Developing tools for high-accuracy \textit{ab initio} relativistic modeling of excited states and spectra of actinide molecules and impurity ions

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The XXVII International Scientific Conference of Young Scientists and Specialists (AYSS-2023)  
JINR, Dubna, 31st October, 2023
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:

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

\[ T = \sum_{pq...rs...} t_{pq...rs...} \{a^\dagger_p a^\dagger_q \ldots a_s a_r\} \]

- \( T \) – cluster operator
- \( t_{pq...rs...} \) – cluster amplitudes
- \( a^\dagger_p, a_q \) – 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!
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 \( \tilde{O} \):

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

- 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


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

The EXP-T program package

The EXP-T program package is designed for high-precision modeling of molecular electronic structure using the relativistic Fock space multireference coupled cluster method (F5-RCC). EXP-T is written from scratch in the C99 programming language and is currently focused on Unix-like systems.

Webpage of the EXP-T project:
http://qchem.pnpi.spb.ru/expert

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:

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

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

- 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)

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

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<thead>
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<th>Library</th>
<th>Year</th>
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- `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

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* Lanthanides

|   | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 97 |    |    |    |    |    |    |    |    |    |    |    |    |    |    |

** Actinides

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<th>U</th>
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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
  - 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
  → the accuracy was acceptable for several low-lying states only

- our goal: all electronic states $< 20000 \text{ cm}^{-1}$
Electronic states of the diatomic ThO molecule

Potential energy curves and equilibrium distances $r_e$

- 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

<table>
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<th>State</th>
<th>RPP/IH-IMMS $T_e$, cm$^{-1}$</th>
<th>DC/IH-CMMS* $T_e$, cm$^{-1}$</th>
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<td>700</td>
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<td>Q(i)</td>
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<td>738</td>
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<td>A(ii)</td>
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<td>691</td>
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<tr>
<td>B(ii)</td>
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<td>927</td>
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<td>C(iii)</td>
<td>424</td>
<td>1698</td>
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<tr>
<td>D(iv)</td>
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<td>1698</td>
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<td>E(iii)</td>
<td>312</td>
<td>960</td>
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<tr>
<td>G(iv)</td>
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<tr>
<td>F(iv)</td>
<td>431</td>
<td>-</td>
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<tr>
<td>I(vi)</td>
<td>367</td>
<td>-</td>
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</table>

Electronic states of the diatomic ThO molecule

Radiative lifetimes of excited states

Exptl.     FS-RCCSD/RKR* GRPP     FS-RCCSD GRPP

$H \rightarrow X$    $4.2 \pm 0.5$ ms$^a$          3.82 ms          3.57 ms

$Q \rightarrow X$    $> 62$ ms$^b$             177 ms          182 ms

$C \rightarrow ...$    $> 480$ ns$^c$        468 $\pm$ 30 ns$^d$  400 ns          364 ns

$C \rightarrow Q$    $5.4 \pm 1.3$ ms$^b$          5.49 $\mu$s        4.87 $\mu$s

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


Ground electronic states of the UO$_2$ molecule and its ion UO$_2^+$; ionization potential calculation

<table>
<thead>
<tr>
<th></th>
<th>CASPT2$^a$</th>
<th>FS-CCSD</th>
<th>SR-CCSD</th>
<th>SR-CCSD(T)</th>
<th>Exptl.</th>
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<td>5.799</td>
<td>5.947</td>
<td>6.062</td>
<td>6.128$^b$</td>
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<tr>
<td>$r_e$(UO$_2^+$), Å</td>
<td>1.771</td>
<td>1.731</td>
<td>1.737</td>
<td>1.753</td>
<td>1.758$^c$</td>
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<tr>
<td>$r_e$(UO$_2$), Å</td>
<td>1.806</td>
<td>1.760</td>
<td>1.774</td>
<td>1.790</td>
<td>1.790$^c$</td>
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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 ⇒ searches for the New physics beyond the Standard model

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 $^{225}\text{Ac}$, $^{227}\text{Ac}$
  
  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)

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

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

- 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)
Bibliography: generalized relativistic pseudopotentials

  Generalized relativistic effective core potential: Gaussian expansions of potentials and pseudospinors for atoms Hg through Rn

  Generalized relativistic effective core potential: Theoretical grounds

  Accounting for the Breit interaction in relativistic effective core potential calculations of actinides

  Generalized relativistic effective core potentials for superheavy elements

  Generalized relativistic small-core pseudopotentials accounting for quantum electrodynamic effects: Construction and pilot applications

  LIBGRPP: a library for the evaluation of molecular integrals of the generalized relativistic pseudopotential operator over Gaussian functions
Bibliography: relativistic coupled cluster theory

  Padé extrapolated effective Hamiltonians in the Fock space relativistic coupled cluster method.

  Generalized relativistic small-core pseudopotentials accounting for quantum electrodynamic effects: Construction and pilot applications

  Electronic transition dipole moments in relativistic coupled-cluster theory: the finite-field method.

  Relativistic fock space coupled cluster method for many-electron systems: non-perturbative account for connected triple excitations.

  Relativistic Fock space coupled-cluster study of bismuth electronic structure to extract the Bi nuclear quadrupole moment.

  Relativistic Fock-space coupled cluster method: Theory and recent applications
thanks to

M. G. Kozlov
D. A. Maltsev
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)


**Correlation calculations:**

- relativistic Fock space coupled cluster method (FS-RCCSD)
- intermediate Hamiltonian for incomplete model spaces (IH-IMMS)


- 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: 6\(sp\), 5\(spd\), 4\(spdf\)
- valence shells: 7\(sp\), 6\(d\), 5\(f\)

<table>
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<th>Excitation energies, cm(^{-1})</th>
<th>5(f^36d^17s^2) →</th>
<th>Absolute errors, cm(^{-1})</th>
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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) → ThO$^+$ (0h1p) → 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)

![Graph](image_url)

deviation from Dirac-Coulomb-Gaunt, cm$^{-1}$
excitation energy, cm$^{-1}$

contribution to excitation energy, cm$^{-1}$

QED + retardation
Gaunt
Summary

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

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<td>rms</td>
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- 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?