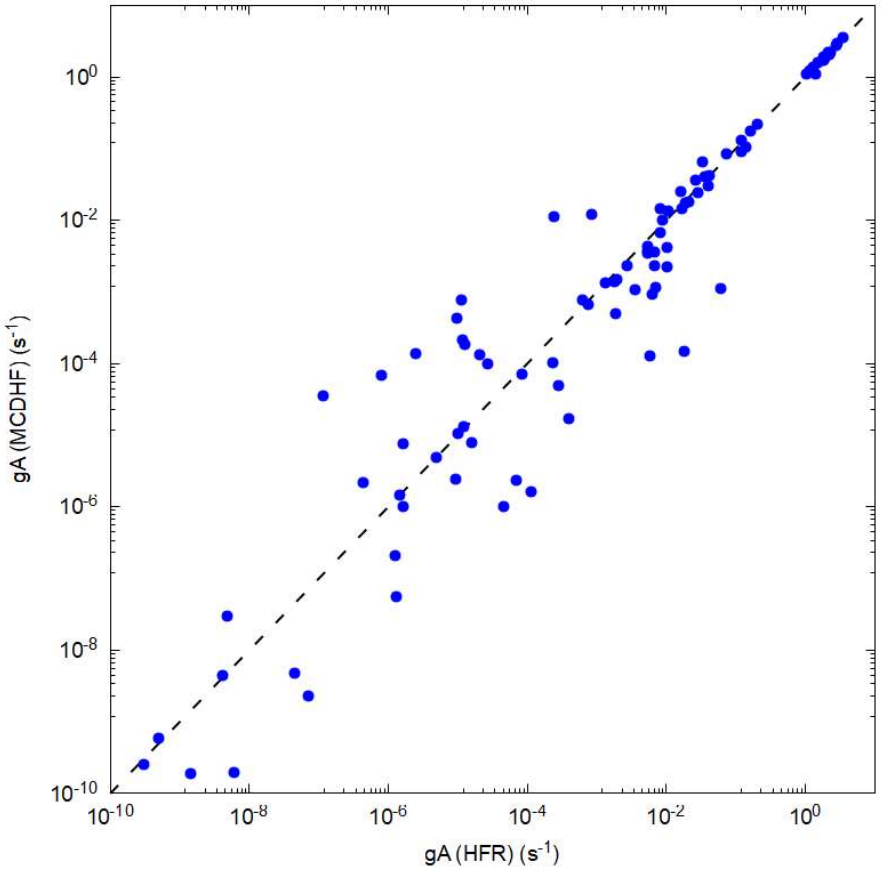
Forbidden lines: results

Example of [Pr II]

HFR

Pr II	
$4f^3 6s^*$	$4f^3 5d$
$4f^3 7s$	$4f^3 6d$
$4f^2 6s6p$	$4f^2 5d6p$
$4f^2 6p7s$	$4f5d^3$
$4f5d^2 6s$	$4f5d^2 7s$
$4f5d6s^2$	$4f5d7s^2$
$4f5d6p^2$	$4f6s^2 6d$
$4f6s^2 7s$	$4f6s6p^2$
$4f6s7s^2$	

$$\left|\frac{\overline{\Delta E}}{E}\right| = 0.22\ \%$$



Forbidden lines: results

Strong forbidden transitions (gA>1E-01 s^{-1}) between experimentally known levels falling close to the two spectral features observed in AT2023vfi at ~2.1 µm and ~4.4 µm

Spectrum	λ (Å)	Mode	gA_{HFR} (s^{-1})	gA_{MCHDF} (s^{-1})
[Ho II]	20082	M1	3.21E+00	3.95E+00
[Lu II]	20419	M1	1.38E-01	1.32E-01
[Pr II]	20755	M1	2.04E-01	2.22E-01
[Pr II]	20802	M1	1.63E-01	1.79E-01
[Pr II]	20969	M1	1.21E-01	1.33E-01
[Pr II]	21117	M1	1.39E-01	1.08E-01
[Ho III]	21345	M1	9.10E+00	3.26E+00

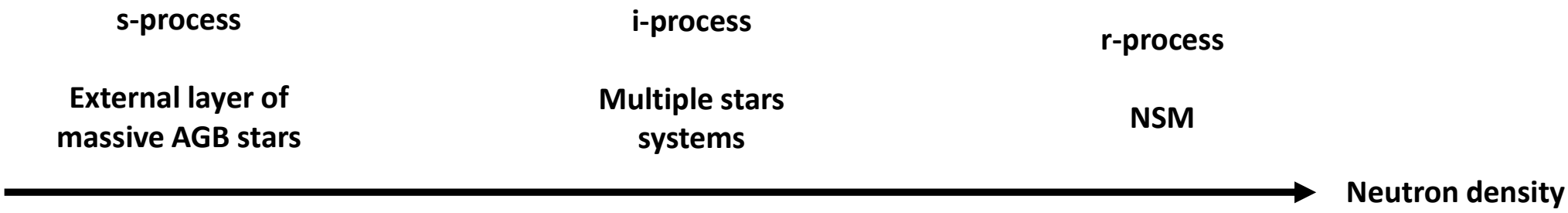
Spectrum	λ (Å)	Mode	gA_{HFR} (s^{-1})	gA_{MCHDF} (s^{-1})
[Ho III]	21540	M1	1.68E+00	5.59E+00
[Nd III]	21855	M1	3.18E-01	2.30E-01
[Ho III]	22031	M1	1.72E+01	1.98E+01
[Tm II]	22137	M1	5.32E+00	5.74E+00
[Sm III]	43563	M1	3.93E+00	3.89E+00
[Ho II]	45396	M1	6.92E-01	7.07E-01
[Dy III]	45828	M1	9.85E+00	9.99E+00

>1000 forbidden transitions for Ce-Pr-Nd-Sm-Eu-Tb-Dy-Er-Tm-Lu III and Nd-Pr-Ho-Er-Lu II

Other singly and doubly lanthanides ongoing

HFS: astrophysical context

Nucleosynthesis of heavy elements (Z>26) by different neutron capture processes



HFS: astrophysical context

Example of barium (Z=56)

82% of Ba produced by s-process in Solar System (Arlandini+, 1999)

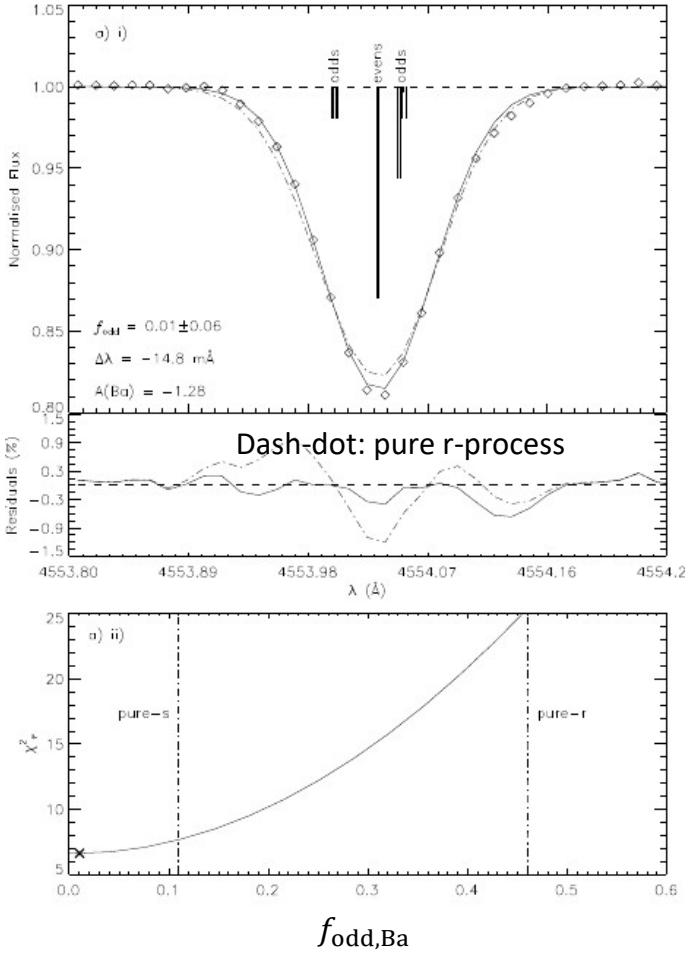
^{135,137,138}Ba produced by a mixture of s- and r-processes

^{134,136}Ba are pure s-processed

Isotopic ratio: $f_{\mathrm{odd,Ba}} = \frac{N(^{135}\mathrm{Ba}) + N(^{13}\ \mathrm{Ba})}{\sum N(\mathrm{Ba\ isotopes})}$

Odd isotopes HFS affect the line profiles more than the IS

Metal-poor subgiant star HD 140283, Ba II 6s $^2S_{1/2}$ – 6p $^2P^o_{3/2}$ (Ghallager+, 2010)



HFS: computational strategy

- Start from a Single Reference (SR) or a Multi Reference (MR) + optimization of the spectroscopic orbitals

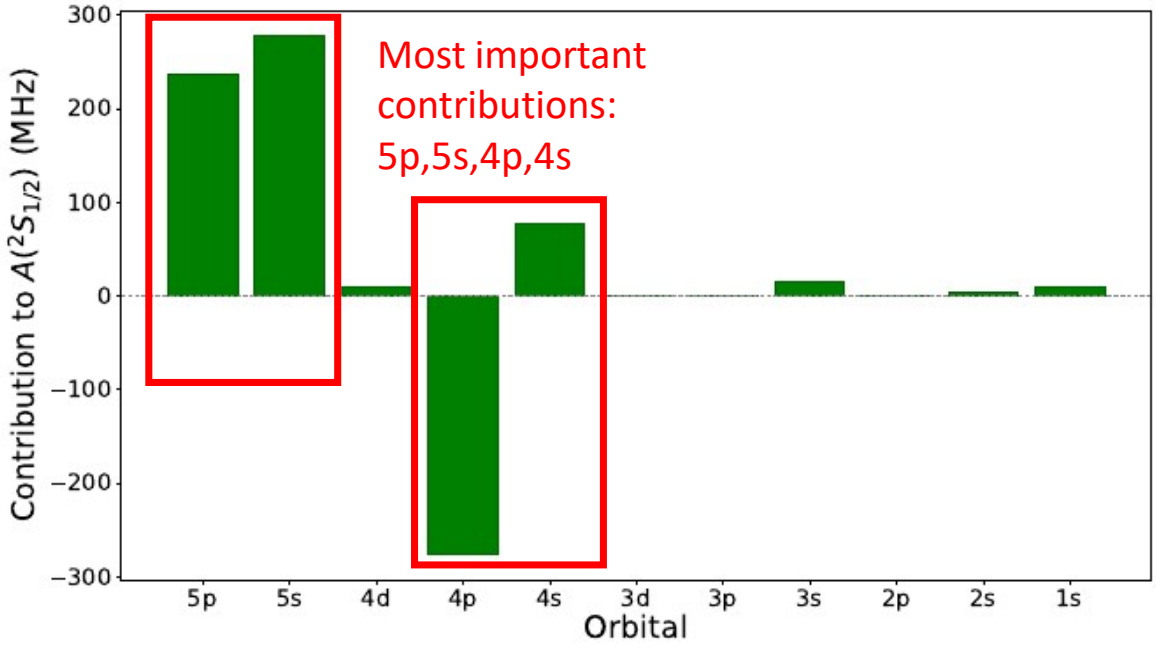
- Add + optimize the correlation orbitals by considering VV (CV) correlations with SD (SrD) substitutions of valence spectroscopic orbitals. One layer at a time until convergence of HFS A & B constants

- RCI step to include (other) core correlation contributions

HFS: computational strategy

Example of ^{137}Ba II:

S substitution contribution to the HFS A constant of the 6s $^2S_{1/2}$ with respect to the DHF value



HFS: computational strategy

Example of ^{135,137}Ba II:

Active sets considered for the 6s $^2S_{1/2}$, 5d $^2D_{3/2,5/2}$ and 6p $^2P^o_{1/2,3/2}$ levels in Ba II

Correlation Layer	$^2S_{1/2}$	$^2D_{3/2,5/2}$	$^2P^o_{1/2,3/2}$
DHF (SR)	$\{6s,5p,4d\}$	$\{5s,5p,5d\}$	$\{5s,6p,4d\}$
AS1	$\{7s,6p,5d,4f\}$	$\{6s,6p,6d,4f\}$	$\{6s,7p,5d,4f\}$
AS2	$\{8s,7p,6d,5f,5g\}$	$\{7s,7p,7d,5f,5g\}$	$\{7s,8p,6d,5f,5g\}$
AS3	$\{9s,8p,7d,6f,6g\}$	$\{8s,8p,8d,6f,6g\}$	$\{8s,9p,7d,6f,6g\}$
AS4	$\{10s,9p,8d,7f,7g\}$	$\{9s,9p,9d,7f,7g\}$	$\{9s,10p,8d,7f,7g\}$
AS5	$\{11s,10p,9d,8f,8g\}$	$\{10s,10p,10d,8f,8g\}$	$\{10s,11p,9d,8f,8g\}$
AS6	$\{12s,11p,10d,9f,9g\}$	$\{11s,11p,11d,9f,9g\}$	$\{11s,12p,10d,9f,9g\}$
AS7	$\{13s,12p,11d,10f,10g\}$	$\{12s,12p,12d,10f,10g\}$	$\{12s,13p,11d,10f,10g\}$

→Up to seven layers of correlation orbitals

HFS: results

Example of ^{137}Ba II:

HFS A constant (in MHz)
of ground level 6s $^2S_{1/2}$

I = 3/2
μ = 0.9375 μ_N
Q = 0.236 b
(Mertzimekis+, 2016)

Step	$^2S_{1/2}$	
	N_{CSFs}	A
Optimization CV SrD nl ≥ 5s		
DHF	1	3060
MCDHF (+AS1)	54	3735
MCDHF (+AS2)	217	3885
MCDHF (+AS3)	494	3992
MCDHF (+AS4)	885	3963
MCDHF (+AS5)	1390	3974
MCDHF (+AS6)	2009	3963
MCDHF (+AS7)	2742	3964
RCI CC SD $nl \geq 5s$ (+AS7)	12,385	3636
RCI CC SD $nl \in \{5p, 5s, 4p, 4s\}$ (+AS7)	24,762	3773
Optimization CV SrD nl ≥ 4p		
DHF	1	3060
MCDHF (+AS1)	135	3823
MCDHF (+AS2)	572	4114
MCDHF (+AS3)	1323	4382
MCDHF (+AS4)	2388	4364
MCDHF (+AS5)	3767	4414
MCDHF (+AS6)	5460	4409
MCDHF (+AS7)	7467	4412
RCI CC SD $nl \geq 5s$ (+AS7)	17,110	3972
RCI CC SD $nl \in \{5p, 5s, 4p, 4s\}$ (+AS7)	27,513	4031
This work, recommended		3902 ± 364

Two independent optimization schemes/ models

Recommended = mean ± 2 x standard dev. (95% confidence level)

Following Papoulia+(2021)

HFS: results

Example of ^{137}Ba II:

Comparison of our HFS constant recommended values (in MHz) with other published ones

Step		$^2S_{1/2}$	$^2D_{3/2}$		$^2D_{5/2}$	
	N_{CSFs}	A	A	B	A	B
This work, recommended		3901.77 ± 182.01	178.47 ± 14.62	42.56 ± 5.30	0.51 ± 6.12	56.69 ± 6.99
Sahoo *et al.* (RCC)	Th.[a]	4078.2	189.92	46.23	-11.67	62.17
Safronova (RMBPT)	Th.[b]	3997.39	191.53	46.23	-9.99	60.8
Itano (MCDHF)	Th.[c]		192.99	51.32	9.39	68.16
	Expt.	4018.87 ± 0.18[d]	189.7288 ± 0.0006[e]	44.54 ± 0.16[e]	-12.028 ± 0.011[e]	59.533 ± 0.043[e]

Step		$^2P^o_{1/2}$		$^2P^o_{3/2}$	
	N_{CSFs}	A	N_{CSFs}	A	B
This work, recommended		667.18 ± 34.43		118.33 ± 2.93	82.43 ± 3.97
Sahoo *et al.* (RCC)	Th.[a]	740.77		128.27	92.87
Safronova (RMBPT)	Th.[b]	733.98		121.35	93.13
Itano (MCDHF)	Th.[c]				
	Expt.	743.7 ± 0.3[f]		127.2 ± 0.2[f]	92.5 ± 0.2[f]

Big disagreement
Small value
Same for
4d $^2D_{5/2}$ in ^{87}Sr II

HFS: results

Example of ^{87}Sr II:

MCHF values of HFS A constants of 4d $^2D_{3/2,5/2}$ (in MHz)
MCHF CV *nl* ≥ 4s one layer (AS1 = {5s,5p,5d})

Level	Term Contribution			
	Orbital	Spin-Dipolar	Contact	Total *A*
		HF		
$^2D_{3/2}$	−26.7	−8.9	0.0	−35.7
$^2D_{5/2}$	−17.8	2.5	0.0	−15.3
		MCHF CV		
$^2D_{3/2}$	−19.9	−3.7	−14.6	−38.2
$^2D_{5/2}$	−13.3	1.1	14.6	2.4

Destructive interference for 4d $^2D_{5/2}$

I = 9/2
μ = -1.09316 μ_N
Q = 0.305 b
(Mertzimekis+, 2016)

HFS: results (preliminary)

Example of ^{43}Ca II and ^{223}Ra II:

Comparison of MCDHF values of HFS A constants of nd $^2D_{5/2}$ levels with published values

^{43}Ca
I = 7/2
μ = -1.31733 μ_N
Q = -0.0408 b
(IAEA)

Method	Ca II (n=3)	Ra II (n=6)
This work (LBL)	-5 ± 0	-22 ± 3
This work (NO)	-5 ± 0	-25 ± 4
Sahoo+ (RCC)	/	-24
Yu+(RMBPT)	-4	/
Itano (MCDHF)	-5	/
Expt.	-3.8 ± 0.6	/

^{223}Ra
I = 3/2
μ = 0.2692 μ_N
Q = 1.22 b
(IAEA)

→No more big disagreements. But still small values and destructive interferences seen in MCHF calculations (Ra II)

Conclusions & Prospects

Forbidden lines in lanthanides:

- HFR and MCDHF transition probabilities for >1000 forbidden transitions in Ce-Pr-Nd-Sm-Eu-Tb-Dy-Ho-Er-Tm-Lu III + Nd-Pr-Ho-Er-Lu II → strong M1 transitions predicted close to the AT2023vfi observed features at ~2.1 μm (5 [Pr II], 1 [Ho II], 1 [Lu II], 1 [Tm II], 3 [Ho III], 1 [Nd III]) and at 4.4 μm (1 [Ho II], 1 [Dy III], 1 [Sm III])

- Lifetime measurements in Sm II at DESIREE (data processing ongoing)

- Prospect: forbidden lines in other singly and doubly ionized lanthanides ongoing; lifetime measurements (DESIREE measurements in Ce II and Nd II)

Conclusions & Prospects

HFS in neutron-capture elements:

- HFS A and B constants computed with two independent MCDHF optimization scheme/model to provide recommended values with uncertainty estimates in ^{135,137}Ba I-II and ^{87}Sr II (published in Nezosi+(2025))
- Importance of MR in Ba I (2 valence electrons)
- Good agreement with published values except for the HFS A constant of the $^{2}D_{5/2}$ level in Ba II and in Sr II
- MCHF computation in Sr II shows an destructive interference between the orbital and contact HFS terms resulting in small and sensitive total A constant
- Not seen in Ca II and Ra II although same destructive interference seen in MCHF calculation in Ra II (preliminary results!)
- Propects: use GRASPG for other neutron-capture elements (3 valence electrons)

Thank you for your attention!

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