Developing tools for high-accuracy *ab initio* relativistic modeling of excited states and spectra of actinide molecules and impurity ions

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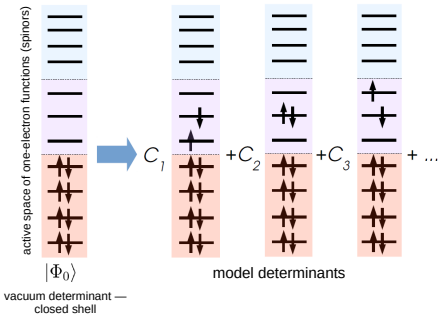
Introduction: the goals of relativistic quantum chemistry

- chemistry and spectroscopy of actinides and superheavy elements
- active laser media; sources of light; chromophores, luminophores
- searches for $\mathcal{P}$,$\mathcal{T}$-odd fundamental interactions (physics beyond the Standard model)
- thermodynamics, physical and chemical properties of actinide compounds
- fine structure effects in spectra of light elements; spin-forbidden transitions
- the Periodic table for the most heavy chemical elements
- optical and magnetic properties of f-element compounds
- laser cooling and assembly of cold molecules
- ...

a clear understanding of the experiment is impossible without a theoretical model!

but: models for d- and f-elements have to be very complicated...

Electron correlation: coupled cluster theory



- Wave function:

$$\psi_n = \{\exp(T)\}\ \tilde{\psi}_n$$

$$T = \sum_{pq\ldots rs\ldots} t_{pq\ldots rs\ldots} \{a_p^\dagger\, a_q^\dagger\, \ldots\, a_s\, a_r\}$$

T – cluster operator
$t_{pq\ldots rs\ldots}$ – cluster amplitudes
$a_p^\dagger$, a_q – creation and annihilation operators

- The most effective account for electron correlation
- Computational complexity:
  time – min $O(N^6)$
  memory – min $O(N^4)$
- Relativistic calculations = complex arithmetic + low symmetry!

E. Eliav, A. Borschevsky, A. Zaitsevskii, A. V. Oleynichenko, U. Kaldor. Relativistic Fock-space Coupled Cluster Method: Theory and Recent Applications. *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering* (2023).

Finite-order method to calculate property operator matrix elements

- General idea:

$$\psi_n = \{\exp(T)\}\ \tilde{\psi}_n \approx \left(1 + T + \frac{T^2}{2}\right)\tilde{\psi}_n$$

- 2nd order approximation to an effective property operator $\tilde{O}$:

$$\tilde{O} \approx \left(O + T^\dagger O + OT + \frac{\{(T^\dagger)^2\}}{2}O + T^\dagger O T + O\frac{\{T^2\}}{2} - (T^\dagger T)_{cl} O\right)_{cl,conn}$$

- Disconnected diagrams cancel each other
- Line intensities in absorption and emission spectra $\sim |\langle\psi_n|\hat{d}|\psi_m\rangle|^2$
- Error $\leq 10\%$ in calculated matrix elements
- The analogous approach was previously used in atomic calculations

B. K. Sahoo et al, *J. Phys. B*, 39(2), 355 (2005)
G. Gopakumar et al, *Phys. Rev. A*, 66(3), 032505 (2002)

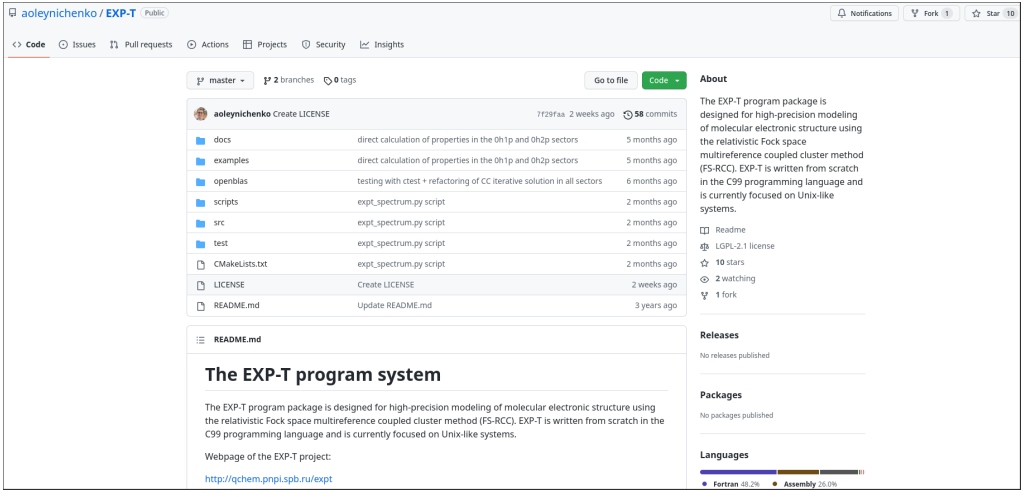
Implementation of the relativistic coupled cluster theory: the EXP-T program package

The new program package EXP-T for coupled cluster calculations was developed at NRC "Kurchatov Institute" – PNPI

- electronic structure of atoms, molecules and defects in crystals
- Kramers-unrestricted relativistic coupled cluster theory
- open shells: Fock-space multireference coupled cluster
- CCSD, CCSD(T), CCSDT-1,2,3, CCSDT models
- analytic density matrices for single-reference CCSD and CCSD(T)
- molecular integrals are imported from the DIRAC package
  relativistic Hamiltonians: Schrödinger, Dirac-Coulomb(-Gaunt) DC(G), **(generalized) pseudopotentials**
- property calculations, e. g. transition dipole moments → intensities in spectra
- fast and flexible implementation of new models

A. V. Oleynichenko, A. Zaitsevskii, E. Eliav, *Commun. Comp. Inf. Sci.* 1331, 375 (2020)

The EXP-T program package



https://github.com/aoleynichenko/EXP-T

Pseudopotential operator as a part of relativistic Hamiltonian

- core electronic shells are replaced with the some potential $\hat{U}$ acting on valence electrons (the Pauli principle is accounted for)
- the valence electrons are described by the Schrödinger equation:

$$\hat{H}^{RPP} = \sum_i \left(-\frac{\Delta_i}{2} + \sum_\alpha \left(-\frac{z_\alpha}{r_{\alpha i}} + \hat{U}_\alpha(i) \right) \right) + \sum_{i>j} \frac{1}{r_{ij}}$$

i, j – sum over electrons
α – sum over nuclei
z_α – effective charge of the atomic core α, $z_\alpha = Z_\alpha - N_{\text{inner core el-s}}$

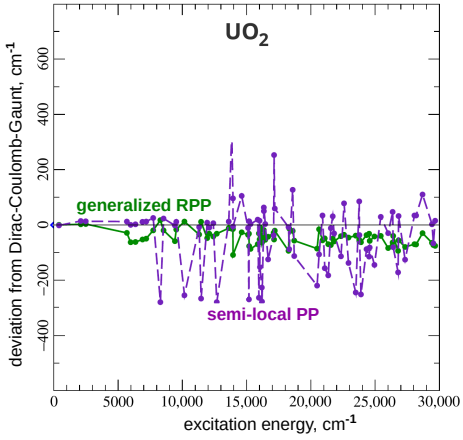
- potential $\hat{U}$ can effectively account for:
  - scalar-relativistic effects
  - spin-orbit interaction
  - Breit interaction of electrons
  - finite nuclear charge distribution (the Fermi model)
  - QED contributions (electron self-energy + vacuum polarization)

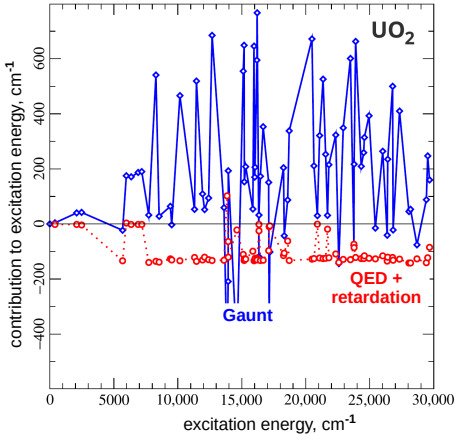
- The most accurate version of the method – generalized relativistic pseudopotential (GRPP)

A. V. Titov, N. S. Mosyagin, *IJQC* 71, 359 (1999); M. Dolg, X. Cao, *Chem. Rev.* 112, 403 (2012)

Accuracy of the generalized relativistic pseudopotential (GRPP) model

Vertical excitation energies of the UO_2 molecule; compared to the 4-component Dirac-Coulomb-Gaunt calculations





FS-RCCSD calculation: UO_2^{2+} $(0h0p) \rightarrow UO_2^{+}$ $(0h1p) \rightarrow UO_2$ $(0h2p)$

Main model space comprised the $\approx 7s5f$, $5f^2$, $6d5f$, $7p5f$ configurations of U

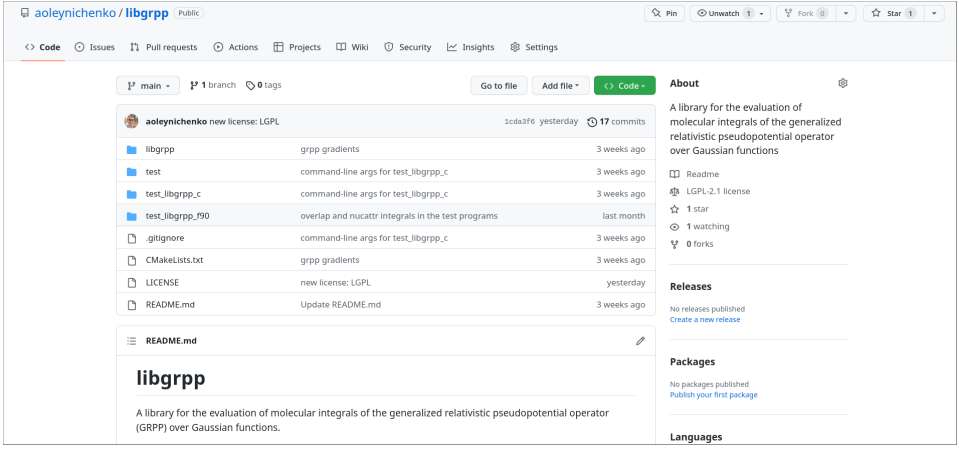
For details, see: A. V. Oleynichenko et al, *Symmetry*, 15, 197 (2023)

The `libgrpp` library for evaluation of molecular integrals of the GRPP operator over Gaussian basis functions

		scal.-rel.	spin-orbit	outercore	open source	written in
ARGOS	1981	+	+	−	+	Fortran
MOLGEP	1991	+	+	+	−	Fortran
Turbomole	2005	+	+	−	−	Fortran
libECP	2015	+	−	−	+	C
libecpint	2021	+	−	−	+	C++
libgrpp	**2022**	+	+	+	+	**C**

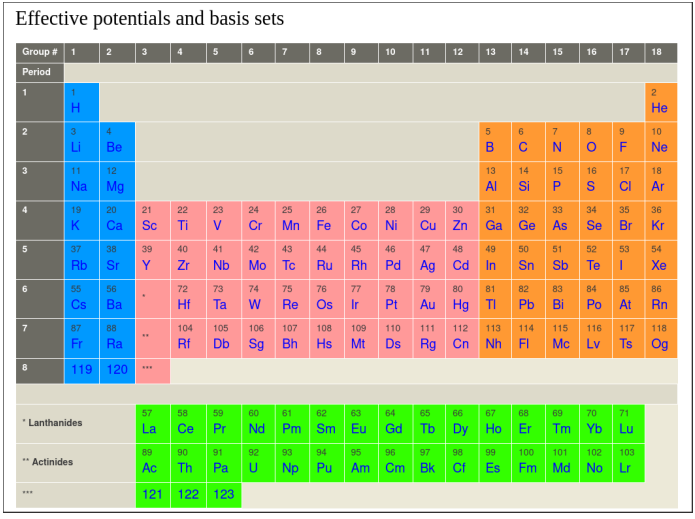
- **libgrpp** is written from scratch in C99
- no restrictions on maximum angular momenta of GRPP and basis functions
- analytic gradients of GRPP integrals
- libgrpp is available in the home version of DIRAC!

The `libgrpp` library for evaluation of molecular integrals of the GRPP operator over Gaussian basis functions



https://github.com/aoleynichenko/libgrpp

Library of relativistic pseudopotentials – by N. S. Mosyagin



http://qchem.pnpi.spb.ru/recp

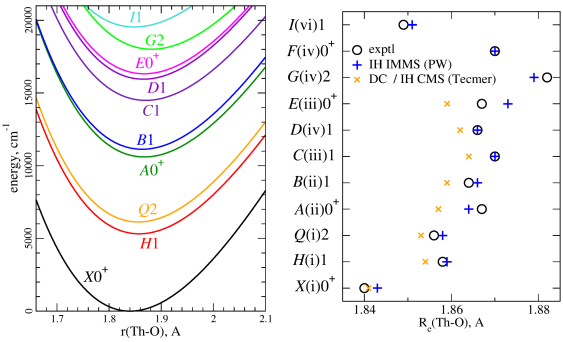
Pilot applications

The ThO molecule as a pilot application

- one of the most well-studied actinide molecules:
  - experimental searches of the electron electric dipole moment
    ACME Collaboration, *Nature*, 562, 355 (2018)
  - term energies T_e and equilibrium distances r_e
  - permanent dipole moments in ground and excited electronic states
  - radiative lifetimes of excited electronic states
- previous works: Dirac-Coulomb Hamiltonian
  $\rightarrow$ the accuracy was acceptable for several low-lying states only
  P. Tecmer, C. E. González-Espinoza, *Phys. Chem. Chem. Phys.* 20, 23424 (2018)
- our goal: all electronic states < 20000 cm^{-1}

Electronic states of the diatomic ThO molecule

Potential energy curves and equilibrium distances r_e



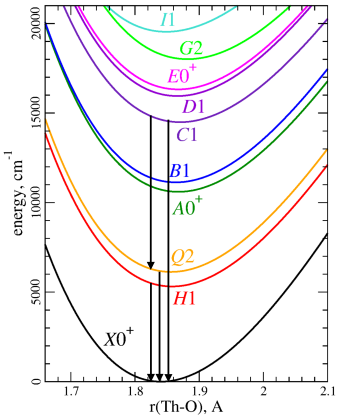
	deviation from experimental T_e, cm^{-1}		
	RPP/IH-IMMS	DC/IH-CMMS*	
	0h2p	0h2p	1h1p
H(i)1	104	700	-149
Q(i)2	97	738	-62
A(ii)0^+	242	691	1098
B(ii)1	302	927	–
C(iii)1	424	1698	-39
D(iv)1	440	1698	–
E(iii)0^+	312	960	-1950
G(iv)2	165	–	–
F(iv)0^+	431	–	–
I(vi)1	367	–	–

- Relativistic Hamiltonian: GRPP accounting for Breit and QED
- Ground state calculations: single-reference coupled cluster CCSD(T)
- Excited states: Fock space coupled cluster FS-CCSD

* P. Tecmer, C. E. González-Espinoza, *Phys. Chem. Chem. Phys.* 20, 23424 (2018)

Electronic states of the diatomic ThO molecule

Radiative lifetimes of excited states



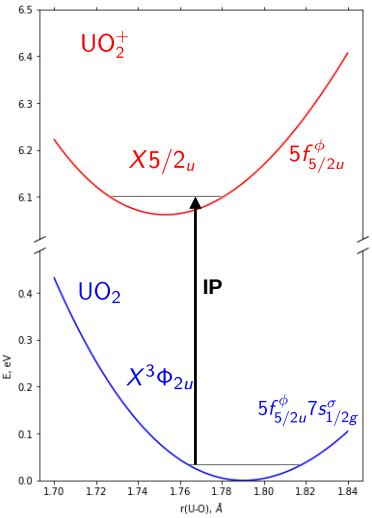
	Exptl.	FS-RCCSD/RKR* GRPP	FS-RCCSD GRPP
$H \to X$	4.2 ± 0.5 ms[a]	3.82 ms	3.57 ms
$Q \to X$	> 62 ms[b]	177 ms	182 ms
$C \to ...$	> 480 ns[c] 468 ± 30 ns[d]	400 ns	364 ns
$C \to Q$	5.4 ± 1.3 ms[b]	5.49 μs	4.87 μs

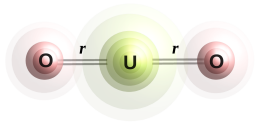
* FS-RCCSD/RKR – potential energy curve for the ground state was constructed using the Rydberg-Klein-Rees method based on experimental data

[a] D. G. Ang et al, Phys. Rev. A 106, 022808 (2022) [b] X. Wu et al, New J. Phys. 22, 023013 (2020)

[c] N. R. Hutzler et al, Phys. Chem. Chem. Phys. 13, 18976 (2011) [d] D. L. Kokkin et al, Phys. Rev. A 91, 042508 (2015)

Ground electronic states of the UO_2 molecule and its ion UO_2^+; ionization potential calculation

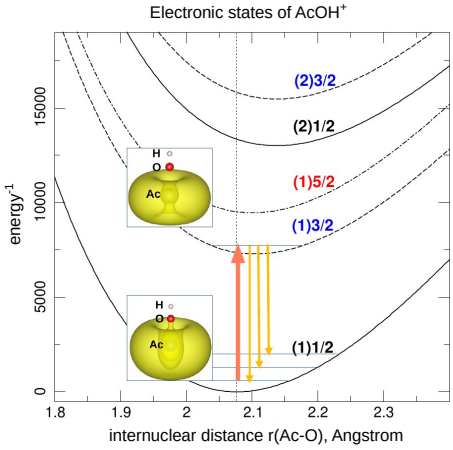




	CASPT2[a] DK, sc-rel	FS-CCSD GRPP	SR-CCSD GRPP	SR-CCSD(T) GRPP	Exptl.
IP, eV	6.17	5.799	5.947	6.062	6.128[b]
$r_e(UO_2^+)$, Å	1.771	1.731	1.737	1.753	1.758[c]
$r_e(UO_2)$, Å	1.806	1.760	1.774	1.790	1.790[c]

[a] L. Gagliardi et al, *J. Phys. Chem. A*, 105, 10602 (2001)
[b] J. Han et al, *J. Chem. Phys.* 120, 5155 (2004)
[c] A. Kovacs, R. J. M. Konings *J. Phys. Chem. A*, 115, 6646 (2011)

$AcOH^+$ – the first prediction of a laser-coolable polyatomic ion

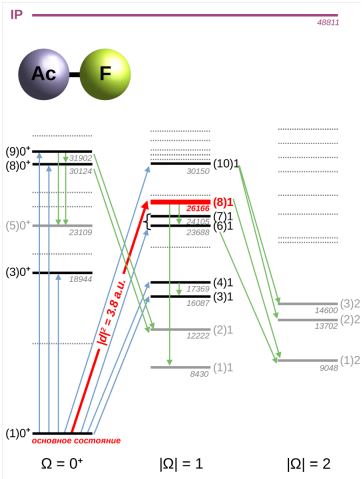


A promising system for a new generation of experiments searching for P, T-odd effects

$\Rightarrow$ searches for the New physics beyond the Standard model

A. V. Oleynichenko, L. V. Skripnikov, A. V. Zaitsevskii, V. V. Flambaum *Phys. Rev. A*, 105, 022825 (2022).

Spectroscopy of the AcF molecule: relativistic modeling makes spectroscopic experiment possible



- a promising object for the searches of the P,T-odd nuclear Schiff moment on ^{225}Ac, ^{227}Ac

  L. V. Skripnikov et al, *PCCP* 22, 18374 (2020)
- Low-lying electronic states: 2 electrons over the closed-shell vacuum state (AcF^{2+})
- $\sim$ 80 electronic states $<$ 43000 cm^{-1}
- The most intense transitions were predicted
- The (8)1 state was experimentally observed at CRIS/ISOLDE (CERN)

L. V. Skripnikov, A. V. Oleynichenko, A. Zaitsevskii, N. S. Mosyagin, M. Athanasakis-Kaklamanakis, M. Au, G. Neyens. *J. Chem. Phys.*, in press (2023)

Localized excitations on f-element ions Ce^{3+}, Th^{3+} in xenotime YPO_4 crystals

- tetragonal crystal system, $I4_1/amd$
- local symmetry of the Y^{3+} site: D_{2d}
- natural xenotime contains Th and U impurities
- radiation resistant, no metamictization
- very wide bandgap (> 8.6 eV)

- YPO_4 doped with lanthanide ions:
  - laser active media, scintillators, luminophores ...
  - large amount of experimental data: YPO_4:Ce^{3+}, YPO_4:Pr^{3+}, YPO_4:Nd^{3+}, YPO_4:Yb^{3+}, ...
  - energy and charge transfer processes between lanthanide sites
- YPO_4 doped with actinide ions:
  - immobilization of highly radioactive waste
  - nuclear clock on the isomeric transition in ^{229}Th

M. G. Kozlov, A. V. Oleynichenko et al, arXiv:2308.05173 (2023)

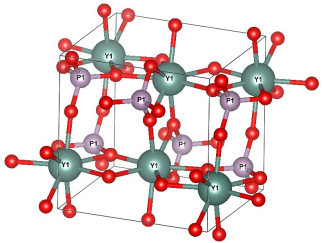
Xenotime crystal

Locality: Novo Horizonte, Brazil

Minimal cluster model of an impurity center

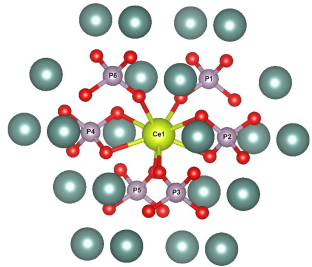
periodic model (crystal)

- **DFT/PBE0**
- optimize geometry
- optimize compound-tunable PPs



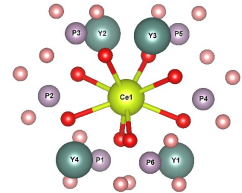
extended cluster model with impurity ion

- **DFT/PBE0**
- optimize CTEP charges
- insert impurity + optimize geometry
- local vibrational modes



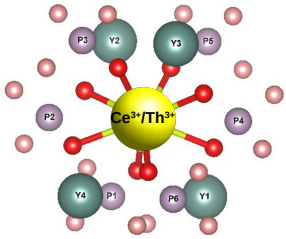
minimal cluster model with impurity ion

- reoptimize CTEP charges (**MP2**)
- spin-orbit is included
- excitation energies (**rel FS CCSD**)
- radiative lifetimes

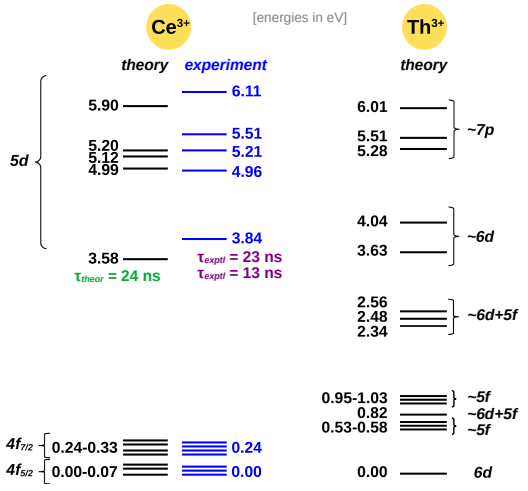


CTEP = Compound-Tunable Effective Potential

Excitation energies and radiative lifetimes of excited states



minimal cluster model



- errors of order $0.2 - 0.3$ eV
- ground state of Th^{3+} in crystal – $6d^1$
- minimal cluster model calculations: FS RCCSD
- correction for the cluster model size: TD-DFT☹
- the interplay of the crystal field and spin-orbit interaction

[1] Y. V. Lomachuk, D. A. Maltsev, N. S. Mosyagin, L. V. Skripnikov, R. V. Bogdanov, A. V. Titov, *PCCP*, 22, 17922 (2020)

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  Generalized relativistic small-core pseudopotentials accounting for quantum electrodynamic effects: Construction and pilot applications
- A. V. Oleynichenko, A. Zaitsevskii, N. S. Mosyagin, A. N. Petrov, E. Eliav, A. V. Titov. *Symmetry*, 15, 197 (2023)
  LIBGRPP: a library for the evaluation of molecular integrals of the generalized relativistic pseudopotential operator over Gaussian functions

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  Generalized relativistic small-core pseudopotentials accounting for quantum electrodynamic effects: Construction and pilot applications
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  Electronic transition dipole moments in relativistic coupled-cluster theory: the finite-field method.
- A. V. Oleynichenko, A. Zaitsevskii, L. V. Skripnikov, E. Eliav. *Symmetry*, 12(7) (2020)
  Relativistic fock space coupled cluster method for many-electron systems: non-perturbative account for connected triple excitations.
- L. V. Skripnikov, A. V. Oleynichenko, A. V. Zaitsevskii, D. E. Maison, A. E. Barzakh. *PRC*, 104, 034316, (2021)
  Relativistic Fock space coupled-cluster study of bismuth electronic structure to extract the Bi nuclear quadrupole moment.
- E. Eliav, A. Borschevsky, A. Zaitsevskii, A. V. Oleynichenko, U. Kaldor. *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, Elsevier* (2022)
  Relativistic Fock-space coupled cluster method: Theory and recent applications

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A. N. Petrov

M. Athanasakis-Kaklamanakis
M. Au
A. Borschevsky
V. V. Flambaum
G. Neyens

Questions?

Appendix

How to assess an accuracy of GRPP?

Problem: taking into account QED and Breit in 4c calculations is extremely difficult

Solution: to construct a special GRPP for testing only (N. S. Mosyagin)

- \+ atomic Dirac-Hartree-Fock-Gaunt calculation (4c)
- \+ Gaussian nuclear charge distribution (instead of Fermi)
- – retardation
- – QED contributions

Reference 4c calculation: Dirac-Coulomb-Gaunt (DCG-x2cmmf)

more: J. Sikkema et al, *J. Chem. Phys.* 131, 124116 (2009); https://doi.org/10.1063/1.3239505

Correlation calculations:

- relativistic Fock space coupled cluster method (FS-RCCSD)
- intermediate Hamiltonian for incomplete model spaces (IH-IMMS)
  A. Zaitsevskii et al, *IJQC*, e27077 (2022), https://doi.org/10.1002/qua.27077
- the EXP-T program package
  http://qchem.pnpi.spb.ru/expt

Example: uranium atom in the SCF approximation

Consider the 64e small core pseudopotential for the U atom:

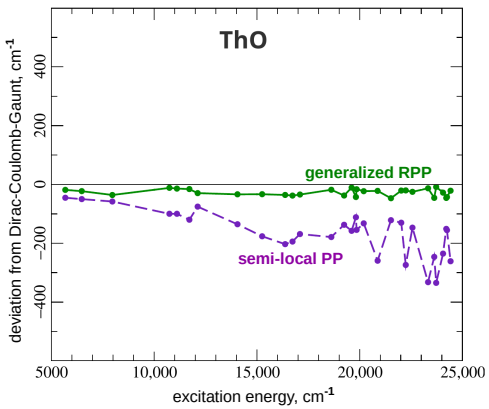
- outercore shells: 6sp, 5spd, 4$spdf$
- valence shells: 7sp, 6d, 5f

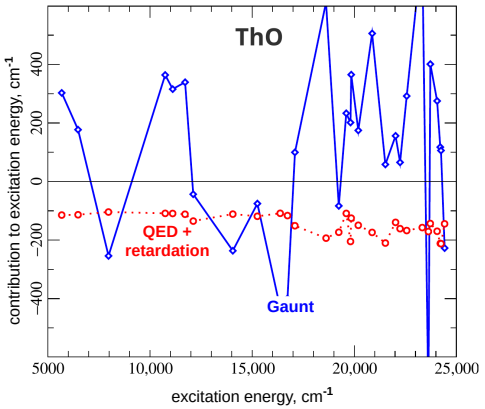
Excitation energies, cm^{-1}		Absolute errors, cm^{-1}				
$5f^3 6d^1 7s^2 \rightarrow$	DFB	no QED	point nuc.	no Breit	GRPP	semilocal
$5f^3 7s^2 7p^1$	7589	-72	-40	-93	-1	-6
$5f^3 6d^2 7s^1$	12990	133	96	78	2	1
$5f^3 6d^1 7s^1 7p^1$	17109	90	74	14	1	-9
$5f^2 6d^2 7s^2$	4809	-169	-85	-780	52	554
$5f^2 6d^2 7s^1 7p^1$	23920	-64	1	-765	53	546
$5f^4 7s^2$	15634	147	75	628	-44	-407
$5f^4 7s^1 7p^1$	30491	221	137	649	-45	-423
$5f^1 6d^3 7s^2$	31804	-354	-175	-1675	111	1238
$5f^1 6d^4 7s^1$	38957	-176	-49	-1552	113	1216

Excitation energies were derived from all-electron numerical SCF calculations for the states averaged over nonrelativistic configurations.
Data by N. S. Mosyagin

Vertical excitation energies of ThO

FS-RCCSD calculation: ThO^{2+} $(0h0p) \rightarrow ThO^{+}$ $(0h1p) \rightarrow ThO$ $(0h2p)$
Active space: 24 lowest virtual Kramers pairs of ThO^{2+}
Main model space: CAS 2e / 12 spinors, $\approx 7s + 6d$ Th
Basis sets: $[19s17p15d15f5g4h3i]$ (Th), aug-cc-pVQZ-DK (O)





Summary

- Deviation from the 4-component Dirac-Coulomb-Gaunt model:

		GRPP	semilocal	DC	Ret.+QED
ThO	max abs	46	335	802	212
	rms	29	181	341	151
UO_2	max abs	110	345	767	142
	rms	51	128	316	112

- the error of GRPP is balanced for all electronic states
- the Dirac-Coulomb Hamiltonian is inherently less accurate than even a semi-local potential
- the contributions of retardation and QED effects are greater than the error of GRPP
- our future: pseudopotentials accounting for QED

GRPP seems to be the most precise Hamiltonian for real-life molecular calculations?