Relativistic coupled cluster applications

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Research interests

Relativistic WFT

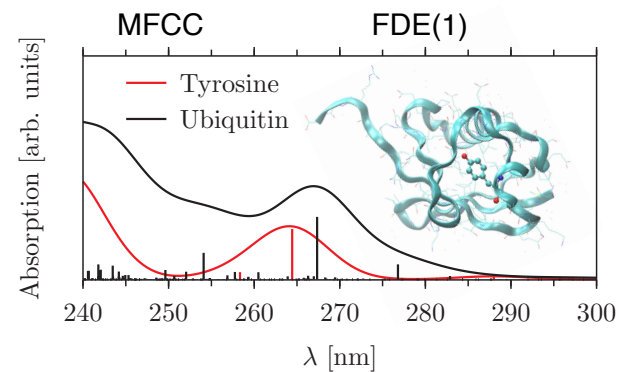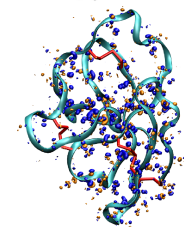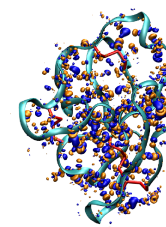WFT-in-DFT

Fast DFT
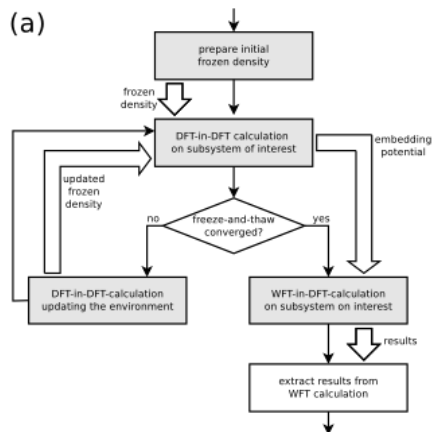
Subsystem DFT

DFTB

Approximations

System size

MFCC   FDE(1)

Absorption [arb. units]

— Tyrosine
— Ubiquitin

240   250   260   270   280   290   300

λ [nm]
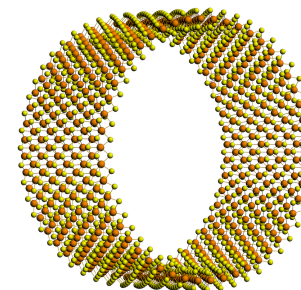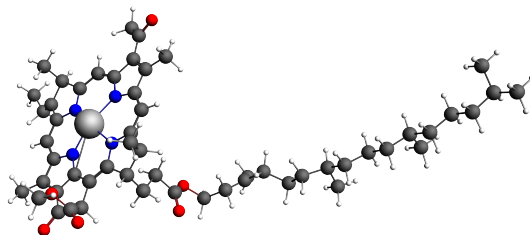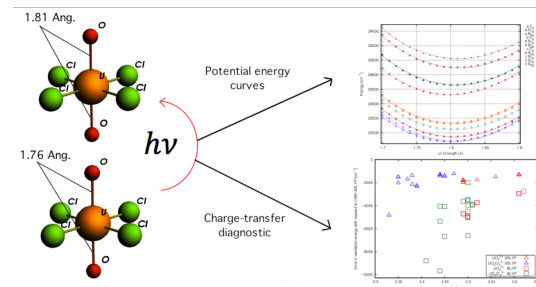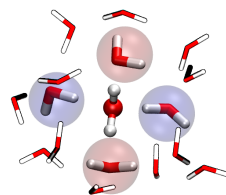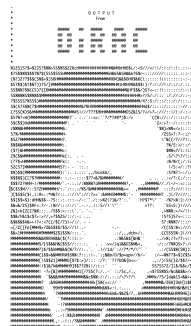
Some selected applications

1. The precision of aluminum

2. Benchmarks for actinide chemistry

3. Relativistic coupled cluster properties

Al$^+$ atomic clock

Fig. 1: Accuracy of atomic clocks based on different species of atoms.

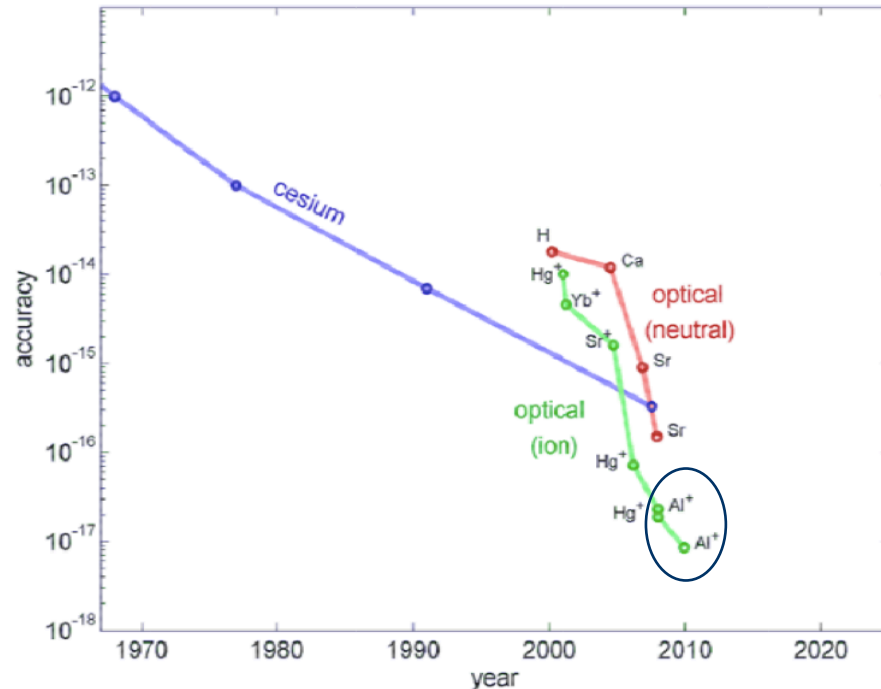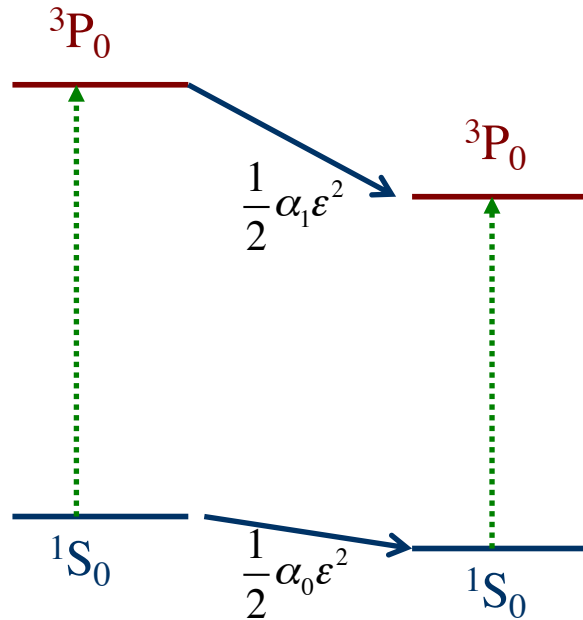TABLE I. Systematic effects that shift the clock from its ideal unperturbed frequency. Shifts and uncertainties given are in fractional frequency units ($\Delta\nu/\nu$).

Effect	Shift (10^{-18})	Uncertainty (10^{-18})
Excess micromotion	−9	6
Secular motion	−16.3	5
Blackbody radiation shift	−9	3
Cooling laser Stark shift	−3.6	1.5
Quad. Zeeman shift	−1079.9	0.7
Linear Doppler shift	0	0.3
Clock laser Stark shift	0	0.2
Background-gas collisions	0	0.5
AOM freq. error	0	0.2
Total	−1117.8	8.6

T. Rosenband, C. W. Chou, D. B. Hume, D. J. Wineland, *Laser Science* (2010);C. W. Chou, D. B. Hume, J. C. J. Koelemeij, D. J. Wineland, T. Rosenband, *Phys. Rev. Lett.*, **104** (2010) 070802.

- Based on $^1S_0 \longrightarrow {}^3P_0$ transition in Al$^+$
- Relative accuracy 8.6 10^{-18} (3.7 seconds / age of the universe)
- Blackbody radiation shift (BBRS) responsible for 35% of this uncertainty

- Precise calculation of BBR shift using relativistic coupled cluster approach

Blackbody Radiation Shift

$^3P_0$

$\frac{1}{2}\alpha_1\varepsilon^2$

$^3P_0$

$^1S_0$

$\frac{1}{2}\alpha_0\varepsilon^2$

$^1S_0$

Energy levels of the Al$^+$ ion:

State		Excitation energy [cm^{-1}]
$3s^2$	$^1S_0$	–
$3s3p$	$^3P_0$	37393
$3s3p$	$^3P_1$	37454
$3s3p$	$^3P_2$	37578

Clock transition: $3s^2\,^1S_0 \rightarrow 3s3p\,^3P_0$

- BBR shift is calculated from the difference in polarizabilities of the ground and excited state:

$$\Delta E_{ij}^{BBR} = -\frac{1}{2}(831.9\,V/m)^2\left(\frac{T(K)}{300}\right)^4\left(\alpha_i - \alpha_j\right)$$

- Finite field differentiation for the DC contribution

$$\alpha_i^{DC} = \frac{2}{\varepsilon^2}\left[E_i^{CC}(\hat{H}^{DC} + \varepsilon\hat{z}) - E_i^{CC}(\hat{H}^{DC})\right]$$

- Breit + QED correction from numerical relativistic MCSCF calculation

$$\Delta\alpha_{ij} = \left(\alpha_i^{DC} - \alpha_j^{DC}\right) + \left(\alpha_i^{BQED} - \alpha_j^{BQED}\right)$$

Results and convergence

Basis set	α ($^1S_0$)	α ($^3P_0$)	$\Delta\alpha$	$\Delta\Delta\alpha$
DZ	24.203	24.261	0.058	
TZ	24.143	25.040	0.897	0.839
QZ	24.273	24.700	0.427	0.470
5Z	24.251	24.656	0.406	0.021
CCSD	24.251±0.044	24.656±0.88	0.406±0.042	

Correlation+QED	α ($^1S_0$)	α ($^3P_0$)	$\Delta\alpha$
CCSD	24.251±0.044	24.656±0.088	0.406±0.042
ΔT	-0.126±0.011	-0.061±0.015	0.065±0.026
ΔQ	-0.002±0.005	0.001±0.002	0.003±0.007
ΔBQED	0.015±0.015	0.018±0.018	0.003±0.003
Total	24.137±0.075	24.614±0.123	0.477±0.078

M. Kallay, H. S. Nataraj, B. K. Sahoo, B. P. Das, L. Visscher, Phys. Rev. A, **83** (2011) 030503.

Modeling actinide systems

- Actinide atoms and ions
  - ✔ Test treatment of relativity
  - ✔ Basis set convergence

- Triatomic actinyls
  - ✔ Test description of strong bonds
  - ✔ Ordering of electronic states

- Seven-atom complexes
  - ✔ Test description of weaker bonds
  - ✔ Charge donation, ligand-to-metal excitations

- Larger models
  - ✔ Computational efficiency of the methods
  - ✔ Direct comparison with experimental data
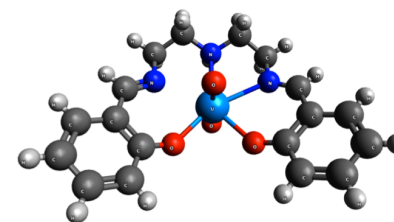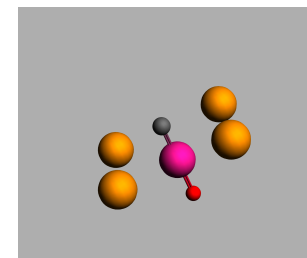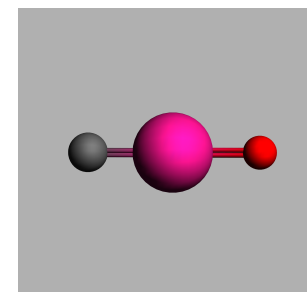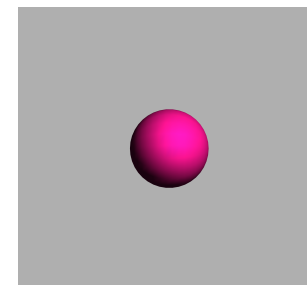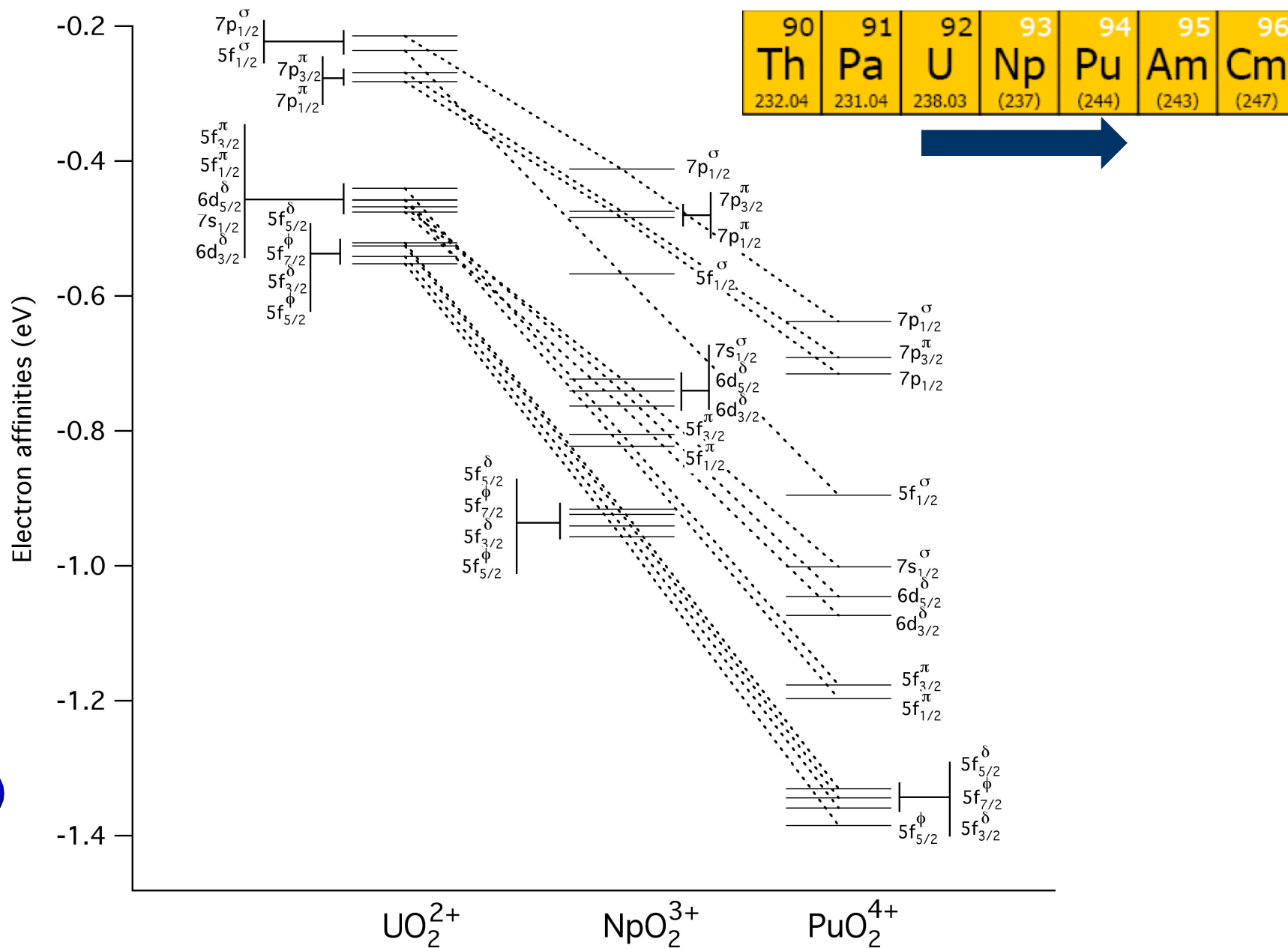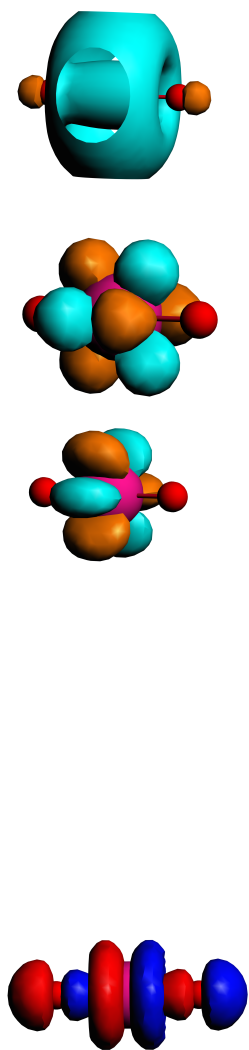
An easy case: PuO_2^{2+}

Configuration	State	SO-CISD+Q[1]	SO-CASPT2[2]	DC-IHFSCCSD[3]	Experiment[4]
$5f^2$	$^3H_g(4g)$	0	0	0	0
$5f^2$	$^3\Sigma_g^-$ (0g)	4,295	4,190	2,530	-
$5f^2$	$^3\Sigma_g^-$ (1g)	7,044	6,065	4,870	-
$5f^2$	^3H_g (5g)	6,593	8,034	6,700	-
$5f^2$	$^3\Pi_g$ (0g)	7,393	12,874	10,334	10,185
$5f^2$	$^3\Sigma_g^+$ (1g)	12,874	12,906	10,983	10,500
$5f^2$	$^3\Pi_g$ (0g)	9,415	14,606	11,225	10,700
$5f^2$	$^3H_g(6g)$	7,848	14,326	11,651	-
$5f^2$	$^3\Pi_g$ (2g)	14,169	14,910	12,236	12,037
$5f^2$	0g			16,713	16,075
$5f^2$	1g			17,737	17,800
$5f^2$	4g			18,565	15,420
$5f^2$	0g			20,029	19,810

[1] Maron et. Al Chem. Phys. 244 (1999) 195
[2] Clavaguéra-Sarrio et al. JCP 121 (2004) 5312
[3] Infante et al. J. Chem. Phys. 125 (2006) 074301
[4] Gmelin Handbooks of Inorganic Chemistry 8th ed. A2 (1973)

Results

- Excellent agreement of FSCC method for most of the states, improves upon previous theoretical work (in part due to reoptimized bond length)

- Charge transfer quintet states require annihilation of an electron and are not accessible with the current method

Theoretical actinide spectroscopy

- Favorite guinea pig: Uranyl
  - $[O=U=O]^{2+}$
  - Formally U(VI) or f^0
  - Important in solution and sorption processes: many experimental studies
  - Simple electronic structure: many theoretical studies
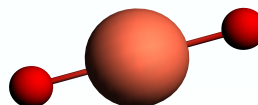
- Electronic ground state
  - Closed shell with large HOMO-LUMO gap
  - Spin-orbit coupling effects not important
  - Molecular structures are well reproduced with standard DFT functionals
  - Correct trends in vibrational spectra (IRMPD)

- Excited states
  - Experimental data only for species in a (strongly) perturbing environment
  - Use IHFS-CCSD as benchmark tool, complemented by LR-CCSD and CASPT2
  - Goal: check accuracy of the available functionals for TD-DFT for actinides
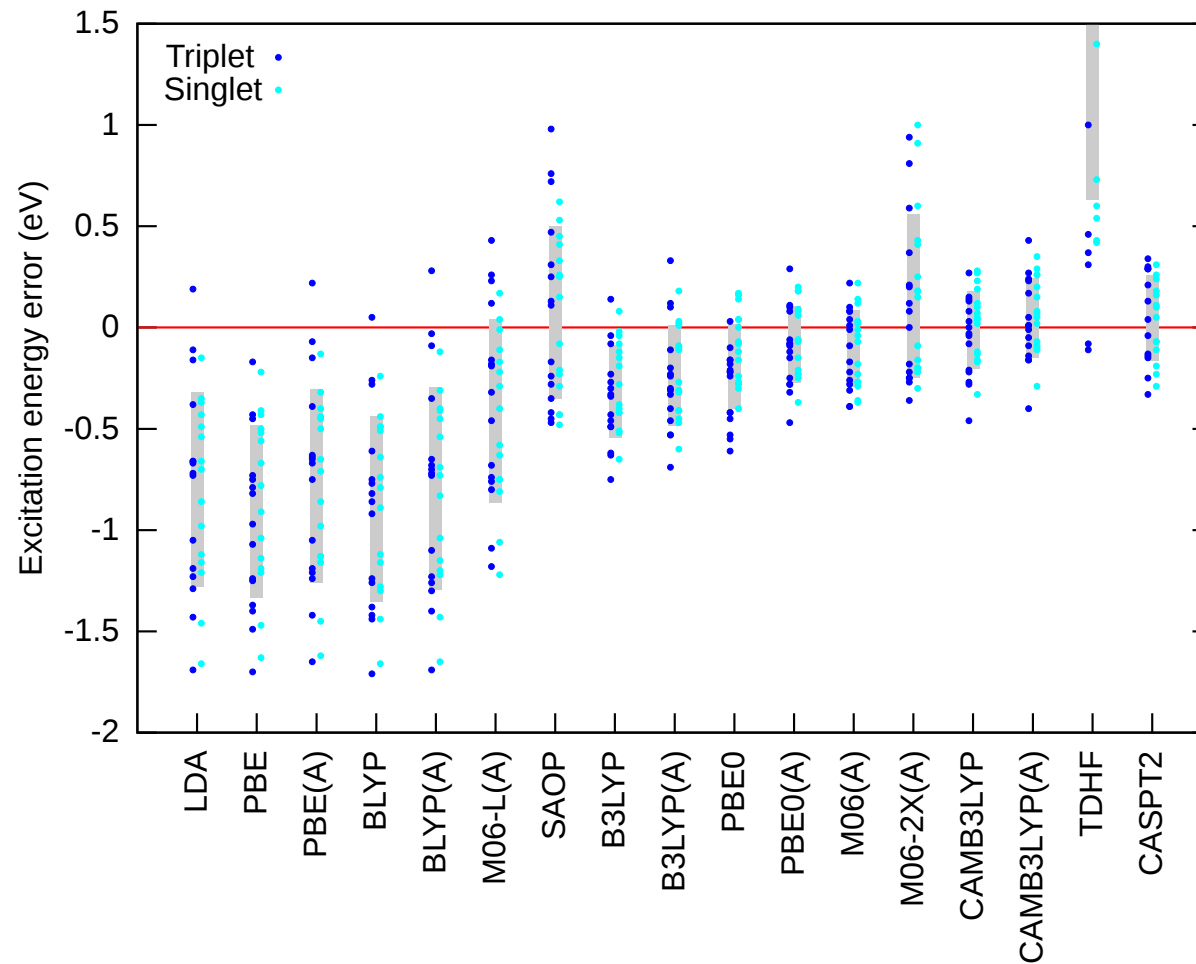
Excited states of uranyl

- LR-CCSD consistently higher than FS-CCSD, CASPT2 close.
- TD-DFT: no functional gives a consistent picture.
- Influence Hamiltonian small.
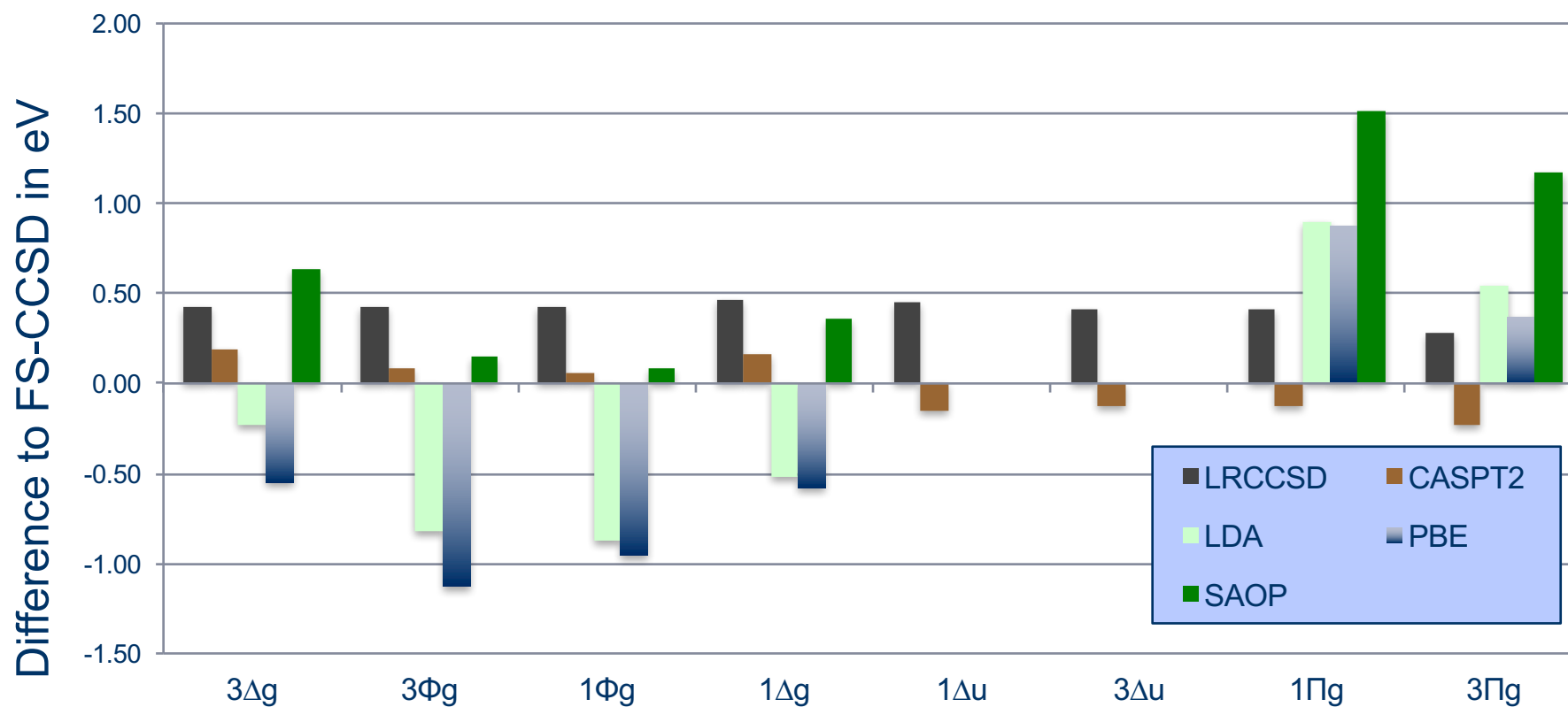
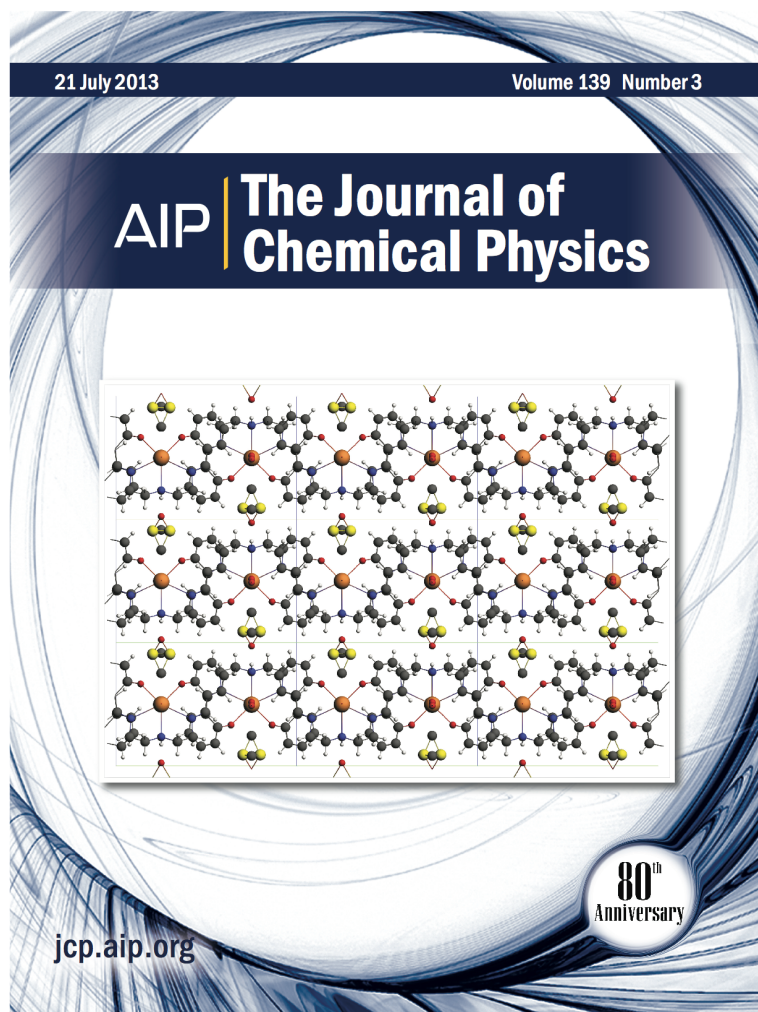F. Réal, A. S. P. Gomes, V. Vallet, LV, E. Eliav, J. Phys. Chem. A **113** (2009) 12504–12511

More actinyls: OUO^{2+}, NUO^+ and NUN

- CASPT2 and FS-CCSD agree again
- TD-DFT: CamB3LYP is the clear winner

P. Tecmer, A. S. P. Gomes, U. Ekström, L. Visscher, 13**6** (2011) 6249.

Beyond small models with CC ?

21 July 2013 — Volume 139 Number 3

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jcp.aip.org

80th Anniversary

- **Interesting U(V) compound reported** (K.Takao, et al. Inorg. Chem. 49 (2010), 2349–2359)
- MRCCSD to benchmark TD-DFT
- DIRAC: 4-component all-electron FSCCSD
- NWCHEM: scalar relativistic (ECP) EOMCCSD(T)

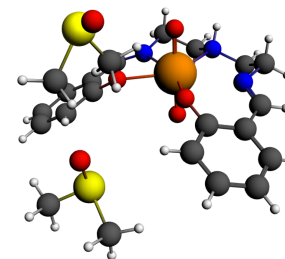- [Uranylsaldien] 45 or 65 (incl. 2 DMSO) atom model
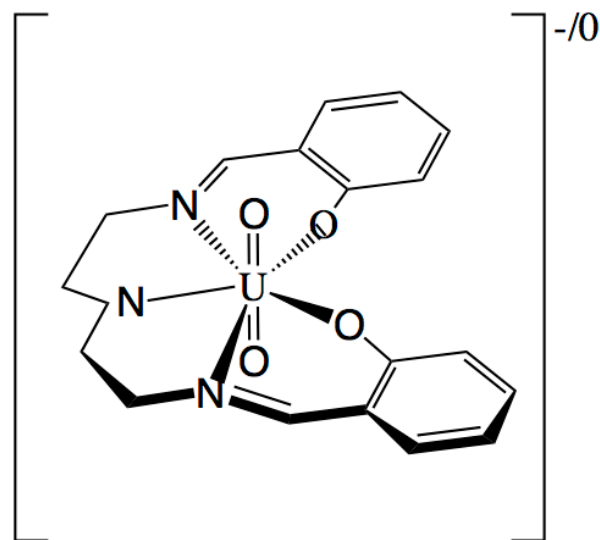
- Test ECP approach and TD-DFT

P. Tecmer, N. Govind, K. Kowalski, W.A. de Jong and LV, JCP **139** (2013) 034301

Testing TD-DFT

Coupled Cluster and experimental data as benchmark

Large Core ECP, DZP, EOMCCSD(t)

2 DMSO molecules included in Uranyl(V) saldien mode

U(VI)	CC	CAM-A	CAM-B
$\sigma \rightarrow \delta$	3.57	2.94	3.39
$\sigma \rightarrow \delta$	3.73	2.96	3.49
$\sigma \rightarrow \phi$	3.74	3.19	3.57

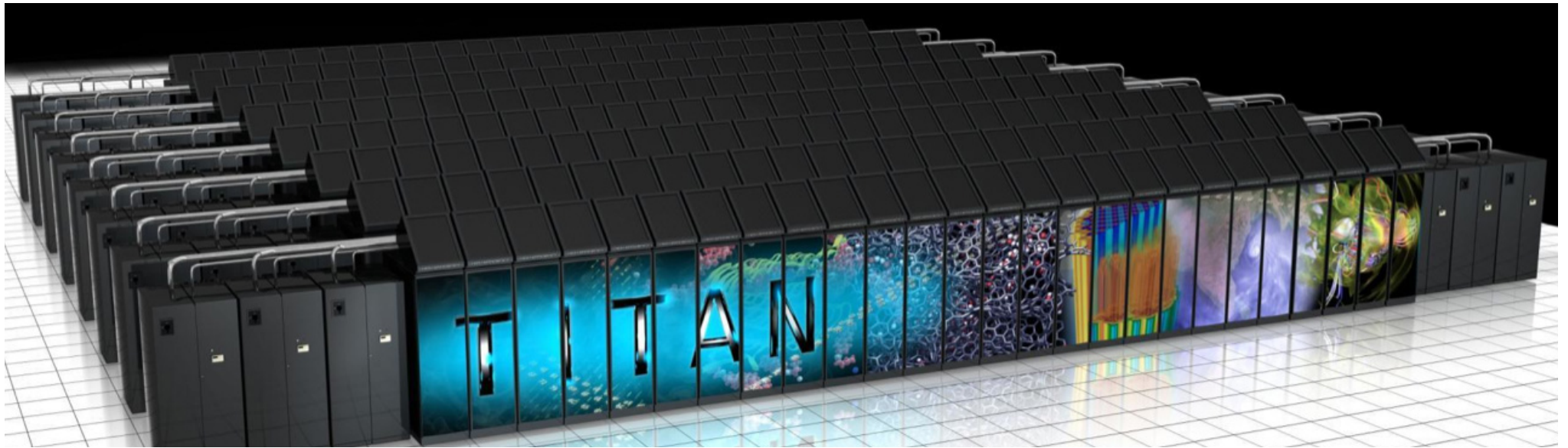| U(V)	Exp	CAM-B
$\delta \rightarrow \sigma$	0.65	0.72
$\delta \rightarrow \sigma$	0.90	1.06
$\delta \rightarrow \phi$	1.49	1.44
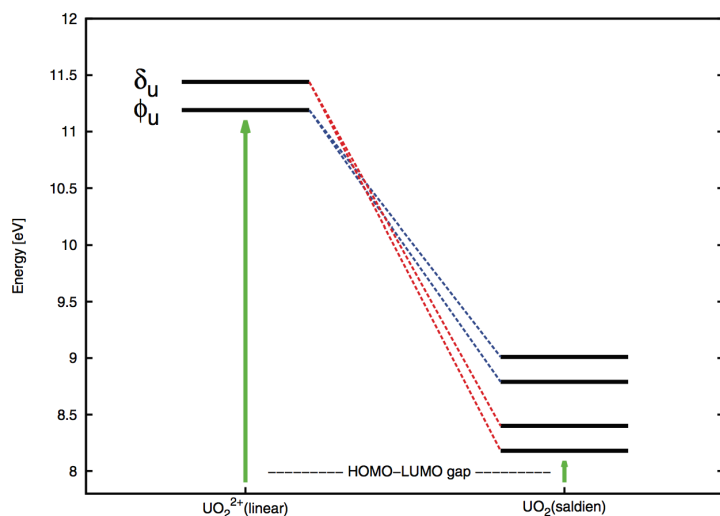
CamB3LYP-B (more exact exchange) gives slightly better results

Conclusions:
- description of actinides with TD-DFT can sometimes be done reliably.
- system size is on the limit of feasibility for coupled cluster theory

Use large computers

- **Key Algorithms**
  - Fock matrix build: easy to parallelize, not a bottleneck
  - Diagonalization of Dirac-Hartree-Fock matrix
    - Can be avoided by direct optimization of the density matrix
    - Can be significant for full 4-component calculations

  - Integral transformation
  - Coupled cluster iterations

$$(PQ|\mu\nu) = \sum_{\lambda} c_{\lambda Q} \sum_{\kappa} c_{\kappa P}^* (\kappa\lambda|\mu\nu) \qquad \mathbb{H} = \mathbb{C}^\dagger \mathbb{G} \mathbb{C}$$

$$-\sum_{C<D} B_{CD}^{AB} \tau_{IJ}^{CD} \qquad \mathbb{S} = \mathbb{B}\mathbb{T}$$

# General purpose tensor contraction library

- Integral transformation

$$(PQ|\mu\nu) = \sum_\lambda c_{\lambda Q} \sum_\kappa c^*_{\kappa P} (\kappa\lambda|\mu\nu) \qquad \mathbb{H} = \mathbb{C}^\dagger \mathbb{G}\mathbb{C}$$

- Coupled cluster iteration (some terms)

$$\sum_{K<L} A^{KL}_{IJ} \tau^{AB}_{KL} + \sum_{C<D} B^{AB}_{CD} \tau^{CD}_{IJ}$$

$$P_{AB}\left(\sum_C G^A_C T^{CB}_{IJ} - \sum_K V^{AK}_{IJ} T^B_K \right).$$

$$\mathbb{S} \leftarrow \mathbb{A}\mathbb{T} + \mathbb{B}\mathbb{T}$$

$$\mathbb{S}' \leftarrow \mathbb{G}\mathbb{T}'$$

$$\mathbb{S}'' \leftarrow \mathbb{V}\mathbb{T}''$$

- Total memory should sufficient to fit all tensor elements
  - Hierarchical block structure to distribute tensors over nodes
  - Library should take care of reordering
  - GPU acceleration within each node
  - Sparsity features nice to have

Coupled cluster properties
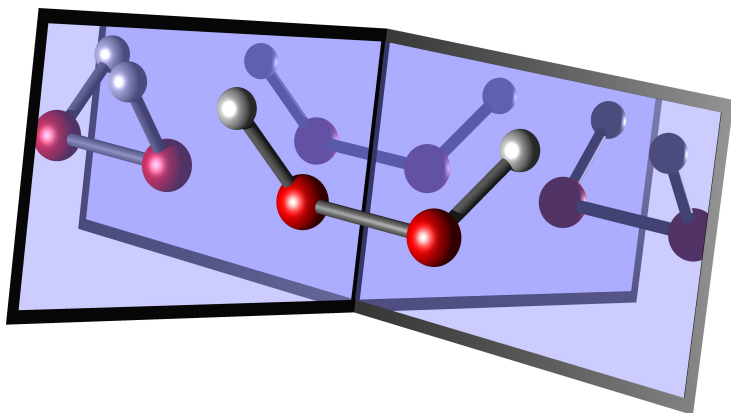
**Implementation of orbital-unrelaxed coupled cluster density matrix for relativistic wave functions**

Access to various properties that can be written as a one-body operator

Exotic example: PV energy difference in chiral molecules.

Tiny energy difference between enantiomers resulting from the electroweak interaction between charged particles.

Observed in atoms (asymmetry of decay processes) but not in molecules yet. Search for suitable candidate molecules to observe this effect.

Correlation effect is visible but not very prominent in (one of the) simplest chiral molecule hydrogenperoxide.

A. Shee, T. Saue, and LV, JCP **145** (2016)
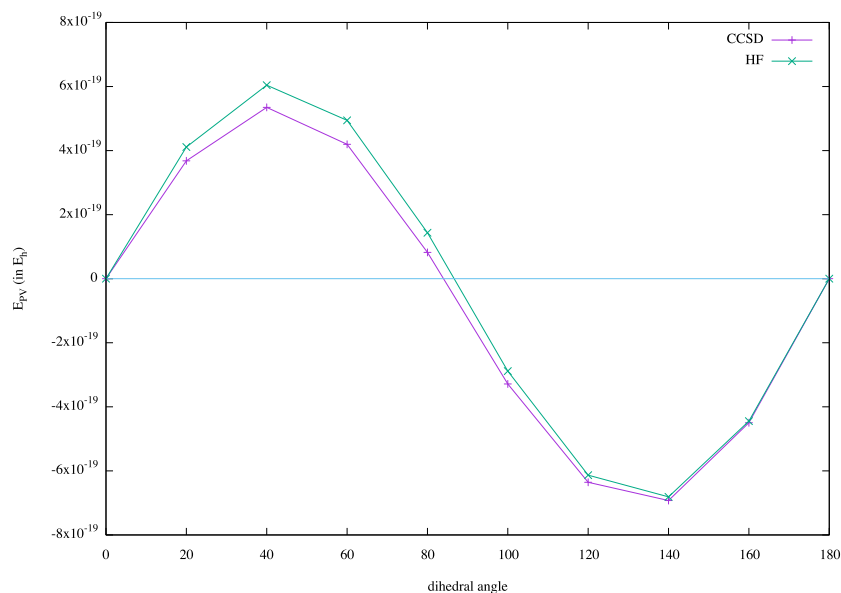
Acknowledgements

- **Actinide Chemistry**
  Ivan Infante, Andre Gomes, Bert de Jong, Pawel Tecmer

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  Mihaly Kállay, Avijit Shee, Dmitry Liakh

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  Trond Saue, Radovan Bast, Hans Jørgen Jensen, Ken Dyall

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