GRASP:

Recent Code Developments and Applications

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Outline

GRASPG -- An extension to Grasp2018

- Performance Tests and Improvements on the rmcdhf and rci Programs of GRASP
  Atoms 11, 12 (2023)
- Reducing the computational load – atomic multiconfiguration calculations based on configuration state function generators
  Comp. Phys. Comm. 283, 108562 (2023)
- Graspg --An extension to Grasp2018 based on configuration state function generators.
  Comp. Phys. Comm. 312, 109604 (2025)

GRASPG is available on GitHub: https://github.com/compas.

srcg	directory with the subdirectories appl, containing the source code for the application programs, lib, containing the source code for the libraries and tool, containing the source code for the tools.
graspgtest	directory containing scripts for all the test runs and examples to be described in later sections of this article

- Multiconfiguration methods

$$\Psi(\Gamma J) = \sum_{i=1}^{N_{CSF}} c_i \Phi(\gamma_i J)$$

Atomic State Function (ASF) — Configuration State Function (CSF)

- Computation of Hamiltonian matrix elements

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

- Radial integrals and effective interaction strengths
- Spin-angular integration (dominate the CPU time)

- Introduction of Configuration State Function Generator (CSFG)

Spin-angular integration is independent of the principal quantum numbers

- **Labeling space**: excitations from reference configurations to a labeling-ordered orbital set of highly occupied orbitals.

MR: $(2s^2 2p^6)3s^2$, $3p^2$, $3s3d$, $3d^2$ $\{1s, 2s, 2p\text{-}, 2p, 3s, 3p\text{-}, 3p, 3d\text{-}, 3d\}$

- **Correlation space**: excitations from reference configurations to a symmetry-ordered orbital set of correlation orbitals.

$$\underbrace{4s,5s}_{\kappa=-1},\ \underbrace{4p-,5p-}_{\kappa=+1},\underbrace{4p,5p}_{\kappa=-2},\underbrace{4d-,5d-}_{\kappa=+2},\underbrace{4d,5d}_{\kappa=-3},\underbrace{4f-,5f-}_{\kappa=+3},\underbrace{4f,5f}_{\kappa=-4},\underbrace{4g-,5g-}_{\kappa=+4},\underbrace{4g,5g}_{\kappa=-5}$$

$$\{5s,5p-,5p,5d-,5d,5f-,5f,5g-,5g\}$$

11 988 CSFGs → 28 055 CSFs

$$\{9s,9p-,9p,9d-,9d,9f-,9f,9g-,9g\}$$

11 988 CSFGs → 380 624 CSFs

- Computer Physics Communications 312 (2025) 109604

1. Programs to generate CSFs/CSFGs list

a) **rcsfggenerate_csfg** – generate a list of CSFs in Graspg format.

b) **rcsfgsplit_csfg** – split a list of CSFs in Graspg format into a number of lists, with the CSFGs built from different user defined sets of symmetry ordered orbitals.

c) **rcsfgblocksplit_csfg** – split a list of CSFs in Graspg format into a number of lists, one for each Jp-block.

d) **rcsfgextend_csfg** – extend the set of symmetry ordered orbitals for a list of CSFs in Graspg format.

e) **rcsfgexpand_csfg** – expand a list of CSFs in Graspg format, to a list of CSFs in ordinary Grasp2018 format.

- **rcsfg.out**
- **CSFs**: first come the CSFs in the labelling space, and then the generating CSFs
- **Peel subshells:** first come the orbitals in the labeling ordered set, and then the orbitals in the symmetry-ordered set

```
Core subshells:

Peel subshells:
  1s    2s    2p-   2p    3s    3p-   3p    3d-   3d    4s    5s    6s    7s
  4p-   5p-   6p-   7p-   4p    5p    6p    7p    4d-   5d-   6d-   7d-   4d
  5d    6d    7d
CSF(s):
  1s ( 2)  2s ( 1)  2p-( 1)      <-- start CSFs in labeling space
              1/2       1/2
                            0-

            ....

  3p-( 1)  3d-( 2)  3d ( 1)      <-- end CSFs in labeling space
     1/2         2      5/2
               5/2          0-
  1s ( 2)  2s ( 1)  7p-( 1)      <-- start generating CSFs in
              1/2       1/2          correlation space
                            0-

            ....

  2s ( 1)  2p-( 1)  7d-( 2)      <-- end generating CSF in
     1/2      1/2         0          correlation space
                  0         0-
```

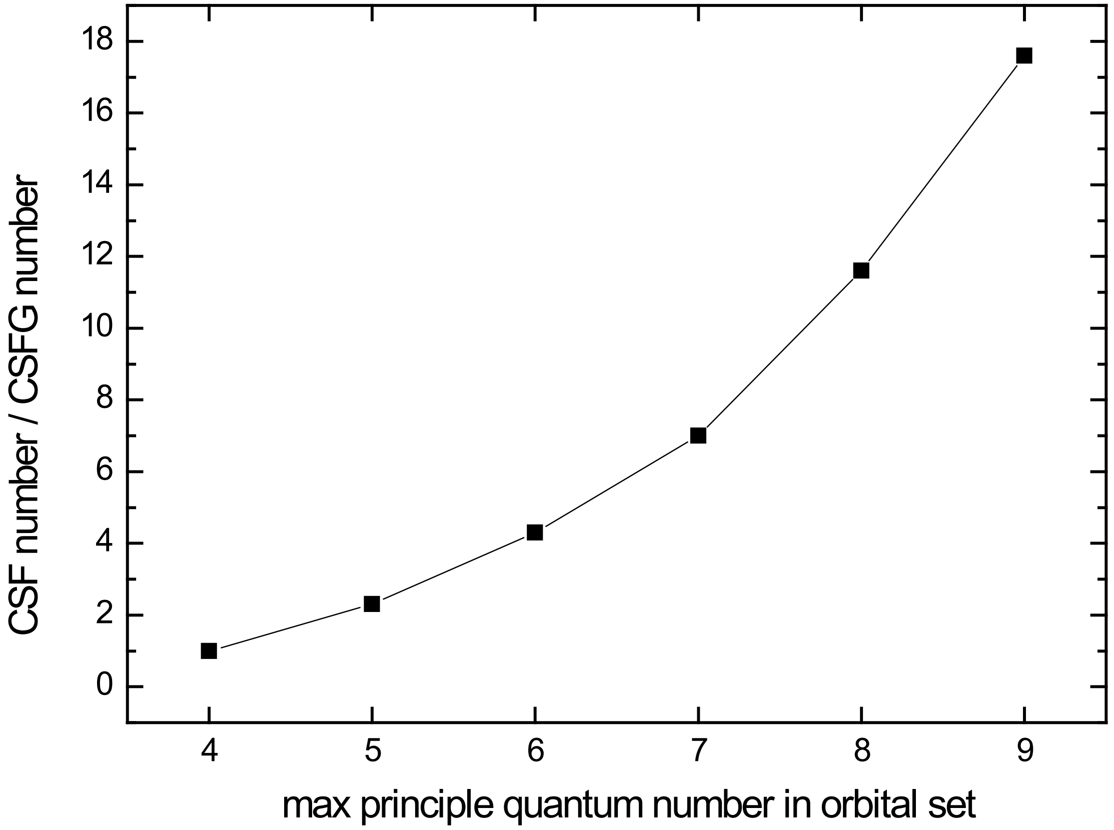
- **filename.l**
- Keep track of the orbitals that are in the labeling ordered set

```
          9    = nonsym
  1s    2s    2p-   2p    3s    3p-   3p    3d-   3d
```

GRASPG -- An extension to Grasp2018

Block averaged labeling and generating CSFs, M', block averaged CSFs in the expanded list, M, and the reduction ratio $R = M/M'$ as functions of the increasing orbital set for the VV and CV MCDHF calculations reported in section 9. Orbitals given in non-relativistic notation.

orbital set	M'	M	R	R^2
$\{5s, 5p, 5d, 5f, 5g\}$	2 431	5 606	2.3	5.3
$\{6s, 6p, 6d, 6f, 6g, 6h\}$	3 322	14 355	4.3	18.7
$\{7s, 7p, 7d, 7f, 7g, 7h, 7i\}$	4 203	29 323	7.0	48.7
$\{8s, 8p, 8d, 8f, 8g, 8h, 8i\}$	4 313	49 915	11.6	133.9
$\{9s, 9p, 9d, 9f, 9g, 9h, 9i\}$	4 313	76 130	17.6	311.5



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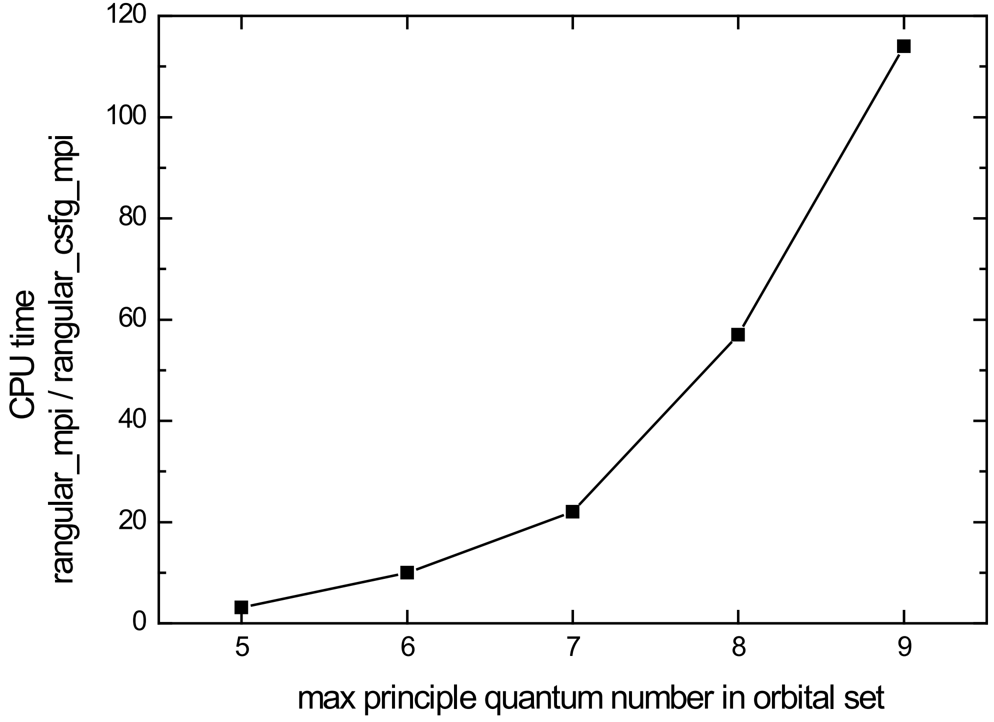
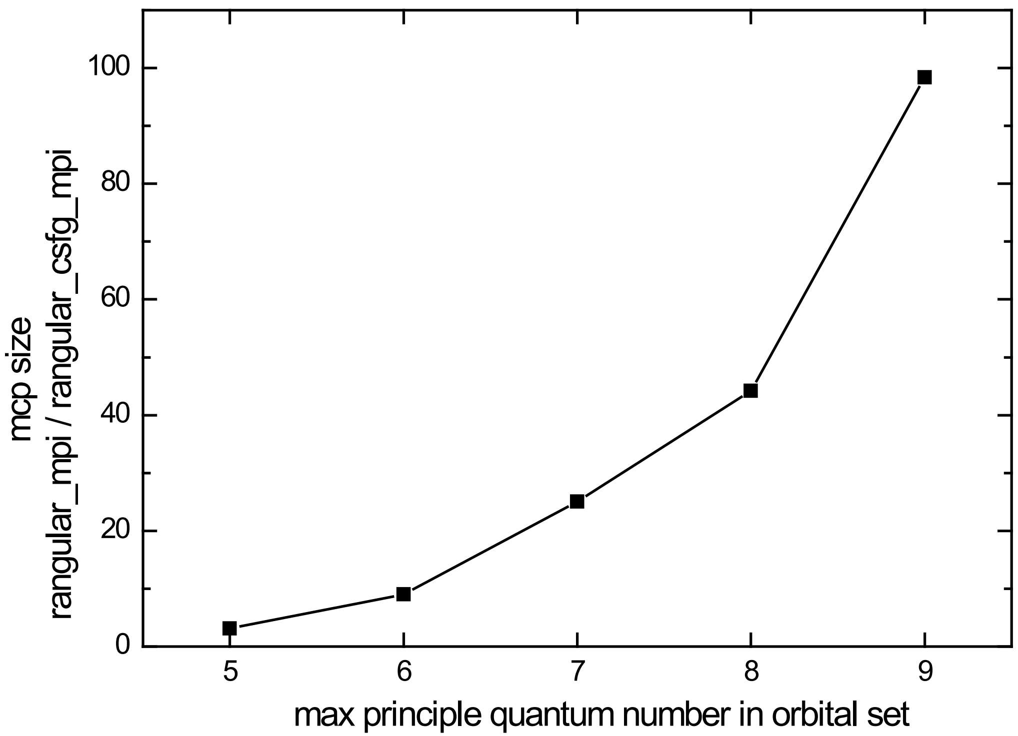
2. Programs to perform spin-angular integration: rangular_csfg_mpi

Reduction in CPU time
for spin-angular integration



Reduction in
spin-angular data size



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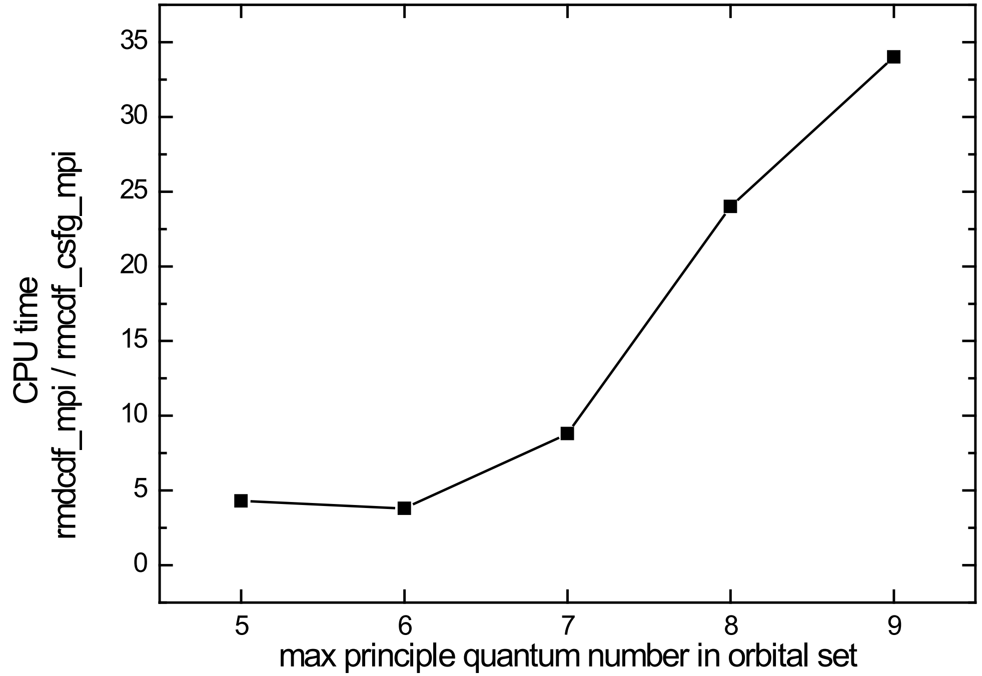
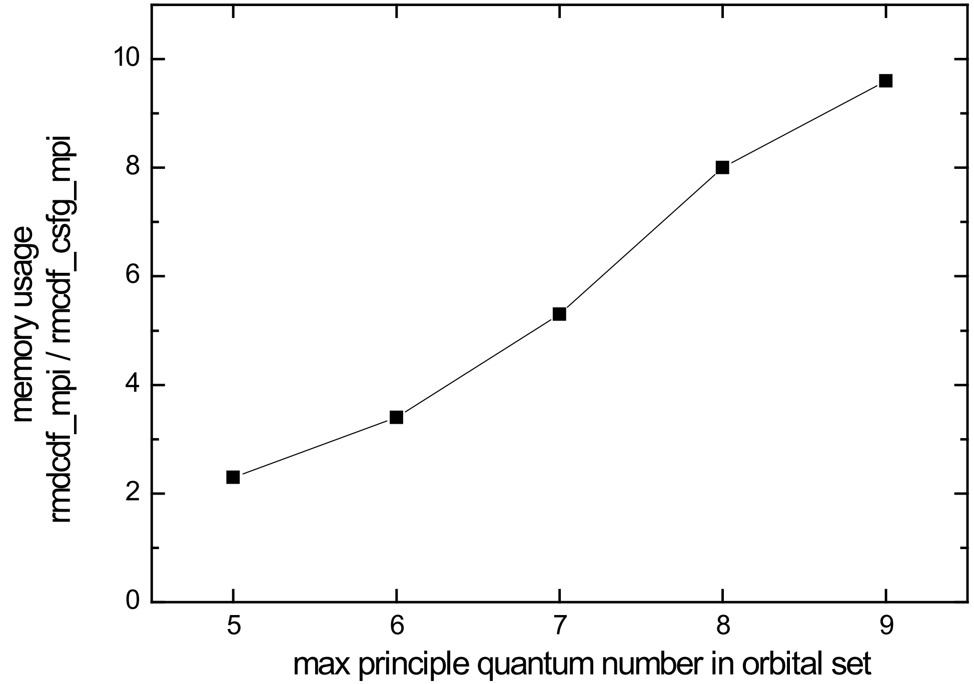
3. Programs to perform rmcdhf calculations: rmcdhf_csfg_mpi

Reduction in CPU time for rmcdhf calculations



Reduction in memory usage for rmcdhf calculations



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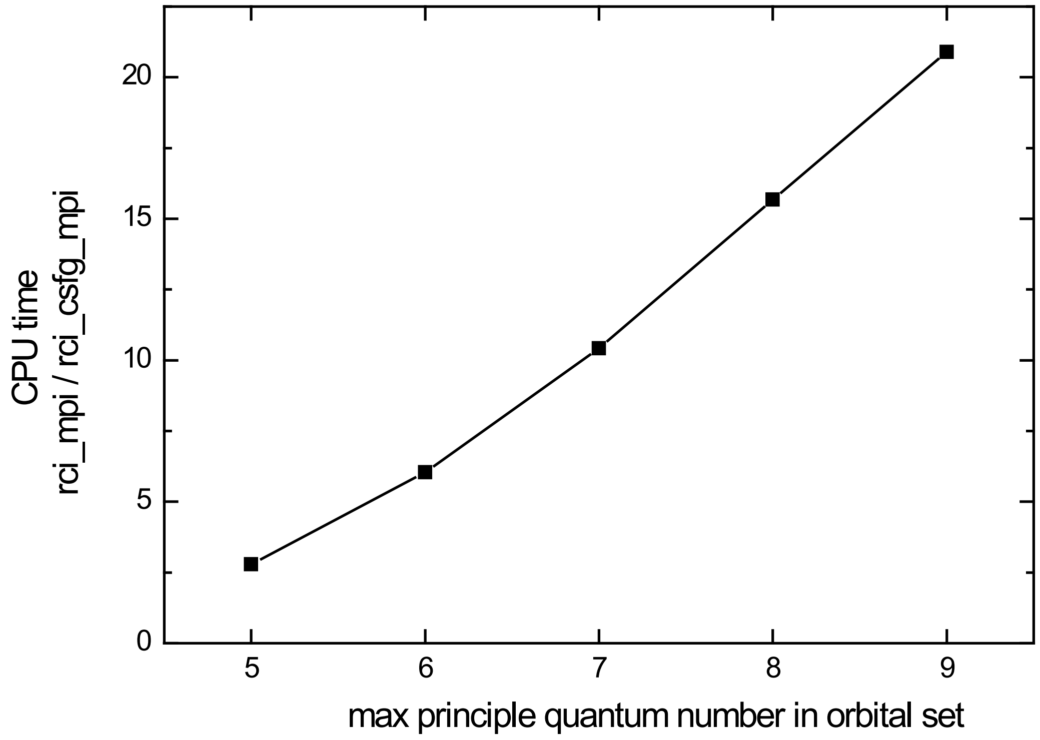
4. Programs to perform CI calcultions: rci_csfg_mpi

Reduction in CPU time for rci calculations



More new features to reduce the consumption of computing resources

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1. Restrictions on Breit interaction

Discard Breit interaction between high n and l orbitals

Orbital Set	rci_mpi	rci_csfg_mpi	ratio
$\{9s, 9p, 9d, 9f, 9g, 9h, 9i\}$	2d 11 h	2 h 50 m	20.9
$\{9s, 9p, 9d, 9f, 9g, 9h, 9i\}^*$		1 h 17 m	46.0

* Breit interaction restricted to CSFs built on *spdf* orbitals.

- Speed-up factor: 2.5
- Deviations: <10 ppm

2. Prior condensation： rmixaccumulate_csfg

(1) Perform calculations using a small set of symmetry-ordered orbitals

(2) Sort the squared weights of the CSFGs, and accumulate to a predefined fraction, e.g., 0.9999999

(3) The surviving CSFGs are used for larger calculations based on extended sets of symmetry-ordered orbitals

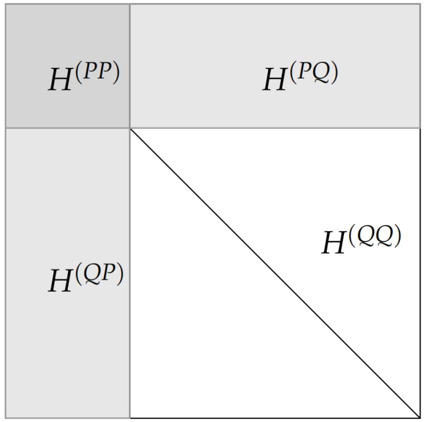
Orbital Set	rci_mpi	rci_csfg_mpi	ratio
$\{9s,9p,9d,9f,9g,9h,9i\}$	2d 11 h	2 h 50 m	20.9
$\{9s,9p,9d,9f,9g,9h,9i\}^{*}$		1 h 17 m	46.0
$\{9s,9p,9d,9f,9g,9h,9i\}^{**}$		17 m 9 s	208

* Breit interaction restricted to CSFs built on *spd f* orbitals.
** Restricted Breit and *a priori* condensation.

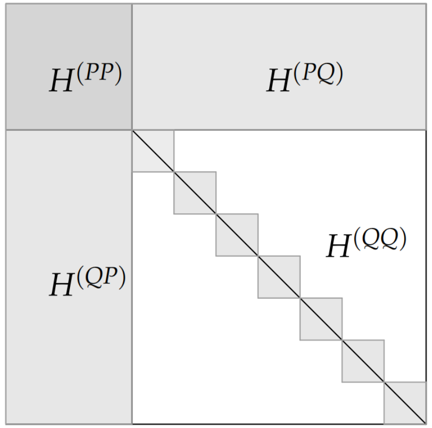
- Speed-up factor: 4.5
- Deviations: <0.2 ppm

3. (CSFG/relativistic/nonrelativistic) blockwise zero-first method

Hamiltonian matrix for the CSF zero-first method



Hamiltonian matrix for the CSFG blockwise zero-first method



- CSFG blockwise
- Relativistic configuration blockwise
- Nonrelativistic configuration blockwise

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4. Redistribute the rci.res files (rdistHmatrix_csfg)

- ➢ The computation of the **Hamiltonian matrix elements** scales almost linearly with the number of processes.
- ✓ **The more processes used, the faster**

- ■ **In restart mode, redistribute the matrix element (rci.res) files into fewer processes**

- ➢ During the **diagonalization**, depending on the available memory per process, the Hamiltonian matrix is loaded into memory or kept on disk.
- ✓ **Fewer processes are preferable**

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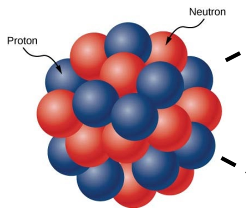
GRASPG -- Some recent applications

- ^{229}Th

Isomeric state



△E~8.4 eV

λ~148.4nm

Half-life~ 20-40min

Ground state

The lowest known nuclear-excited state

Highly-accurate nuclear clock

Quality factor 10^{19}-10^{20}

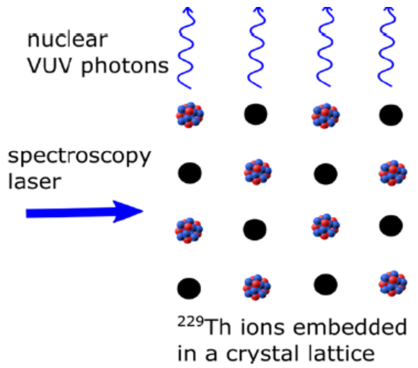
Less sensitive to external perturbations

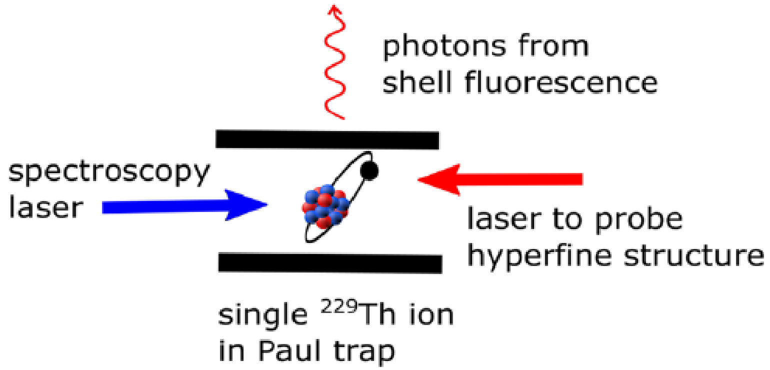
10^{-19} potential accuracy

Sensitive probe for fundamental physics

Strongly enhanced sensitivity for variations of fundamental constants

K factor ~ $-(0.82 \pm 0.25) \times 10^4$





Solid-state nuclear clock

- Embedded in a crystal-lattice environment (CaF2， MgF_2，$LiSrAlF_2$ ···)
- Large number of simultaneously excited thorium nuclei (~10^{18} cm^{-3})
- Cost of achievable accuracy
- $^{229}Th^{4+}$

Ion trap nuclear clock

- Trapped and laser-cooled
- Single or multiple ions
- Expected to provide the higher accuracy
- $^{229}Th^{3+}$

GRASPG -- Some recent applications

- 1976: <100 eV Nucl. Phys. A 259, 29 (1976)

  1990: 1(4) eV Phys. Rev. Lett. 64, 271 (1990)

  1994: 3.5(1.9) eV Phys. Rev. C 49, 1845 (1994)

  2007: 7.6(5) eV Phys. Rev. Lett. 98, 142501 (2007)

  2020: 8.10(17) eV Phys. Rev. Lett. 125, 142503 (2020)

$^{229}Th^{0+}$, γ ray spectrum

- 2019: 8.28(17) eV Nature 573, 243 (2019)

$^{229}Th^{0+}$, internal conversion

- 2023:8.338(24) eV Nature 617, 706 (2023)

  2024: 8.35574(3) Phys. Rev. Lett. 132, 182501 (2024)

  8.355733(2)stat(10)sys eV Phys. Rev. Lett. 133, 013201 (2024)

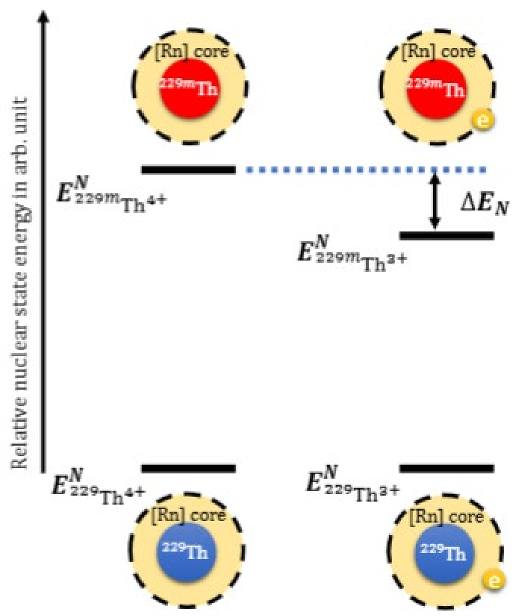
  8.355733554021(8) eV Nature 633, 63 (2024)

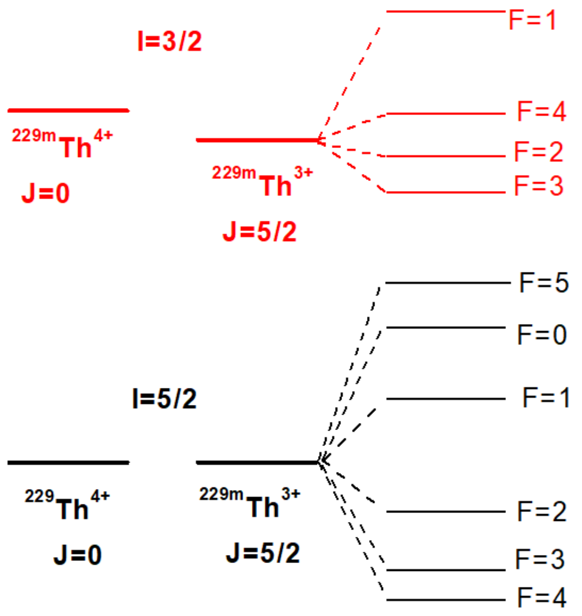
$^{229}Th^{4+}$, radiative decay

$^{229}Th^{4+}$, laser excitation

Laser excitation of $^{229}Th^{3+}$ has not been achieved!

Effects of electrons on nuclear transition frequency





- **Field shift**: Coulomb interaction of atomic electrons with the nucleus
- Hyperfine splitting: interaction between the non-zero J of the electrons and non-zero I of the nucleus

Effects of electrons on nuclear transition frequency

$$\Delta E_N = (E_{g,{}^{229m}Th^{3+}} - E_{g,{}^{229}Th^{3+}}) - (E_{g,{}^{229m}Th^{4+}} - E_{g,{}^{229}Th^{4+}})$$

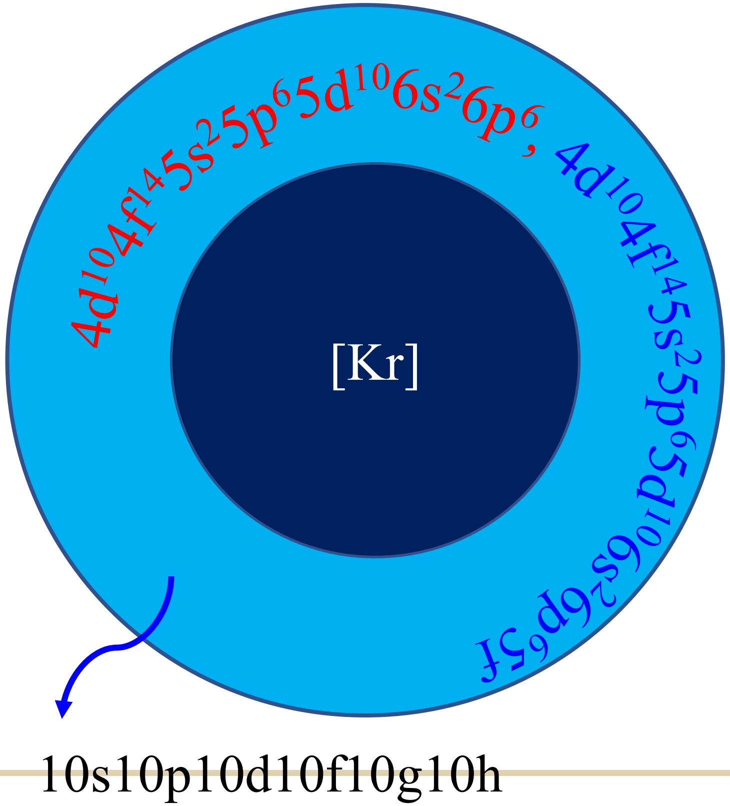
- **Four** independent calculations:
- □ $^{229}Th^{4+}$, $^{229m}Th^{4+}$

  Number of CSFs: 58,779

  Number of CSFGs: 4,890
- □ $^{229}Th^{3+}$, $^{229m}Th^{3+}$

  Number of CSFs: 2,066,564

  Number of CSFGs: 192,999



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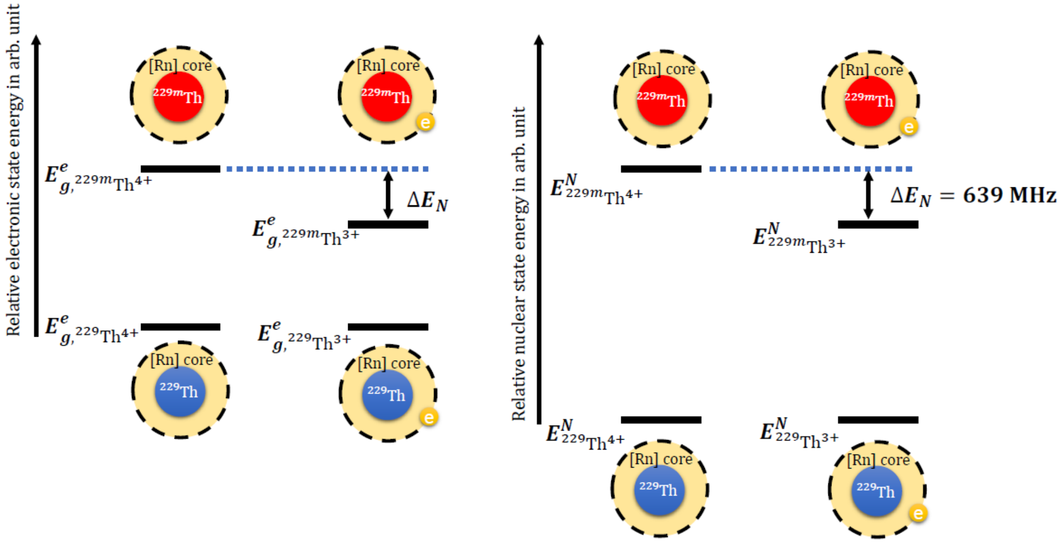
GRASPG -- Some recent applications

➢ Field shift of the nuclear clock transition frequency between Th^{3+} and Th^{4+}

Table 1 Calculated energy of the atomic ground state for $^{229,229m}Th^{3+}$ and $^{229,229m}Th^{4+}$ and the difference $\Delta E_{g,\mathrm{Th\,IV}} = E_{g,^{229m}Th^{3+}} - E_{g,^{229}Th^{3+}}$ and $\Delta E_{g,\mathrm{Th\,V}} = E_{g,^{229m}Th^{4+}} - E_{g,^{229}Th^{4+}}$, as functions of active sets.

ASs	$E_{g,^{229}Th^{3+}}$	$E_{g,^{229m}Th^{3+}}$	$\Delta E_{g,\mathrm{Th\,IV}}$	$E_{g,^{229}Th^{4+}}$	$E_{g,^{229m}Th^{4+}}$	$\Delta E_{g,\mathrm{Th\,V}}$
AS7	-26452.1231423864	-26452.1196339200	0.0035084664	-26451.1352841710	-26451.1317756064	0.0035085646
AS8	-26452.2466260137	-26452.2431175449	0.0035084688	-26451.2059508799	-26451.2024423136	0.0035085663
AS9	-26452.2894648398	-26452.2859563704	0.0035084694	-26451.2365257811	-26451.2330172145	0.0035085666
AS10	-26452.3073192168	-26452.3038107472	0.0035084696	-26451.2517689877	-26451.2482604210	0.0035085667

AS_n	ΔE_N (In Hartree)	$\Delta \nu_N$ (In MHz)
AS_7	−9.82E−08	−646
AS_8	−9.75E−08	−642
AS_9	−9.72E−08	−640
AS_{10}	−9.71E−08	−639



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➢ Hyperfine splitting of Nuclear clock transition frequency of $^{229}Th^{3+}$

$$\Delta E_F^{(1)} = \frac{1}{2} AC + B \frac{\frac{3}{4}C(C+1) - I(I+1)J(J+1)}{2I(2I-1)J(2J-1)} \qquad C = F(F+1) - J(J+1) - I(I+1)$$

$$A = \frac{\mu}{I} \frac{1}{\sqrt{J(J+1)}} \langle \Gamma J || T^{(1)} || \Gamma J \rangle \qquad B = 2Q \sqrt{\frac{J(2J-1)}{(J+1)(2J+3)}} \langle \Gamma J || T^{(2)} || \Gamma J \rangle$$

$$\mu_{is} / \mu_g = -1.04(15), \; Q_{is} / Q_g = 0.57003(1)$$

(Nature 633, 63 (2024) ; Nature 636, 603 (2024))

$$A_g = 82.2(6) MHz, \; B_g = 82.2(6) MHz \Longrightarrow A_{is} = \text{-}142.5\ (20.5)\ \text{MHz}, \; B_{is} = 1293\ (6)\ \text{MHz}$$

(Phys. Rev. Lett. 106, 223001 (2011))

$$I_g = 5/2, \; I_{is} = 3/2$$

In MHz

Isomer	Ground	Energy shift
$F = 1$	$F = 0$	784(117)
$F = 1$	$F = 1$	1247(115)
$F = 1$	$F = 2$	1967(113)
$F = 2$	$F = 1$	−73(71)
$F = 2$	$F = 2$	648(68)
$F = 2$	$F = 3$	1218(69)
$F = 3$	$F = 2$	-362(9)
$F = 3$	$F = 3$	209(10)
$F = 3$	$F = 4$	16(11)
$F = 4$	$F = 3$	673(80)
$F = 4$	$F = 4$	480(81)
$F = 4$	$F = 5$	−1292(80)

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GRASPG -- Some recent applications

- **Be I :** GRASPG + prior condensation
- ✓ **Targeted configurations**: $1s^2nl\,n'l'$ $(n \le 7)$
- ✓ **MR**: $1s^2nl\,n'l'$ $(2 \le n \le n' \le 14, 0 \le l(l') \le n-1, [n(n') \ge 9, l(l') \in \{s,p,d,f\}])$
- ✓ **CSFs**: SD-excitations to $\{22s, 22p, 19d, 17f, 16g, 15h, 15i, 13k, 13l, 11m\}$

  Number of CSFs: 247 482 200

  Number of CSFGs: 85 627 995
- ✓ **Prior condensation**

  Number of CSFs: 13 335 187

  Number of CSFGs: 3 622 609

  Only 5% out of the original CSFs are retained.

Configuration	Energy(cm^{-1}) (original)	Energy(cm^{-1}) (condensed)	ΔE (cm^{-1})
$1s^22s3s\ ^1S_0$	54664.60	54665.02	0.42
$1s^22p^2\ ^3P_0$	59678.61	59678.89	0.28
$1s^22s4s\ ^1S_0$	65231.45	65232.13	0.69
$1s^22s5s\ ^1S_0$	69307.99	69308.83	0.84
$1s^22s6s\ ^1S_0$	71306.77	71307.68	0.91
$1s^22s7s\ ^1S_0$	72434.12	72435.06	0.94

GRASPG -- Some recent applications

- **W^{37+}:** GRASG + Blockwise zero-first method
  - ✓ **Targeted configurations (MR)**: $4s^2 4p^6 4d$, $4s^2 4p^6 4f$, $4s^2 4p^5 4d^2$
  - ✓ **CSFs**: SD-excitations to $\{9s, 9p, 9d, 8f, 8g, 8h, 8i, 8k\}$

    Number of CSFs: 21 691 040

    P Space: 2 586 477

- **Zero-first** based on CSF:

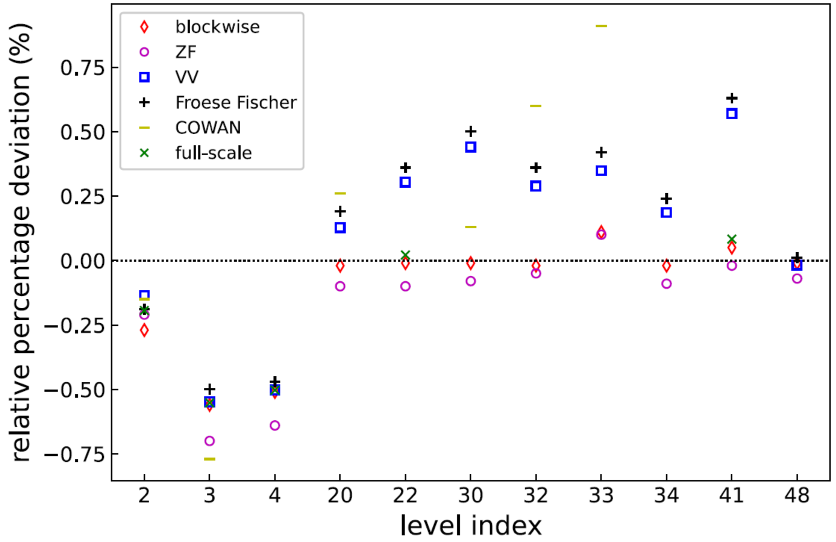
  0.1% agreement with experimental wavelengths

- **Blockwise zero-first** based on CSFG:

  0.01% agreement with experimental wavelengths

- **Blockwise zero-first** based on CSFGs in the same (non)relativistic configurations:

  Similar accuracy with the results based on CSFG



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GRASPG -- Developments on the way

➢ nrconfgenerate_csfg

1. Substitute any number of electrons from the reference configurations to non-relativistic configurations
2. Construct the non-relativistic configurations in "CSFG" format
3. Generate the relativistic configurations in "CSFG" format
4. Generate the jj-coupled CSFGs

➢ Advantages

1. 20 non-relativistic orbitals, 30 relativistic orbitals
2. Speed-up factor in generating the CSFs expansions: 2 order of magnitude
3. Speeds up the zero-first rearrangement of the CSFs expansions
4. The generated information can be used for (CSFG/relativistic/non-relativistic) blockwise zero-first calculations/NN calculations

- GRASPG + Basis selection by machine learning

Details in Chaofan Shi’ s talk!

- A partitioned correlation function interaction approach in GRASP

Details in Sijie Wu’ s talk!

Thanks for your attention!