Accounting for core-core effects in multiconfiguration calculations of isotope shifts

ECT* Workshop
Trento, Italia

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Chimie quantique et Photophysique
Université Libre de Bruxelles

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ECT*
EUROPEAN CENTRE FOR THEORETICAL STUDIES
IN NUCLEAR PHYSICS AND RELATED AREAS

Isotope shifts

Isotope shift (**IS**)

Key role in extracting *nuclear* properties of an isotope such as its **mean-square nuclear radius** $\langle r^2 \rangle$

Atomic transition k with frequency ν_k

Electronic response of the atom to variations of A & $\langle r^2 \rangle$ given by **only 2** parameters :

- **mass-shift** parameter M_k
- **field-shift** parameter F_k

$\delta\nu_k^{A,A'}$ between any pair of isotopes with A & A' related to $\delta\langle r^2 \rangle^{A,A'}$

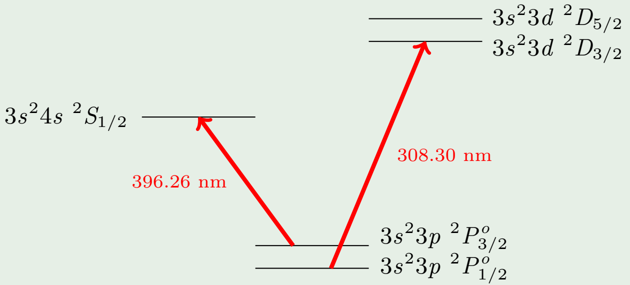
$$\delta\nu_k^{A,A'} \equiv \nu_k^{A} - \nu_k^{A'} \approx M_k \left(\frac{1}{A} - \frac{1}{A'} \right) + F_k \, \delta\langle r^2 \rangle^{A,A'}$$

Motivation of this work

Determination of IS in **Al I**

- Neutral aluminium ($Z = 13$)
  - Ground state [Ne]$3s^2 3p\ ^2P^o_{1/2}$

5 transitions for laser spectroscopy experiments **@ TRIUMF**



⇒ computation of M_k and F_k parameters for each of these transitions

MCDHF Method

Ab initio calculations of IS parameters with **Multi-Configuration Dirac-Hartree-Fock (MCDHF)** method (RIS3/GRASP2K)

- Atomic state function (ASF) as linear combination of CSFs :

$$|\Psi(\Pi J M_J)\rangle = \sum_{\nu=1}^{N_{CSFs}} c_\nu \, |\Phi(\gamma_\nu \, \Pi J M_J)\rangle$$

- CSFs constructed from Slater determinants built on Dirac spinors :

$$\phi_{n\kappa m}(\boldsymbol{r}) = \frac{1}{r} \begin{pmatrix} P_{n\kappa}(r)\chi_{\kappa m}(\hat{r}) \\ i\, Q_{n\kappa}(r)\chi_{-\kappa m}(\hat{r}) \end{pmatrix}$$

- **Variational** method : $P_{n\kappa}(r)$, $Q_{n\kappa}(r)$ and c_ν obtained from *self-consistent* procedure that optimizes the energy functional

$$E = \sum_{\mu=1} \sum_{\nu=1} c_\mu c_\nu \langle \Phi(\gamma_\mu \, \Pi J M_J) | H_{DC} | \Phi(\gamma_\nu \, \Pi J M_J) \rangle$$

with $$H_{DC} = \sum_{i=1}^{N} \left(c\, \boldsymbol{\alpha}_i \cdot \boldsymbol{p}_i + (\beta_i - 1)c^2 + V(r_i) \right) + \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

Computational scheme

- M_k estimated from expectation values of one- and two-body recoil Hamiltonian for **a given isotope** + Shabaev relativistic corrections

$$H_{MS} = \frac{1}{2M} \sum_{i,j}^{N} \left(\boldsymbol{p}_i \cdot \boldsymbol{p}_j - \frac{\alpha Z}{r_i} \left(\boldsymbol{\alpha}_i + \frac{(\boldsymbol{\alpha}_i \cdot \boldsymbol{r}_i)\boldsymbol{r}_i}{r_i^2} \right) \cdot \boldsymbol{p}_j \right)$$

$\Rightarrow$ 3 contributions : $H_{MS} = H^1_{MS} + H^2_{MS} + H^3_{MS}$

$$H^1_{MS} \Rightarrow \begin{cases} \langle H^1_{NMS} \rangle = \langle \sum_i \boldsymbol{p}_i^2 / 2M \rangle \\ \langle H^1_{SMS} \rangle = \langle \sum_{i \neq j} \boldsymbol{p}_i \cdot \boldsymbol{p}_j / 2M \rangle \end{cases}$$

- F_k estimated from theoretical total electron densities at the origin

$$F_k = \frac{2\pi}{3} Z \, \Delta |\Psi(0)|^2_k$$

where $\Delta |\Psi(0)|^2_k = \Delta \rho^e_k(\mathbf{0}) = \rho^e_u(\mathbf{0}) - \rho^e_l(\mathbf{0})$

Active set approach for **Al I**

Building the **MR**

- Common orbital basis for *all* states
- Multi Reference (MR) built from valence-CAS :
  SDT from valence orbitals to $n = \{3, 4\}$ shells
- Extract CSFs with mixing coef. $\geq$ threshold **(0.1)**

States	SR	N_{CSFs}	MR	N_{CSFs}
$^2P^o_J$	$[\mathrm{Ne}]3s^23p$	2	$[\mathrm{Ne}]\{3s^23p, 3s3p3d, 3p^3\}$	8
$^2S_{1/2}$	$[\mathrm{Ne}]3s^24s$	1	$[\mathrm{Ne}]\{3s^24s, 3s3p^2, 3p^24s\}$	4
^2D_J	$[\mathrm{Ne}]\{3s^23d, 3s3p^2\}$	7	$[\mathrm{Ne}]\{3s^23d, 3s^24d, 3s3p^2, 3p^23d\}$	13

(VV + CV) correlations

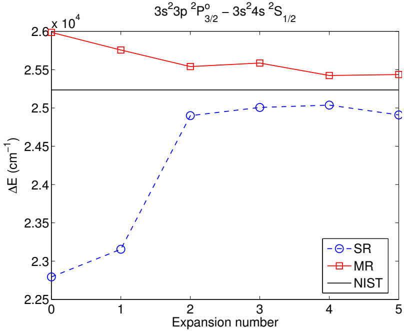
- SD from valence orbitals + S from $\{2s, 2p\}$ core
- Active orbital set successively extended, including for each new layer one extra l-orbital
- SR-I or MR-I expansions : all CSFs interacting to 1st order with the CSFs defining the SR or the MR

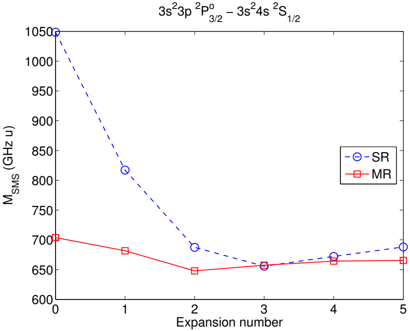
$3s^23p\ ^2P^o_{3/2} \rightarrow 3s^24s\ ^2S_{1/2}$ (1)

(VV + CV) correlations

Table 1 : ΔE (cm^{-1}), M_{MS} (GHz u) & F (MHz/fm^2)

Model	N_{CSFs}	ΔE	M_{NMS}	M_{SMS}	M_{MS}	F
$n=9$ (VV+CV) SR	53 780	24 909	-479.1	688.1	209.0	75.0
$n=9$ (VV+CV) MR	213 875	25 436	-422.5	665.4	242.9	78.7
Expt.		25 236				





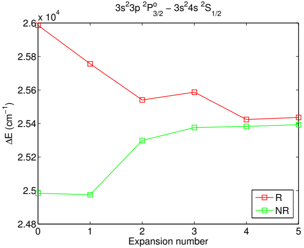
$3s^23p\ ^2P^o_{3/2} \rightarrow 3s^24s\ ^2S_{1/2}$ (2)

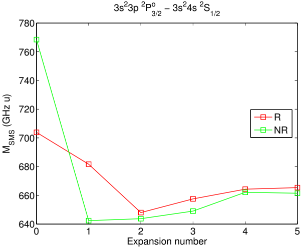
Comparison between **SR & MR** results

- ΔE : better results with MR (**0.8%** error with NIST)
- M_{MS} : 15% difference **but**
  - M_{NMS} : MR value **much closer** to scaling law (-415.0)
  - M_{SMS} : good agreement (3% difference)

Comparison with **Non-relativistic** results

- ΔE : Relativistic correction of 43 cm^{-1} (**0.2%**)
- M_{SMS} : Relativistic correction of 3.9 GHz u (**0.6%**)



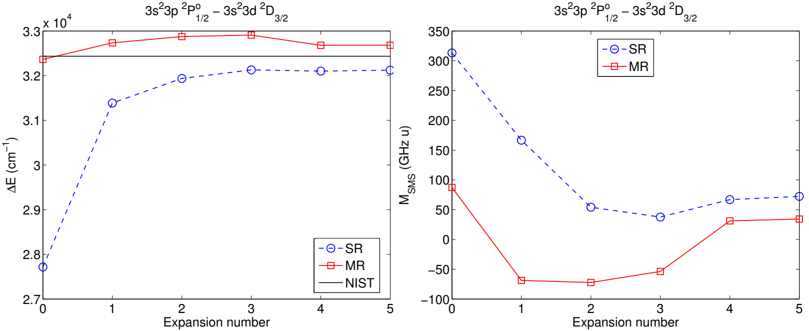


$3s^2 3p\ ^2P^o_{1/2} \rightarrow 3s^2 3d\ ^2D_{3/2}$ (1)

(VV + CV) correlations

Table 2 : ΔE (cm^{-1}), M_{MS} (GHz u) & F (MHz/fm^2)

Model	N_{CSFs}	ΔE	M_{NMS}	M_{SMS}	M_{MS}	F
$n = 9$ (VV+CV) SR	79 464	32 122	-541.2	72.4	-468.8	-2.6
$n = 9$ (VV+CV) MR	239 443	32 681	-522.9	34.3	-488.6	1.8
Expt.		32 435				



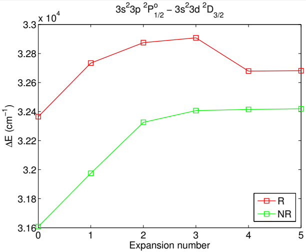
$3s^23p\ ^2P^o_{1/2} \rightarrow 3s^23d\ ^2D_{3/2}$ (2)

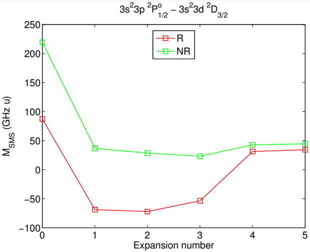
Comparison between **SR** & **MR** results

- ΔE : better results with MR (**0.8%** error with NIST)
- M_{MS} : good agreement (3% difference) **but**
  - M_{NMS} : MR value **as close** to scaling law (-533.4) as SR value
  - M_{SMS} : **50%** difference **!!!**

Comparison with **Non-relativistic** results

- ΔE : Relativistic correction of 262 cm^{-1} (**0.8%**)
- M_{SMS} : Relativistic correction of -10.2 GHz u (**-23%**)



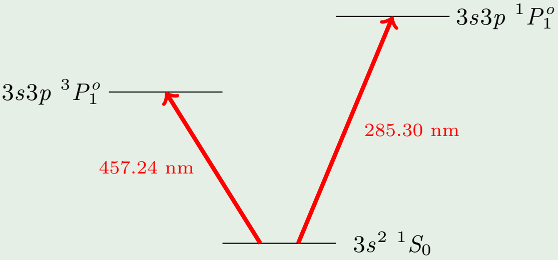


Core-core effects in Mg I

Determination of IS in **Mg I**

- Neutral magnesium $(Z = 12)$
  - Ground state $[\mathrm{Ne}]3s^2\ ^1S_0$

2 well known transitions from experiments (1979, 2006)



⇒ computation of M_k and F_k parameters for these transitions

Active set approach for Mg I

Building the **MR**

- Common orbital basis for *all* states
- Multi Reference (MR) built from valence-CAS : SD from valence orbitals to $n = \{3, 4\}$ shells
- Extract CSFs with mixing coef. $\geq$ threshold **(0.05)**

States	MR	N_{CSFs}
$^1S_0$	$[\mathrm{Ne}]\{3s^2, 3p^2, 3p4p\}$	5
$^{1,3}P^o_1$	$[\mathrm{Ne}]\{3s3p, 3s4p, 3p3d, 3p4s, 3d4p\}$	9

(VV + CV + CCd) correlations

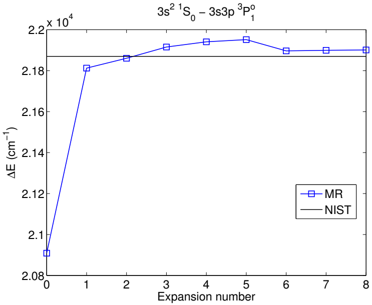
- Convergence reached in (VV + CV) with SD to $n = 9$ shell
  $\Rightarrow$ **add CCd contribution** by CI computation
    - only **doubly occupied** correlation orbitals
- SD from ground $1s^22s^22p^6\,{}^1S_0$ of Mg^{2+} to $n = \{10, 11\}$ shells
  $\Rightarrow$ **capture only CC contributions**
- CI on each new set of CSFs

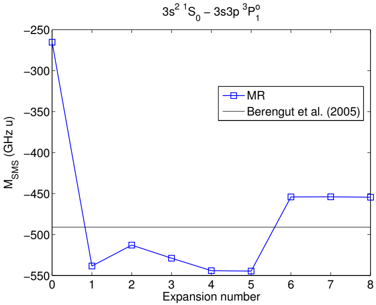
$3s^2\ ^1S_0 \rightarrow 3s3p\ ^3P^o_1$ (1)

(VV + CV + CCd) correlations

Table 3 : ΔE (cm^{-1}), M_{MS} (GHz u) & F (MHz/fm^2)

Model	ΔE	M_{NMS}	M_{SMS}	M_{MS}	F
$n = 9$ (VV + CV)	21 952	-286.2	-544.7	-830.9	-77.0
$n = 9$ CI (VV + CV + CCd)	21 897	-356.1	-454.1	-810.2	-76.7
$n = 9$ + 1 layer CI (VV + CV + CCd)	21 900	-356.6	-454.0	-810.6	-76.8
$n = 9$ + 2 layers CI (VV + CV + CCd)	21 901	-356.4	-454.5	-810.9	-76.8
Expt.	21 870				





$3s^2\ ^1S_0 \rightarrow 3s3p\ ^3P^o_1$ (2)

Comparison with **Non-relativistic** results

- **Not the same** configurations in the MR : valence-CAS
- Non-relativistic results include **full CC** contribution
  - ΔE : Relativistic correction of 234 cm^{-1} (**1.1%**)
  - M_{SMS} : Relativistic correction of -28 GHz u (-**6.6%**)

Table 4 : ΔE (cm^{-1}) & M_{SMS} (GHz u)

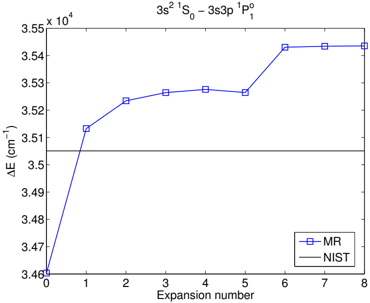
	Non-relativistic		**Relativistic**	
Model	ΔE	M_{SMS}	ΔE	M_{SMS}
$n = 9$ (VV + CV)			21 952	-544.7
$n = 9$ CI (VV + CV + CCd)			21 897	-454.1
$n = 9 + 1$ layer CI (VV + CV + CCd)			21 900	-454.0
$n = 9 + 2$ layers CI (VV + CV + CCd)	21 667	-426.5	21 901	-454.5

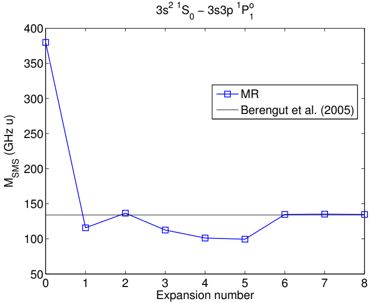
$3s^2\ ^1S_0 \rightarrow 3s3p\ ^1P^o_1$ (1)

(VV + CV + CCd) correlations

Table 5 : ΔE (cm^{-1}), M_{MS} (GHz u) & F (MHz/fm^2)

Model	ΔE	M_{NMS}	M_{SMS}	M_{MS}	F
$n = 9$ (VV + CV)	35 265	-506.9	99.5	-407.4	-60.9
$n = 9$ CI (VV + CV + CCd)	35 431	-583.2	134.8	-448.4	-62.0
$n = 9$ + 1 layer CI (VV + CV + CCd)	35 434	-583.7	135.2	-448.5	-62.0
$n = 9$ + 2 layers CI (VV + CV + CCd)	35 435	-583.7	134.8	-448.9	-62.0
Expt.	35 051				





$3s^2\ ^1S_0 \rightarrow 3s3p\ ^1P_1^o$ (2)

Comparison with **Non-relativistic** results

- **Not the same** configurations in the MR : valence-CAS
- Non-relativistic results include **full CC** contribution
  - ΔE : Relativistic correction of 509 cm^{-1} (**1.5%**)
  - M_{SMS} : Relativistic correction of -39.3 GHz u (-**22%**)

Table 6 : ΔE (cm^{-1}) & M_{SMS} (GHz u)

	Non-relativistic		**Relativistic**	
Model	ΔE	M_{SMS}	ΔE	M_{SMS}
$n = 9$ (VV + CV)			35 265	99.5
$n = 9$ CI (VV + CV + CCd)			35 431	134.8
$n = 9 + 1$ layer CI (VV + CV + CCd)			35 434	135.2
$n = 9 + 2$ layers CI (VV + CV + CCd)	34 926	174.1	35 435	134.8

Comparison with expt. & Berengut *et al.*

Observed IS between ^{26}Mg & ^{24}Mg

- Comparison with Berengut *et al.* (2005)
  - **field shift neglected** (order of 20-30 MHz) :

$$\delta\nu_k^{26,24} \equiv \nu_k^{26} - \nu_k^{24} \approx M_k \left(\frac{1}{26} - \frac{1}{24}\right) + \underbrace{F_k \, \delta\langle r^2\rangle^{26,24}}_{\ll MS}$$

Table 7 : IS (MHz) & SMS (MHz) between ^{26}Mg & ^{24}Mg

	IS (MHz)			SMS (MHz)		
Transition	This work	Expt.	Berengut[c]	This work	Expt.	Berengut[c]
$3s^2\,{}^1S_0 - 3s3p\,{}^3P_1^o$	2599	2683(0)[a]	2726	1457	1530[a]	1573
$3s^2\,{}^1S_0 - 3s3p\,{}^1P_1^o$	1439	1412(21)[b] 1413.8(7.5)[d]	1420	-432	-436[b]	-428

[a] U. Sterr *et al.*, Appl. Phys. B : Photophys. Laser Chem. **56**, 62 (1993)

[b] L. Hallstadius *et al.*, Z. Phys. A **291**, 203 (1979)

[c] J. C. Berengut *et al.*, Phys. Rev. A **72**, 044501 (2005)

[d] E. J. Salumbides *et al.*, Mon. Not. R. Astron. Soc. **373**, L41-L44 (2006)

Conclusions & perspectives

Conclusion for **Al I** (VV + CV)

- Comparison between SR & MR results
  - Good agreement for ΔE & F
  - Some differences for M_{MS} (as expected)
- Consistent comparison with NR results (as expected)

Conclusion for **Mg I** (VV + CV + CCd)

- Consistent comparison with NR results (as expected)
- Consistent comparison with theory & expt.

Perspectives for **Al I** (VV + CV + CCd)

- Effect of the MR on the results of Al I with CCd correlations
  ⇒ **need for *systematic* procedure to balance the MR**
- Compare with Al I values from Ratip (Prof. S. Fritzsche)
- Compare Al I results with experimental data (TRIUMF)

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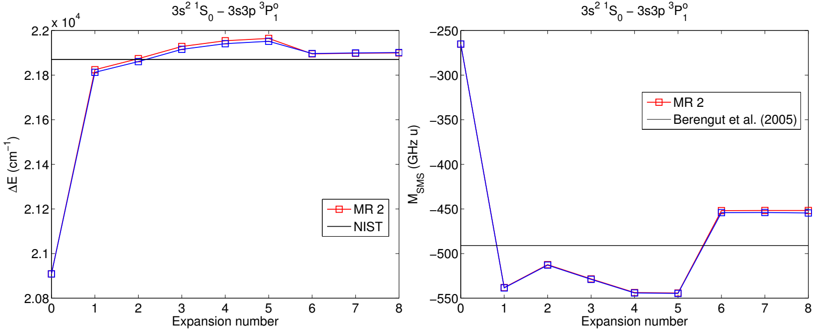
$3s^2\ ^1S_0 \rightarrow 3s3p\ ^3P^o_1$ (3)

Finding a **balanced** MR...

States	MR 1 (blue lines, threshold=0.05)
$3s^2\,^1S_0$	$[\mathrm{Ne}]\{3s^2, 3p^2, 3p4p\}$
$3s3p\,^3P^o_1$	$[\mathrm{Ne}]\{3s3p, 3s4p, 3p3d, 3p4s, 3d4p\}$
States	MR 2 (red lines, threshold=0.025)
$3s^2\,^1S_0$	$[\mathrm{Ne}]\{3s^2, 3s4s, 3p^2, 3p4p, 4s^2, 4p^2\}$
$3s3p\,^3P^o_1$	$[\mathrm{Ne}]\{3s3p, 3s4p, 3p3d, 3p4s, 3d4p, 4s4p\}$



$3s^2\ ^1S_0 \to 3s3p\ ^1P^o_1$ (3)

Finding a **balanced** MR...

States	MR 1 (blue lines, threshold=0.05)
$3s^2\,^1S_0$	$[\mathrm{Ne}]\{3s^2, 3p^2, 3p4p\}$
$3s3p\,^1P^o_1$	$[\mathrm{Ne}]\{3s3p, 3s4p, 3p3d, 3p4s, 3d4p\}$
States	MR 2 (red lines, threshold=0.025)
$3s^2\,^1S_0$	$[\mathrm{Ne}]\{3s^2, 3s4s, 3p^2, 3p4p, 4s^2, 4p^2\}$
$3s3p\,^1P^o_1$	$[\mathrm{Ne}]\{3s3p, 3s4p, 3p3d, 3p4s, 3d4p, 4s4p\}$