# On the use of natural orbitals in GRASP calculations

Per Jönsson

Department of Materials Science and Applied Mathematics
Malmö University, Sweden

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# Dedicated to the memory Ian and Charlotte

# Acknowledgment


- Betul Atalay
- Gediminas Gaigalas
- Michel Godefroid
- Jörgen Ekman
- Jacek Bieron
- Jiguang Li
- Sacha Schiffmann

# Starting point

- I think we are orbital basis limited
- crucial that the orbitals in the MR are as accurate as possible
- the CSFs in the MR should be described by orbitals that are mutually non-orthogonal: example Ti I: $3d^2 4s^2\ ^3F_{2,3,4}$ and $3d^3(^4F)4s\ ^5F_{1,2,3,4,5}$.
- multiple and non-orthogonal orbitals targeted for different pair correlation effects
- the number of allowed orbitals in GRASP should be increased
- transformation to natural orbitals

# Intimidation – hyperfine structure

## Independently Optimized Orbital Sets in GRASP—The Case of Hyperfine Structure in Li I

by Yanting Li [1,2,†], Per Jönsson [2,*,†], Michel Godefroid [3], Gediminas Gaigalas [4], Jacek Bieroń [5], José Pires Marques [6], Paul Indelicato [7] and Chongyang Chen [1]

[1] Shanghai EBIT Lab, Key Laboratory of Nuclear Physics and Ion-Beam Application, Institute of Modern Physics, Department of Nuclear Science and Technology, Fudan University, Shanghai 200433, China

[2] Department of Materials Science and Applied Mathematics, Malmö University, SE-20506 Malmö, Sweden

[3] Spectroscopy, Quantum Chemistry and Atmospheric Remote Sensing, Université Libre de Bruxelles, B-1050 Brussels, Belgium

[4] Institute of Theoretical Physics and Astronomy, Vilnius University, LT-010222 Vilnius, Lithuania

[5] Instytut Fizyki Teoretycznej, Uniwersytet Jagielloński, 30-348 Kraków, Poland

[6] LIP-Laboratório de Instrumentação e Física Experimental de Partículas and Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal

[7] Laboratoire Kastler Brossel, Sorbonne Université, CNRS, ENS-PSL Research University, Collège de France, Case 74, 4, Place Jussieu, 75005 Paris, France

[*] Author to whom correspondence should be addressed.

[†] These authors contributed equally to this work.

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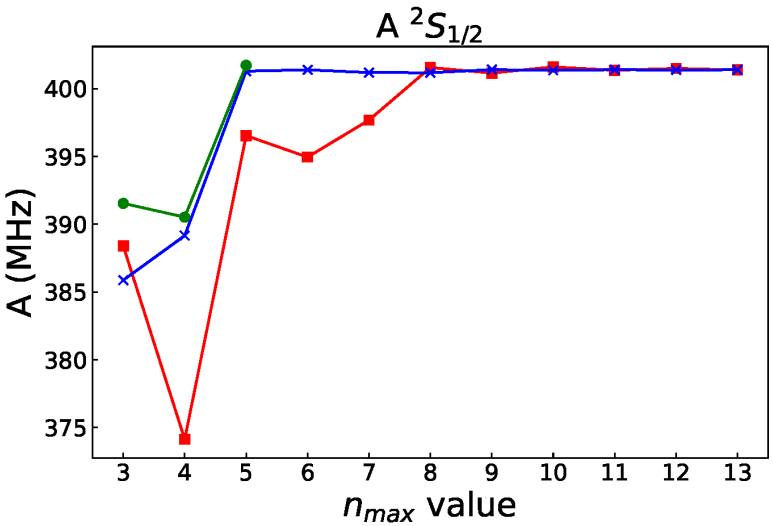
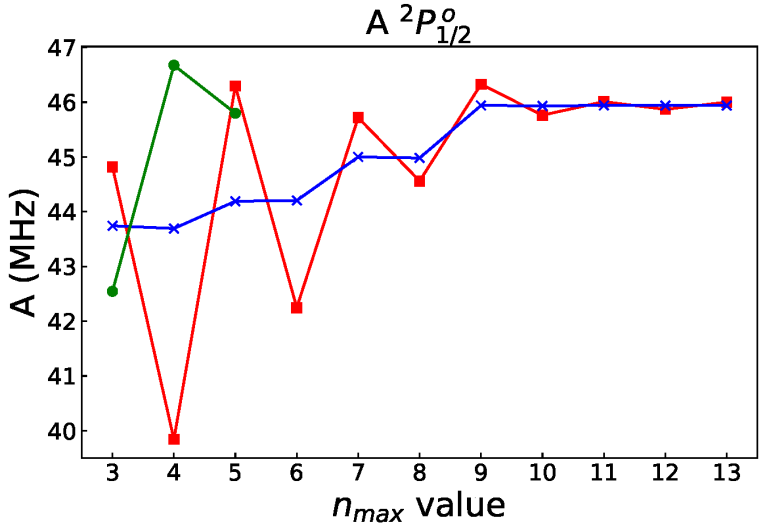
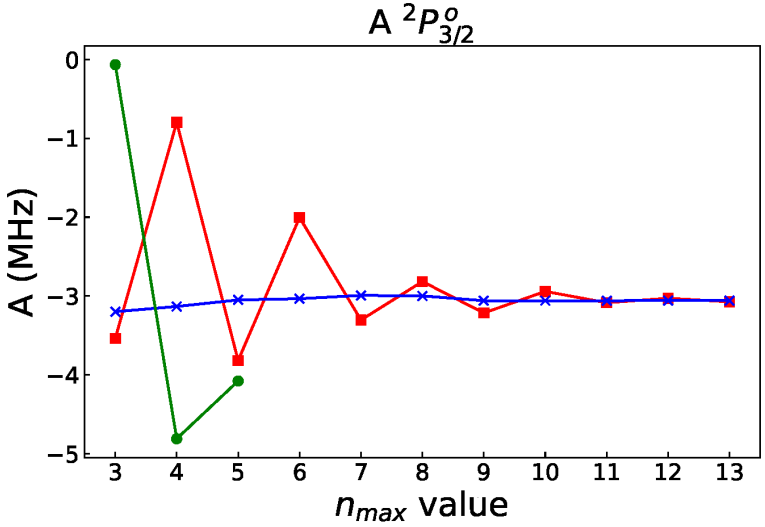
# Intimidation – hyperfine structure



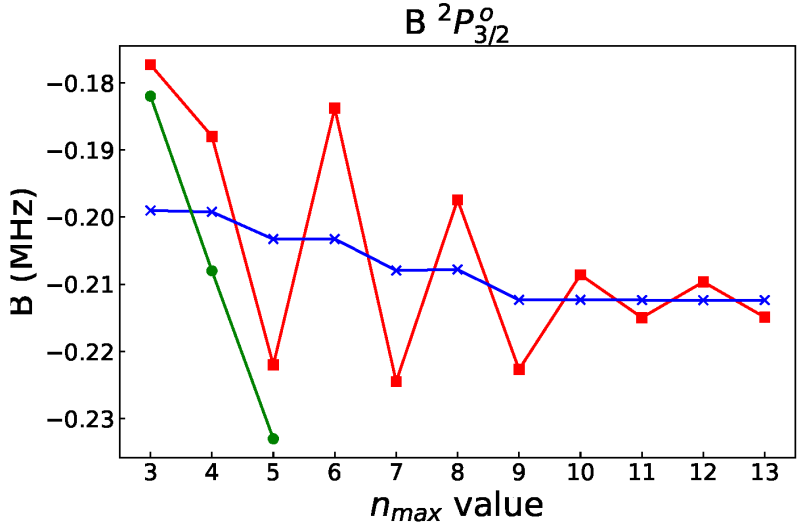

(a)




(b)




(c)




(d)

# Intimidation – transition rates

## Coulomb (Velocity) Gauge Recommended in Multiconfiguration Calculations of Transition Data Involving Rydberg Series

by **Asimina Papoulia** [1,2,*], **Jörgen Ekman** [1], **Gediminas Gaigalas** [3], **Michel Godefroid** [4], **Stefan Gustafsson** [1], **Henrik Hartman** [1], **Wenxian Li** [1], **Laima Radžiūtė** [3], **Pavel Rynkun** [3], **Sacha Schiffmann** [2,4], **Kai Wang** [5] and **Per Jönsson** [1]

[1] Department of Materials Science and Applied Mathematics, Malmö University, SE-20506 Malmö, Sweden
[2] Division of Mathematical Physics, Department of Physics, Lund University, SE-22100 Lund, Sweden
[3] Institute of Theoretical Physics and Astronomy, Vilnius University, Saulėtekio av. 3, LT-10222 Vilnius, Lithuania
[4] Chimie Quantique et Photophysique, Université libre de Bruxelles, B-1050 Brussels, Belgium
[5] Hebei Key Lab of Optic-electronic Information Materials, College of Physics Science and Technology, Hebei University, Baoding 071002, China
[*] Author to whom correspondence should be addressed.

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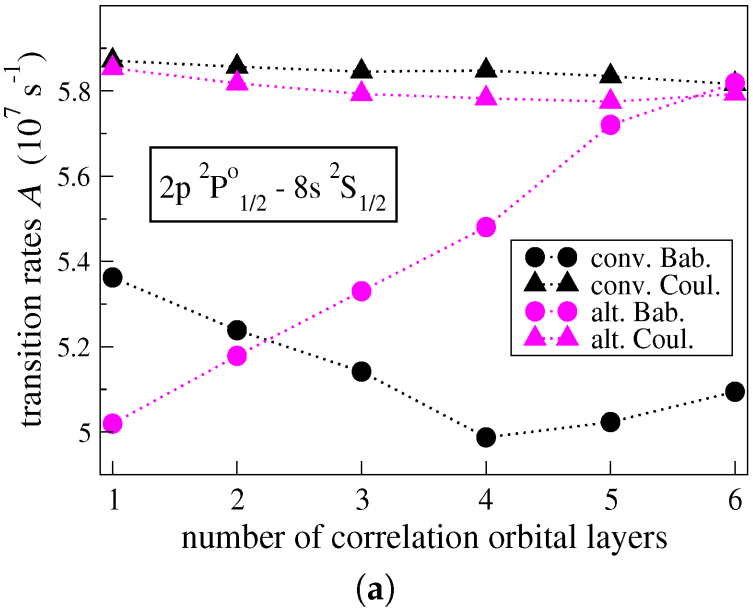
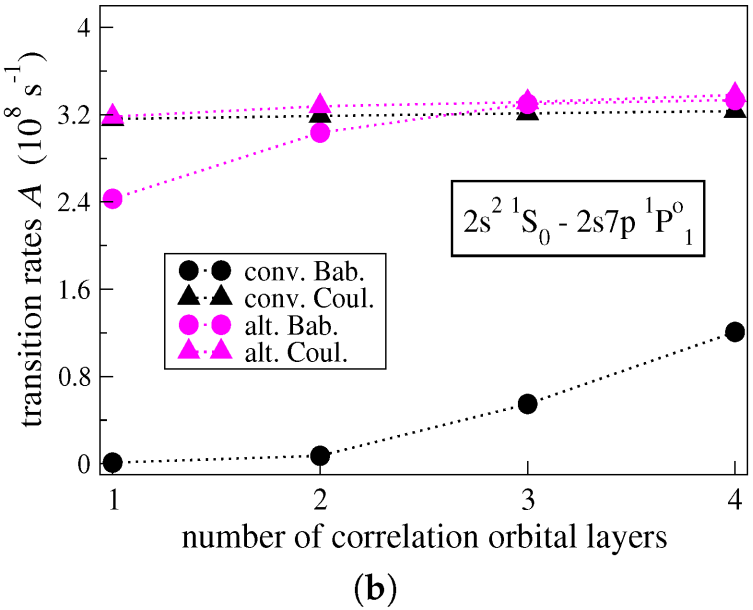
# Intimidation – transition rates




(a)




(b)

# Outline

- transformation to natural orbitals in two electron systems
- computation of natural orbitals in the general case
- Sacha Schiffmann's analysis for hfs
- applications

# $1s^2\ ^1S$ in He I – the beginning

- $\Psi^{l=0}(1s^2\ ^1S) = \sum_{n,n'} c_{nn'}\Phi(nsn's)$
- $\Psi^{l=0}(1s^2\ ^1S) = \left(\sum_{n,n'} c_{nn'}R_{ns}(r_1)R_{n's}(r_2)\right)|ss'\ ^1S\rangle$, where $R_{nl}(r) = P_{nl}(r)/r$ and $c_{nn'} = c_{n'n}$.
- $\left(\sum_{n,n'} c_{nn'}R_{ns}(r_1)R_{n's}(r_2)\right) = \mathbf{R(r_1)\ C\ R(r_2)}^t$, radial factor in matrix vector form
- **C** symmetric, unitary transformation that will diagonalize it
- applying transformation to radial function vectors **R** gives the natural orbitals (NO)
- $\Psi^{l=0}(1s^2\ ^1S) = \sum_n c_n\Phi(ns^2)$
- similar transformations for other $l$, leads to reduced form $\Psi(1s^2\ ^1S) = \sum_l \sum_n c_{nl}\Phi(nl^2)$

# Rdensity program in GRASP

Computer Physics Communications
Volume 278, September 2022, 108403

## Relativistic radial electron density functions and natural orbitals from GRASP2018 ☆, ☆☆

S. Schiffmann [a b], J.G. Li [c], J. Ekman [d], G. Gaigalas [e], M. Godefroid [a], P. Jönsson [d], J. Bieroń [f]

- NOs are obtained, for each $\kappa$, by constructing and diagonalizing the orbital electron density matrix

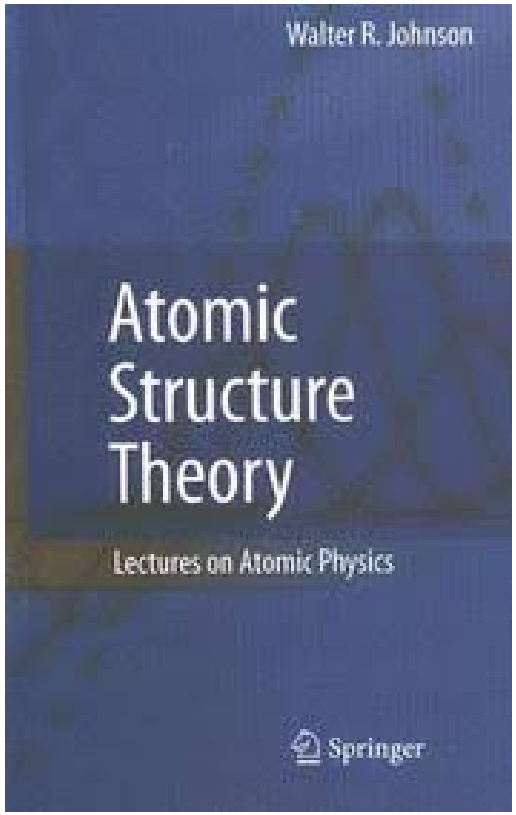
# Effects of natural orbitals

- when CV correlation are included in fully variational calculations, valence orbitals contracts relative to their shapes from DF
- in the layer-by-layer approach the valence orbitals are fixed from the DF calculation, no contraction
- transformation to NO from layer-by-layer wave functions leads to a contraction of the valence orbitals similar to the one from fully variational calculations
- important implications for hfs, IS and transition rates

# Effects of natural orbitals

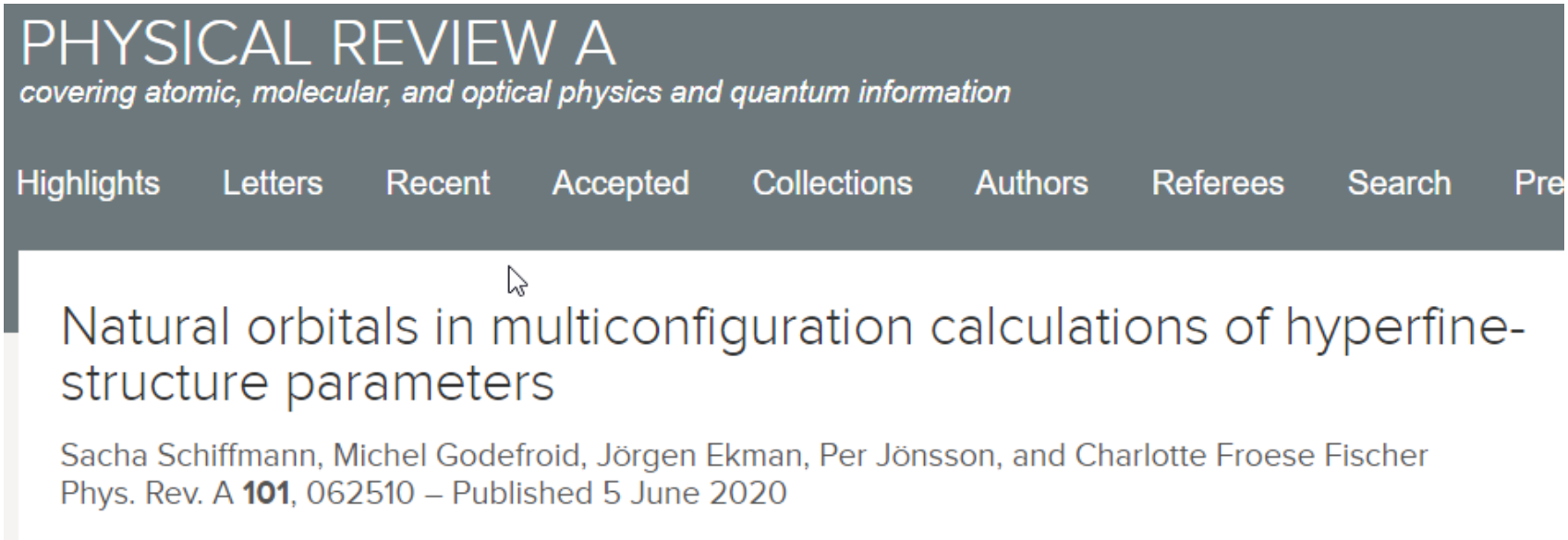
- building CSF expansions on NOs concentrates the weights to fewer CSFs
- more compact representation, we can condense harder
- energies lower in NO basis compared to the ordinary basis
- some terms in Rayleigh-Schrödinger perturbation theory are zero in the NO basis

# Natural orbitals vs Brueckner orbitals




- Similarities with Brueckner orbitals that have a clearer physical interpretation, read section 7.3.3

# Transformation to natural orbitals - Na I



# Computational procedure

- $2s^2 2p^6 3s\ ^2S_{1/2}$ and $2s^2 2p^6 3p\ ^2P_{1/2,3/2}$ in Na I.
- layer-by-layer optimization of correlation orbitals based on SD-CV and SD-CV-CC expansions
- transforming to NOs based on SD-CV expansion
- CI based on SD-CV-CC + TQ expansion in NO basis
- detailed comparisons with corresponding fully variational as well as layer-by-layer MCHF calculations

# Orbital contraction

- Orbital contraction

$$\langle r_{3s} \rangle_{\mathrm{LBL}} = 4.12007 \rightarrow \langle r_{3s} \rangle_{\mathrm{NO}} = 4.05088$$

$$\langle r_{3s}^{-2} \rangle_{\mathrm{LBL}} = 0.43488 \rightarrow \langle r_{3s}^{-2} \rangle_{\mathrm{NO}} = 0.48120$$

# Hyperfine structure

| | $A_{1/2}$(MHz) | |
|---|---|---|
| Active set | LBL | NO |
| DHF | 633.698 | |
| MCDHF+CI CV | | |
| 3 | 691.693 | |
| 4 | 837.150 | |
| 5 | 870.354 | |
| 6*h* | 895.195 | |
| 7*h* | 906.639 | |
| 8*h* | 939.435 | |
| 9*h* | 938.813 | 937.083 |
| MCDHF+CI CV + CC | | |
| 10*h* | 852.679 | 888.676 |
| 11*h* | 852.806 | 888.725 |
| CI CV + CC + T | | |
| SD[11*h*] | | |
| ∪ T[4] | 859.307 | 886.605 |
| ∪ T[5*f*] | 865.388 | 885.925 |
| ∪ T[6*f*] | 866.826 | 883.113 |
| CI CV + CC + T + Q | | |
| SD[11*h*] | | |
| ∪ TQ[4] | 862.146 | 889.111 |
| ∪ T[6*f*] ∪ Q[4] | 869.945 | 885.841 |
| Expt. | 885.813 064 4(5) [34] | |

# Hyperfine structure

TABLE VIII. Relativistic magnetic dipole hyperfine constants $A_{1/2}$ (MHz) and $A_{3/2}$ (MHz) of the $^2P_{1/2}$ and $^2P_{3/2}$ sodium excited states, respectively, along the active space expansion in two different orbital bases. Similar results are given for the electric field gradient EFG = $B_{3/2}/Q$ (MHz/b) of the $J = 3/2$ level.

| | $A_{1/2}$(MHz) | | $A_{3/2}$(MHz) | | $B_{3/2}/Q$(MHz/b) | |
|---|---|---|---|---|---|---|
| Active set | LBL | NO | LBL | NO | LBL | NO |
| DHF | 64.157 | | 12.744 | | 15.939 | |
| MCDHF+CI CV | | | | | | |
| 3 | 69.348 | | 12.054 | | 16.605 | |
| 4 | 91.212 | | 20.611 | | 27.648 | |
| $5f$ | 93.643 | | 21.077 | | 27.291 | |
| $6f$ | 98.294 | | 20.300 | | 27.822 | |
| $7f$ | 100.751 | | 20.770 | | 28.520 | |
| $8f$ | 101.791 | | 20.544 | | 28.562 | |
| $9f$ | 101.861 | 101.817 | 20.554 | 20.543 | 28.453 | 28.433 |
| MCDHF+CI CV + CC | | | | | | |
| $10f$ | 87.740 | 94.655 | 17.184 | 18.592 | 24.424 | 26.274 |
| $11f$ | 87.701 | 94.603 | 17.197 | 18.606 | 24.469 | 26.322 |
| CI CV + CC + T | | | | | | |
| SD[$11f$] | | | | | | |
| $\cup$ T[4] | 88.596 | 94.668 | 17.514 | 18.755 | 24.838 | 26.474 |
| $\cup$ T[$5f$] | 90.073 | 94.594 | 17.943 | 18.874 | 25.395 | 26.616 |
| $\cup$ T[$6f$] | 90.908 | 94.316 | 18.083 | 18.803 | 25.675 | 26.599 |
| Others | | | | | | |
| CI [1] | 94.04 | | 18.80 | | 25.79 | |
| SD [38] | 94.99 | | 18.84 | | 26.85 | |
| SD [37] | 92.4 | | 19.3 | | | |
| CCSD [36] | 93.02 | | 18.318 | | 26.14 | |
| Expt. [43,44] | 94.42(19) | | 18.79(12) | | | |

# Other observations

- Computing along the isoelectronic sequence shows that the effect of the NOs are largest for neutral and near neutral systems

# Transformation to natural orbitals - Si IV

A&A 631, A29 (2019)
https://doi.org/10.1051/0004-6361/201935618


Astronomy & Astrophysics

## MCDHF and RCI calculations of energy levels, lifetimes, and transition rates in Si III and Si IV★

B. Atalay[1,2], T. Brage[1,4], P. Jönsson[3], and H. Hartman[3]

[1] Department of Physics, Lund University, Post Office Box 118, 22100 Lund, Sweden
e-mail: betul.atalay@teorfys.lu.se
[2] Department of Physics, Çanakkale Onsekiz Mart University, Çanakkale, Turkey
e-mail: batalay@comu.edu.tr
[3] Materials Science and Applied Mathematics, Malmö University, 20506 Malmö, Sweden
[4] Institute of Modern Physics, Fudan University, Shanghai, PR China

# Computational procedure

- $2s^2 2p^6 nl$, $n \leq 7$ and $l \leq 6$, configurations in Si IV.
- we performed the calculations for states belonging to $2s^2 2p^6 nl$, $n \leq 9$ and $l \leq 6$, i.e., we added two more layers spectroscopic orbitals in comparison to the states we were targeting.
- two layers aim to correcting the tail of the wave functions for the targeted states
- optimize correlation orbitals on MR-SD-CV
- optimize additional correlation orbitals on the $1s^2 2s^2 2p^6$ core based on SD-CC expansion
- transform to NOs based on SD-CC expansion
- CI based on MR-SD-CV-CC expansion in NO basis

# Compactness of wave function

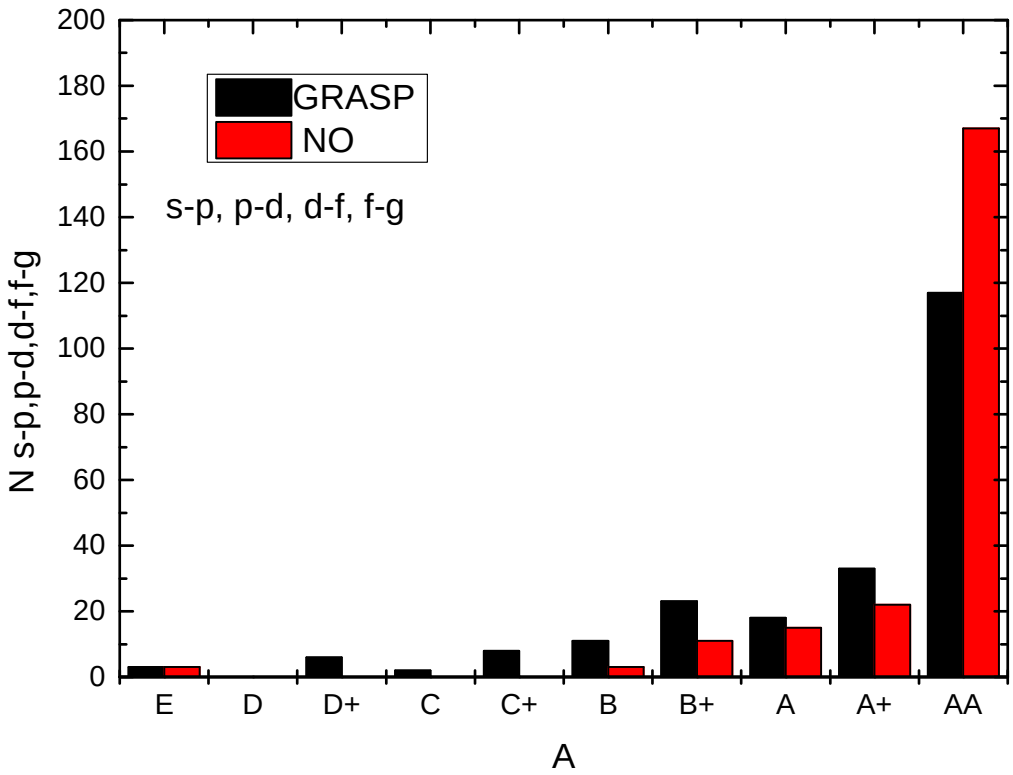
- energy level structure unchanged
- expansion concentrated to fewer CSFs
- take the expansion and accumulate the contributions up to 0.999999 of the full wave function. See how many CSFs survive

| | ordinary | NO |
|---|---|---|
| core | 6163/19253 | 3710/19253 |
| even parity | 437 703/995 020 | 264 047/995 020 |
| odd parity | 425 451/993 501 | 255 974/993 501 |

# Transition rates

- results from original calculation very good
- relative difference between transition rates in length and velocity gauge is halved in NO basis
- rates in velocity gauge more stable with respect to the NO basis, i.e. it is the length gauge that is mostly affected
- Gediminas QQE analysis shows that transitions are promoted to more accurate classes according to NIST definition
- NIST classes: AA $\leq$ 1 %, $A^+ \leq$ 2 %, A $\leq$ 3 %, $B^+ \leq$ 7 %, B $\leq$ 10 %, $C^+ \leq$ 18 %, C $\leq$ 25 %, $D^+ \leq$ 40 %, D $\leq$ 50 %, and E $>$ 50 %

# Transition rates



# Transformation to natural orbitals - In I

Results due to Betul Atalay who unfortunately could not participate

- states of the $5s^2 5p$, $5s^2 6p$, $5s^2 7p$, $5s^2 8p$, $5s^2 4f$ odd and $5s^2 6s$, $5s^2 7s$, $5s^2 8s$, $5s^2 5d$, $5s^2 6d$, $5s5p^2$ even configurations.
- Hybrid strategy: large MR including also $5p^3$, $5p^2 6p$ etc

| layer | orbitals | |
|---|---|---|
| 1 | $\{10s, 10p, 7d, 5f, 5g\}$ | CV $5s^2$ as the core |
| 2 | $\{11s, 11p, 8d, 6f, 6g\}$ | CV $5s^2$ as the core |
| 3 | $\{12s, 12p, 9d, 7f, 7g, 6h\}$ | VV $4s^2 4p^6 4d^{10}$ as core |
| 4 | $\{13s, 13p, 10d, 8f, 8g, 7h, 7i\}$ | VV $4s^2 4p^6 4d^{10}$ as core |
| 5 | $\{14s, 14p, 11d, 9f, 9g, 8h, 8i\}$ | VV $4s^2 4p^6 4d^{10}$ as core |
| 6 | $\{15s, 15p, 12d, 10f, 10g, 9h, 9i\}$ | VV and CV $4s^2 4p^6 4d^{10}$ as core |
| 7 | $\{16s, 16p, 13d, 11f, 11g, 10h, 10i\}$ | VV and CV $4s^2 4p^6 4d^{10}$ as core |
| 8 | $\{17s, 17p, 14d, 12f, 12g, 10h, 10i\}$ | VV and CV $4s^2 4p^6 4d^{10}$ as core |

# Computational procedure

CI calculation

- SDMR-VVCV in hybrid orbital orbital basis plus S MR with $2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}$ as core
- SDMR-VVCV in natural orbital basis plus SMR with $2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}$ as core
- transformation to NOs based on the SMR expansion

# Computational procedure

Transformation to NOs based on different types of expansions in the three examples. Why?

- "Research is what I'm doing when I don't know what I'm doing"
- inclination is that the SMR expansion is the one to use for transformation to NOs

# Energies in $cm^{-1}$

| State | layer8+S | layer 8+S+NO | NIST |
|---|---|---|---|
| $5s^2 5p\ ^2P^o_{1/2}$ | 0 | 0 | 0 |
| $5s^2 5p\ ^2P^o_{3/2}$ | 2 222 | 2 230 | 2 212.599 |
| $5s^2 6s\ ^2S_{1/2}$ | 24 354 | 24 265 | 24 372.957 |
| $5s^2 6p\ ^2P^o_{1/2}$ | 31 785 | 31 703 | 31 816.982 |
| $5s^2 6p\ ^2P^o_{3/2}$ | 32 079 | 31 997 | 32 115.251 |
| $5s^2 5d\ ^2D_{3/2}$ | 32 995 | 32 827 | 32 892.230 |
| $5s^2 5d\ ^2D_{5/2}$ | 33 013 | 32 846 | 32 915.539 |
| $5s5p^2\ ^4P_{1/2}$ | 35 441 | 35 228 | 34 977.678 |
| $5s5p^2\ ^4P_{3/2}$ | 36 498 | 36 277 | 36 020.780 |
| $5s^2 7s\ ^2S_{1/2}$ | 36 239 | 36 147 | 36 301.864 |
| $5s5p^2\ ^4P_{5/2}$ | 37 962 | 37 727 | 37 451.962 |
| $5s^2 7p\ ^2P^o_{1/2}$ | 38 797 | 38 712 | 38 861.43 |
| $5s^2 7p\ ^2P^o_{3/2}$ | 38 907 | 38 822 | 38 972.90 |
| $5s^2 6d\ ^2D_{3/2}$ | 39 124 | 38 931 | 39 048.53 |
| $5s^2 6d\ ^2D_{5/2}$ | 39 163 | 38 985 | 39 098.38 |
| $5s^2 4f\ ^2F^o_{7/2}$ | 39 632 | 39 558 | 39 707.59 |
| $5s^2 4f\ ^2F^o_{5/2}$ | 39 632 | 39 558 | 39 707.59 |
| $5s^2 8s\ ^2S_{1/2}$ | 40 563 | 40 478 | 40 636.98 |
| $5s^2 8p\ ^2P^o_{1/2}$ | 41 752 | 41 670 | 41 827.10 |
| $5s^2 8p\ ^2P^o_{3/2}$ | 41 805 | 41 723 | 41 881.44 |
| $5s^2 9s\ ^2S_{1/2}$ | 42 640 | 42 561 | 42 719.02 |
| $5s^2 9p\ ^2P^o_{1/2}$ | 43 289 | 43 211 | 43 369.09 |
| $5s^2 9p\ ^2P^o_{3/2}$ | 43 319 | 43 241 | 43 399.53 |
| NSCFs | 21 555 509 | 21 555 509 | |

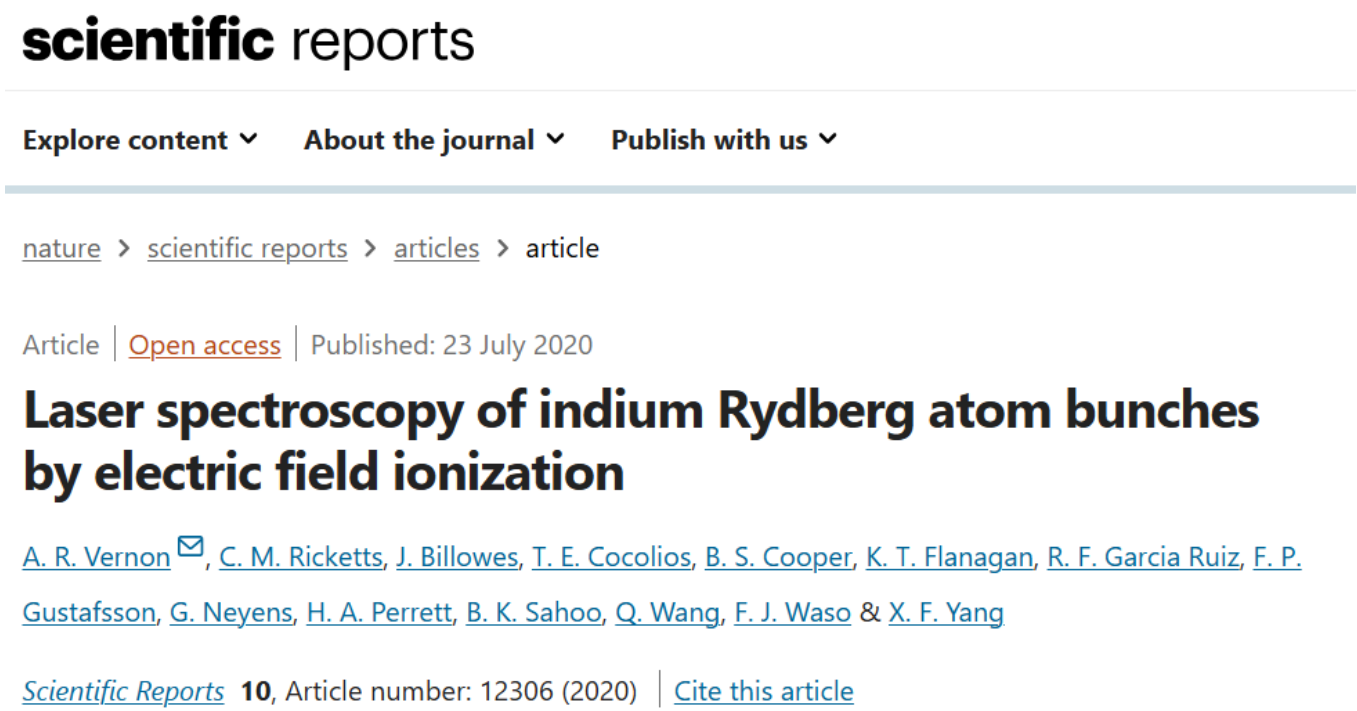
# Energies

Things to note

- $5s^2 5d$ and $5s5p^2$ states that were too high are brought down.
- ground state energy lowered from
  $-5873.7598418$ H to $-5874.0479647$ H.
  gain HUGE compared to what we gain by adding layers of correlation orbitals!

# Hyperfine structure, $A$ constants

Important paper



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Article | Open access | Published: 23 July 2020

## Laser spectroscopy of indium Rydberg atom bunches by electric field ionization

A. R. Vernon ✉, C. M. Ricketts, J. Billowes, T. E. Cocolios, B. S. Cooper, K. T. Flanagan, R. F. Garcia Ruiz, F. P. Gustafsson, G. Neyens, H. A. Perrett, B. K. Sahoo, Q. Wang, F. J. Waso & X. F. Yang

*Scientific Reports* **10**, Article number: 12306 (2020) | Cite this article

# Hyperfine structure, $A$ constants

| State | 8 + S | 8 + S NO | Saf | Sahoo | Sahoo exp | Exp |
|---|---|---|---|---|---|---|
| $5s^2 5p\ ^2P^o_{1/2}$ | 2417 | 2455 | 2306 | 2274 | 2282.04 | 2282 |
| $5s^2 5p\ ^2P^o_{3/2}$ | 248.2 | 258.5 | 262.4 | 253 | 241.98 | |
| $5s^2 6s\ ^2S_{1/2}$ | 1640 | 1702 | 1812 | 1645 | 1684.75 | 1685 |
| $5s^2 6p\ ^2P^o_{1/2}$ | 249.7 | 280.7 | 263.2 | | | 250.2 |
| $5s^2 6p\ ^2P^o_{3/2}$ | 62.96 | 71.94 | 77.82 | | | 79.33 |
| $5s^2 5d\ ^2D_{3/2}$ | -54.73 | -62.85 | -11.48 | -9.74 | -64 | 62 |
| $5s^2 5d\ ^2D_{5/2}$ | 125.3 | 150.6 | 47.83 | 39.87 | 151.2 | 152 |
| $5s5p^2\ ^4P_{1/2}$ | 9512 | 9471 | | | | 9194 |
| $5s5p^2\ ^4P_{3/2}$ | 4146 | 4132 | | | | 3999 |
| $5s^2 7s\ ^2S_{1/2}$ | 486.7 | 522.7 | 544.5 | 520 | | |
| $5s5p^2\ ^4P_{5/2}$ | 3814 | 3791 | | | 3696 | 3654 |
| $5s^2 7p\ ^2P^o_{1/2}$ | 85.37 | 100.2 | 95.61 | | | 90.7 |
| $5s^2 7p\ ^2P^o_{3/2}$ | 23.02 | 27.40 | 30.83 | | | 32.3 |
| $5s^2 6d\ ^2D_{3/2}$ | -41.68 | -63.59 | -11.2 | | | |
| $5s^2 6d\ ^2D_{5/2}$ | 137.45 | 204.4 | 30.81 | | | |
| $5s^2 4f\ ^2F^o_{7/2}$ | 0.087 | 0.084 | 0.2293 | | | |
| $5s^2 4f\ ^2F^o_{5/2}$ | 0.1243 | 0.142 | 0.1871 | | | |
| $5s^2 8s\ ^2S_{1/2}$ | 199.3 | 220.1 | 240.8 | 233 | 243.85 | |
| $5s^2 8p\ ^2P^o_{1/2}$ | 37.78 | 45.70 | 45.97 | | | 44.2 |
| $5s^2 8p\ ^2P^o_{3/2}$ | 10.46 | 12.85 | 15.42 | | | 16.3 |

# Transition rates - NIST classes

NIST classes: AA $\leq$ 1 %, $A^+ \leq$ 2 %, A $\leq$ 3 %, $B^+ \leq$ 7 %, B $\leq$ 10 %, $C^+ \leq$ 18 %, C $\leq$ 25 %, $D^+ \leq$ 40 %, D $\leq$ 50 %, and E $>$ 50 %

# Transition rates - ordinary orbitals

```
  1-5873.75984180  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).5p_2P
  1-5873.64887616  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).6s_2S
  24354.14 CM-1      4106.08 ANGS(VAC)      4105.65 ANGS(AIR)
E1  S =  3.42574D+00   GF =  2.53426D-01   AKI =  5.01313D+07   dT =  0.05054
         3.25260D+00         2.40618D-01         4.75977D+07   NIST class=B+

  1-5873.64887616  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).6s_2S
  1-5873.61501516  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).6p_2P
   7431.63 CM-1     13456.00 ANGS(VAC)     13454.60 ANGS(AIR)
E1  S =  3.81661D+01   GF =  8.61562D-01   AKI =  1.58696D+07   dT =  0.03090
         3.69867D+01         8.34938D-01         1.53792D+07   NIST class=B+

  1-5873.64887616  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).6s_2S
  1-5873.58306533  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).7p_2P
  14443.81 CM-1      6923.38 ANGS(VAC)      6922.66 ANGS(AIR)
E1  S =  5.36848D-01   GF =  2.35536D-02   AKI =  1.63883D+06   dT =  0.17660
         4.42041D-01         1.93941D-02         1.34941D+06   NIST class=C

  1-5873.75984180  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).5p_2P
  1-5873.59472037  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).7s_2S
  36239.96 CM-1      2759.38 ANGS(VAC)      2759.09 ANGS(AIR)
E1  S =  2.68608D-01   GF =  2.95686D-02   AKI =  1.29514D+07   dT =  0.06453
         2.51275D-01         2.76606D-02         1.21157D+07   NIST class=B+

  1-5873.61501516  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).6p_2P
  1-5873.59472037  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).7s_2S
   4454.19 CM-1     22450.76 ANGS(VAC)     22448.44 ANGS(AIR)
E1  S =  3.96306D+01   GF =  5.36196D-01   AKI =  3.54792D+06   dT =  0.06663
         3.69902D+01         5.00472D-01         3.31154D+06   NIST class=B
```

# Transition rates - NOs

```
  3-5874.03780394  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).5p_2P
  1-5873.93740296  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).6s_2S
  22035.47 CM-1      4538.14 ANGS(VAC)      4537.66 ANGS(AIR)
E1   S =  8.28790D+00   GF =  5.54742D-01   AKI =  8.98355D+07   dT =  0.02105
         8.11343D+00         5.43064D-01         8.79443D+07   NIST class=A

  1-5873.93740296  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).6s_2S
  3-5873.90217166  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).6p_2P
   7732.38 CM-1     12932.64 ANGS(VAC)     12931.30 ANGS(AIR)
E1   S =  7.36341D+01   GF =  1.72948D+00   AKI =  1.72435D+07   dT =  0.00500
         7.40044D+01         1.73818D+00         1.73302D+07   NIST class=AA

  1-5873.93740296  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).6s_2S
  3-5873.87107450  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).7p_2P
  14557.41 CM-1      6869.35 ANGS(VAC)      6868.64 ANGS(AIR)
E1   S =  1.30939D+00   GF =  5.78998D-02   AKI =  2.04610D+06   dT =  0.01201
         1.32531D+00         5.86038D-02         2.07098D+06   NIST class=A+

  3-5874.03780394  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).5p_2P
  1-5873.88326461  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).7s_2S
  33917.46 CM-1      2948.33 ANGS(VAC)      2948.02 ANGS(AIR)
E1   S =  5.60932D-01   GF =  5.77907D-02   AKI =  2.21726D+07   dT =  0.01252
         5.68042D-01         5.85232D-02         2.24536D+07   NIST class=A+

  3-5873.90217166  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).6p_2P
  1-5873.88326461  2s(2).2p(6).3s(2).3p(6).3d(10).4s(2).4p(6).4d(10).5s(2).7s_2S
   4149.62 CM-1     24098.61 ANGS(VAC)     24096.12 ANGS(AIR)
E1   S =  8.87672D+01   GF =  1.11888D+00   AKI =  6.42559D+06   dT =  0.01503
         8.74331D+01         1.10207D+00         6.32902D+06   NIST class=A+
```

# Summary and conclusions

- layer-by-layer approach has limitations as the valence orbitals fixed from DF
- NO basis accounts for the valence orbital contraction due to interaction with the core
- sizeable effects on hyperfine structure and transition rates
- effect largest for neutral systems
- transformation to NOs can (should?) be done based on SMR expansion (good since these expansions are small)
- systematic analysis of the effect of NOs can be done using perturbation theory, Gediminas has preliminary results

Thank you for listening!