Towards a software ecosystem for high-precision multi-scale *ab initio* relativistic quantum modeling of atoms, molecules, and materials

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A. S. Rumiantsev, L. V. Skripnikov, M. M. Seregin, M. I. Losev, A. V. Zaitsevskii, E. Eliav, V. S. Galigerov, Yu. V. Kashpurovich, V. V. Stegailov, A. V. Titov

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JINR, Dubna, 30th October, 2024

What is quantum chemistry?

- electronic Hamiltonian of a N-electron system:

$$\hat{H}_e = -\frac{1}{2}\sum_{i=1}^{N_{\text{elec}}} \Delta_i + \sum_{i=1}^{N_{\text{elec}}}\sum_{\alpha=1}^{N_{\text{nuc}}} \left(-\frac{Z_\alpha}{|\boldsymbol{R}_\alpha - \boldsymbol{r}_i|} + \hat{U}_\alpha(i) \right) + \sum_{i<j} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

$\hat{U}_\alpha(i)$	pseudopotential operator = relativistic effects
$\sum_{i<j} \frac{1}{\lvert \boldsymbol{r}_i - \boldsymbol{r}_j \rvert}$	interelectronic interaction (Coulomb)
$\boldsymbol{r}_i$	coordinates of electrons
$\boldsymbol{R}_\alpha$	coordinates of nuclei
Z_α	charges of nuclei (or atomic cores)

- electronic Schrödinger equation (or its relativistic counterpart):

$$\hat{H}_e \, |\psi_n\rangle = E_n \, |\psi_n\rangle$$

$$\Downarrow \quad \Downarrow \quad \Downarrow$$

$$\{\psi_1, E_1\}, \quad \{\psi_2, E_2\}, \quad \{\psi_3, E_3\}, \quad \ldots$$

Yet another quantum chemistry package – why?

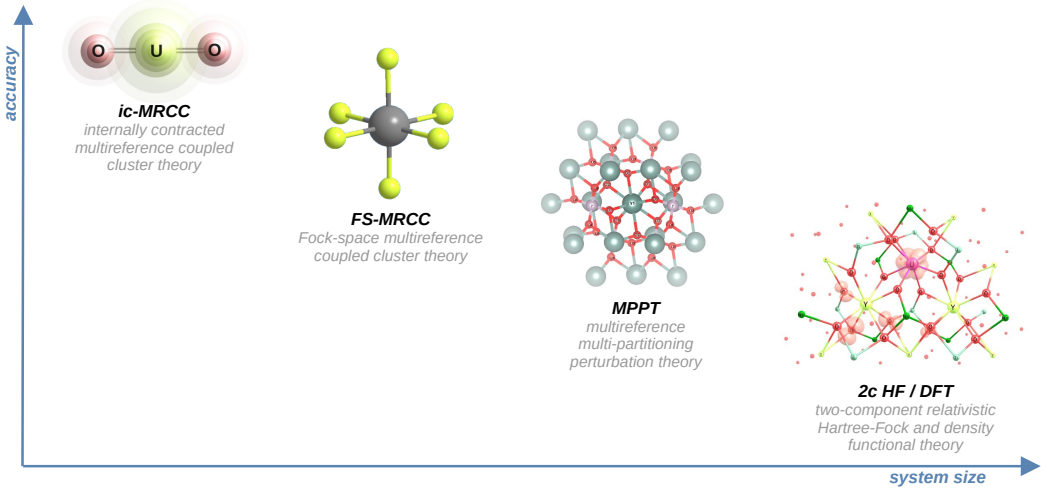
Our focus point: *d*-elements, lanthanides, actinides, superheavy elements (SHEs)

- very strong relativistic (and possibly QED) effects
- open shells, several unpaired electrons
- complicated structure of electronic wavefunctions
  (multireference nature = several leading Slater determinants)
- very dense electronic spectrum
  desired accuracy < 0.1 eV
- very wide range of problems to be solved: from atoms to materials

Yet another QC package – why?

- optical and magnetic properties of f-element compounds
- active laser media; sources of light; chromophores, luminophores
- chemistry and spectroscopy of actinides and superheavy elements
- searches for $\mathcal{P}$,$\mathcal{T}$-odd fundamental interactions (physics beyond the Standard model)
- optical spectroscopy of atoms and molecules to extract properties of nuclei
- 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
- laser cooling and assembly of cold molecules
- ...

Ab initio multi-scale / multi-level modeling of electronic structure



our dream: one software ecosystem – all systems!

Relativistic model: generalized relativistic pseudopotential (GRPP)

- 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:

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

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

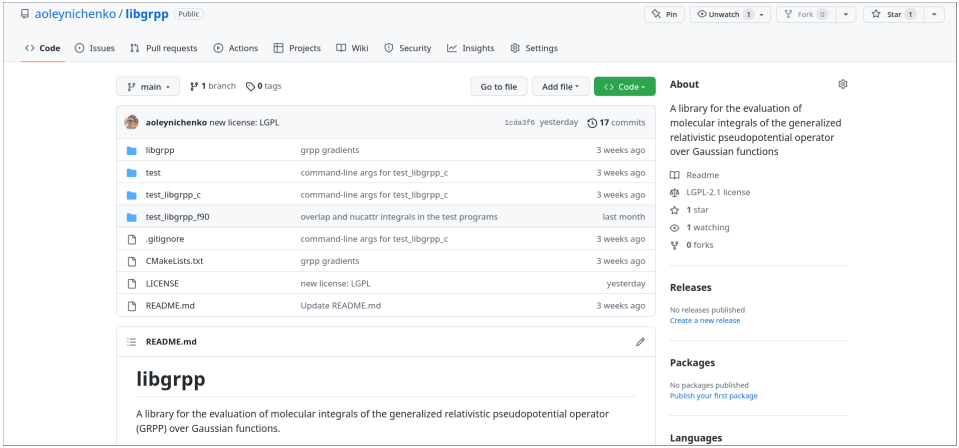
- potential $\hat{U}$ can effectively account for:
  → scalar-relativistic effects
  → spin-orbit interaction
  → Breit interaction of electrons
  → finite nuclear charge distribution (the Fermi model)
  → QED contributions (electron self-energy + vacuum polarization)

- 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)

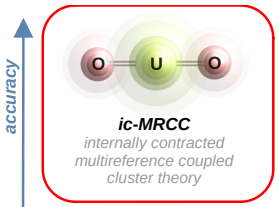
Relativistic model: generalized relativistic pseudopotential (GRPP)

the `libgrpp` library



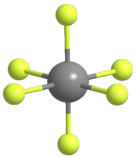
https://github.com/aoleynichenko/libgrpp

Ab initio multi-scale / multi-level modeling of electronic structure

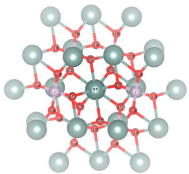


ic-MRCC
internally contracted multireference coupled cluster theory

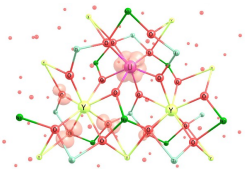
level 1



FS-MRCC
Fock-space multireference coupled cluster theory



MPPT
multireference multi-partitioning perturbation theory



2c HF / DFT
two-component relativistic Hartree-Fock and density functional theory

accuracy

system size

Level 1. Small molecules and atoms: internally contracted multireference coupled cluster theory (ic-MRCC) (M. I. Losev, A. V. Oleynichenko)

$$|\psi_n\rangle = \exp(T)\ |\tilde{\psi}_n\rangle \qquad |\tilde{\psi}_n\rangle = \sum_\mu c_\mu\, |\Phi_\mu\rangle$$

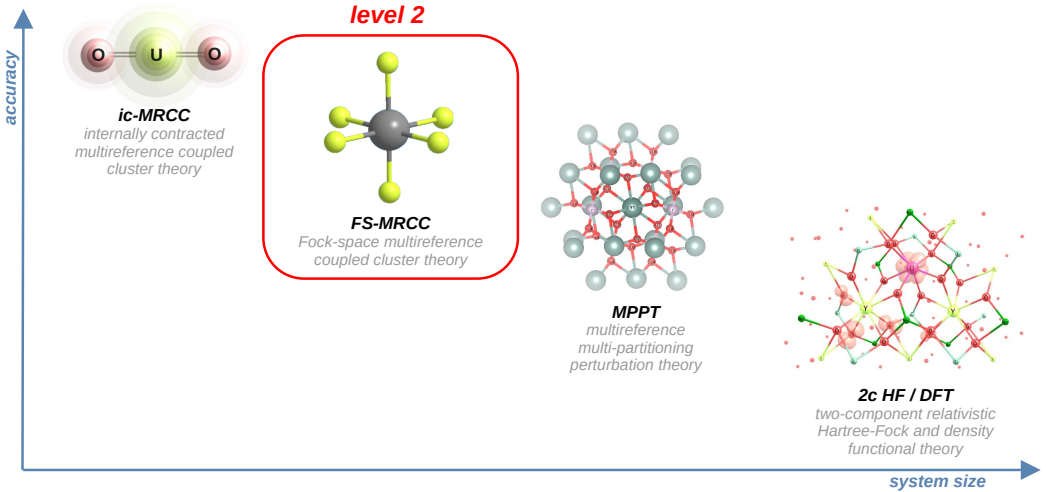
- more flexible Ansatz: contractions between the T operators are allowed
- acceptable computational complexity: $O(N^6)$
- (nearly) arbitrary open shells
- a path towards subtle nuclear properties from optical spectra
  (isotope shifts, octupole deformations, magnetic & quadrupole moments, ...)

Program implementation:

- non-relativistic implementation GeCCo exists
  `https://github.com/ak-ustutt/GeCCo-public`
- 2024: interface to PySCF
- planned: relativistic version

M. Hanauer, A. Köhn, *J. Chem. Phys.* 134, 204111 (2011)

Ab initio multi-scale / multi-level modeling of electronic structure



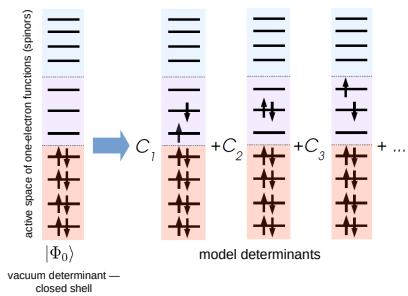
Level 2. Small cluster models of solids and small molecules: multireference Fock space coupled cluster theory (FS-MRCC)

- wave function:

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

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

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

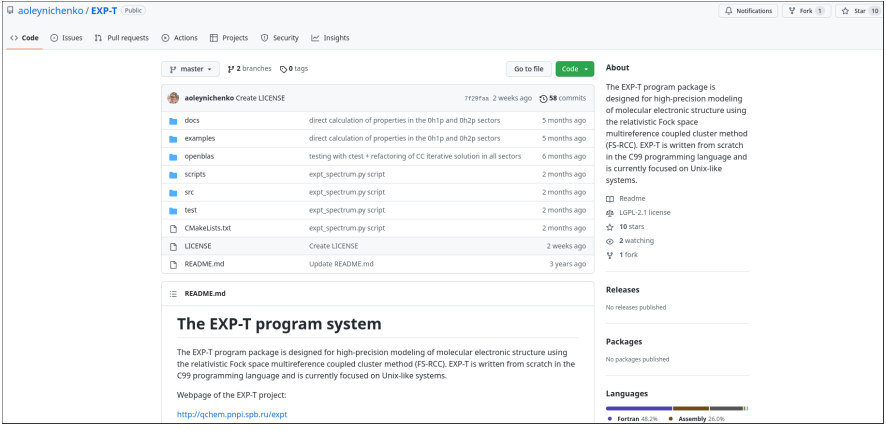


- the most effective account for electron correlation
- computational complexity:
  time – min $O(N^6)$
  memory – min $O(N^4)$
- relativistic calculations = complex arithmetic + low symmetry!

E. Eliav, A. Borschevsky, A. Zaitsevskii, A. V. Oleynichenko, U. Kaldor. *Comprehensive Computational Chemistry*, 3, 79 (2024)

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

(A. V. Oleynichenko, A. S. Rumiantsev, A. V. Zaitsevskii, E. Eliav)



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

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

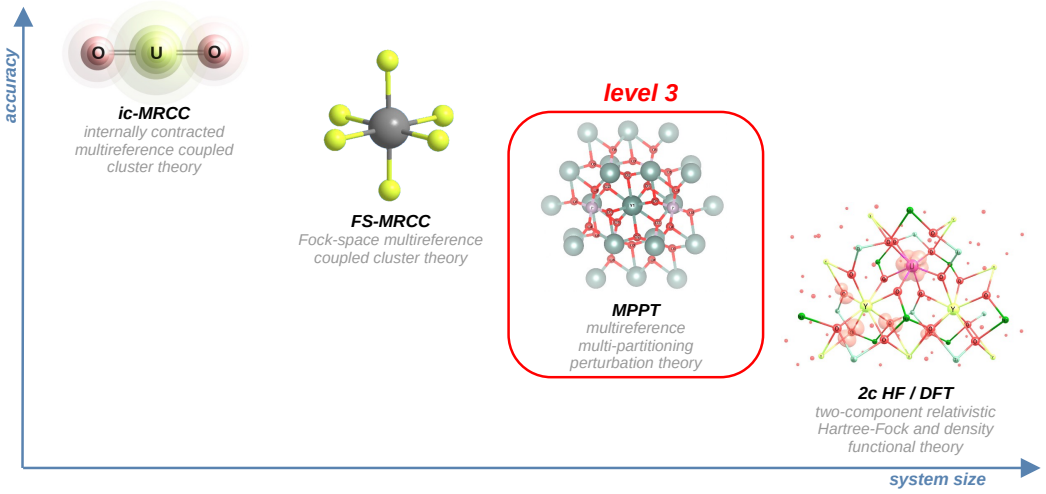
(A. V. Oleynichenko, A. S. Rumiantsev, A. V. Zaitsevskii, E. Eliav)

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
- analytic density matrices

- flexible and enabling fast implementation of new models!

Ab initio multi-scale / multi-level modeling of electronic structure



Level 3. Cluster models of solids and medium-sized molecules: multireference multi-partitioning perturbation theory (MPPT)

(M. M. Seregin, A. V. Oleynichenko, A. V. Zaitsevskii)

- Schrödinger equation $\Rightarrow$ des Cloizeaux equation:

$$H\,|\psi_n\rangle = E_n\,|\psi_n\rangle \quad \Rightarrow \quad H_{\text{eff}} = \Omega^\dagger H \Omega \quad \text{and} \quad H_{\text{eff}}\,|\tilde{\psi}_n\rangle = E_n\,|\tilde{\psi}_n\rangle \quad \text{and} \quad |\tilde{\psi}_n\rangle = \sum_J c_{Jn}\,|\Phi_J\rangle$$

Ω – wave operator, $\Omega\,|\tilde{\psi_n}\rangle = |\psi_n\rangle$

H_{eff} – effective Hamiltonian, its diagonalization gives E_n

- Partitioning of the Hamiltonian depends on a model determinant $|\Phi_J\rangle$ chosen as a vacuum:

$$H = H_0(J) + V(J) \qquad H_0 = \sum_h^{\text{occ in } |\phi_J\rangle} \varepsilon_h^{\oplus}\, a_h^\dagger a_h + \sum_p^{\text{virt in } |\phi_J\rangle} \varepsilon_p^{\odot}\, a_p^\dagger a_p$$

- Second-order PT contribution to H_{eff}:

$$\langle \Phi_J | H_{\text{eff}} | \Phi_{J'} \rangle = \frac{1}{2} \sum_{|\Phi_A\rangle \in Q} \frac{\langle \Phi_J | H | \Phi_A \rangle \langle \Phi_A | H | \Phi_{J'} \rangle}{\sum_i \varepsilon_i^{\oplus} - \sum_a \varepsilon_a^{\odot}} + \text{h.c.}$$

Q – orthogonal complement to the model space $P = \text{span}\{|\Phi_J\rangle\}$

A. Zaitsevskii, J.-P. Malrieu, *Chem. Phys. Lett.*, 233, 597 (1995)

Level 3. Cluster models of solids and medium-sized molecules: multireference multi-partitioning perturbation theory (MPPT)

(M. M. Seregin, A. V. Oleynichenko, A. V. Zaitsevskii)

Summary for non-quantum-chemists:

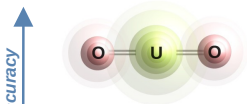
- determinant-based multireference perturbation theory
- incomplete model spaces $\Rightarrow$ compact representation
- arbitrary open shells
- acceptable computational complexity:
  four-index transformation: $O(N^5)$
  H_{eff} construction: $O(MN^4)$
  (M – number of model-space determinants)

Program implementation:

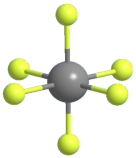
- written by A. V. Zaitsevskii and R. Cimiraglia in 1990s
- 2024: code refactoring
- 2024: modern interface to PySCF

A. Zaitsevskii, J.-P. Malrieu, *Chem. Phys. Lett.*, 233, 597 (1995)

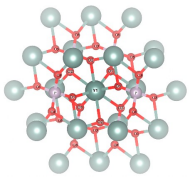
Ab initio multi-scale / multi-level modeling of electronic structure



ic-MRCC
internally contracted multireference coupled cluster theory

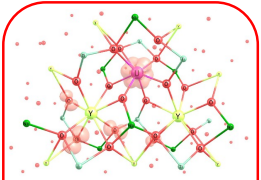


FS-MRCC
Fock-space multireference coupled cluster theory



MPPT
multireference multi-partitioning perturbation theory

level 4



2c HF / DFT
two-component relativistic Hartree-Fock and density functional theory

accuracy

system size

Level 4. Cluster models of solids and large molecules: two-component Kramers-unrestricted density functional theory

- one-electron functions – molecular spinors $\psi_i(\boldsymbol{r})$ with mixed $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ components

$$\psi_i(\boldsymbol{r}) = \sum_\mu C_{\mu i}^{(\alpha)} \begin{pmatrix} \chi_\mu \\ 0 \end{pmatrix} + \sum_\mu C_{\mu i}^{(\beta)} \begin{pmatrix} 0 \\ \chi_\mu \end{pmatrix}$$

$\chi_\mu(\boldsymbol{r})$ – Gaussian basis functions
$C_{\mu i}^{(\alpha,\beta)}$ – complex-valued coefficients

- two-component Kohn-Sham equations

$$\left(h^{GRPP} + J - a_x K + v_{xc}\right)\psi_i = \varepsilon_i \psi_i$$

v_{xc} – exchange-correlation potential
a_x – fraction of exact exchange
Hartree-Fock: $v_{xc} = 0$, $a_x = 1$

- resolution of identity (RI) approximation (example: Coulomb term)

$$J_{\mu\nu} = \sum_{\rho\sigma} D_{\rho\sigma}\ (\mu\nu|\rho\sigma) \quad \Rightarrow \quad J_{\mu\nu} = \sum_{\rho\sigma PQ} D_{\rho\sigma}\ (\mu\nu|P)\ (V^{-1})_{PQ}\ (\rho\sigma|Q)$$

computational scaling $O(N^4) \Rightarrow O(N^3)$
or even O(N) for spatially extended systems

2cDFT: C. van Wüllen, *Z. Phys. Chem.* 224, 413 (2010); RI: I. O. Glebov, V. V. Poddubnyi, *Russ. J. Phys. Chem.*, 98, 617 (2024).

BUFO – a two-component density functional and Hartree-Fock program

(A. V. Oleynichenko, Yu. V. Kashpurovich, V. S. Galigerov, V. V. Stegailov)

Implemented features:

- restricted (RHF), unrestricted (UHF), two-component Hartree-Fock (2c SCF)
- resolution of identity (RI) approximation for RHF
- pseudopotentials

Planned features:

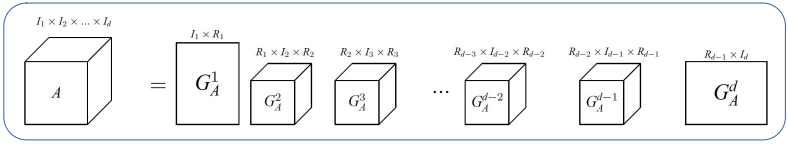
- RI approximation for UHF and 2c SCF
- analytic gradients
- density functional theory
- periodic boundary conditions
- Born-Oppenheimer molecular dynamics

(bufo bufo = common toad in Latin)

making it faster!

Tensor decompositions to reduce computational cost of the coupled cluster theories (A. S. Rumiantsev)

- all molecular integrals and amplitudes are represented by multidimensional arrays – tensors
- tensor train (TT) representation
  [I. V. Oseledets, *SIAM J. Sci. Comput.*, 33, 2295 (2011)]



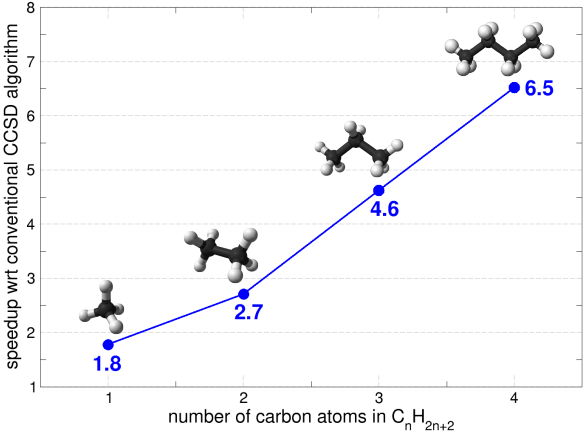
$$A[i_1, i_2, ..., i_d] = \sum_{\alpha_1, \ldots, \alpha_{d-1}}^{R_1, \ldots, R_{d-1}} \underbrace{G_1[1, i_1, \alpha_1]}_{TT-core} \times G_2[\alpha_1, i_2, \alpha_2] \times \ldots \times G_d[\alpha_{d-1}, i_d, 1]$$

$$\mathbf{N^d \rightarrow dNR^2}$$

- new library has been written in Rust (tensor contractions, transpositions, sparse arrays...)
- the first implementation of the CCSD method employing tensor trains

Tensor decompositions to reduce computational cost of the coupled cluster theories (A. S. Rumiantsev)

Classical algorithm *vs* tensor trains: speedup, times
(linear alkanes)



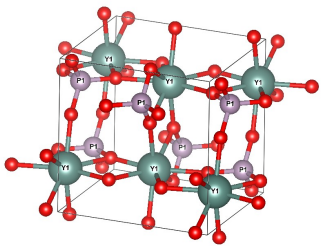
ab initio multi-scale modeling of electronic structure: practice!

Ab initio multi-scale modeling of electronic structure: practical illustration

Localized excitations in Ce^{3+} and Th^{3+}-doped xenotime YPO_4

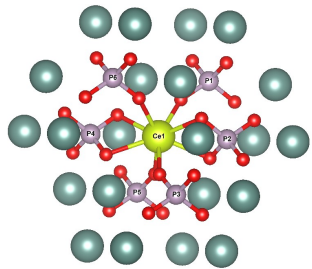
periodic model (crystal)

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



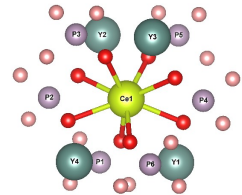
extended cluster model with impurity ion

- **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

Ab initio multi-scale modeling of electronic structure: practical illustration

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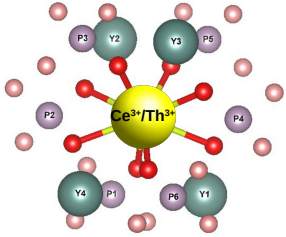
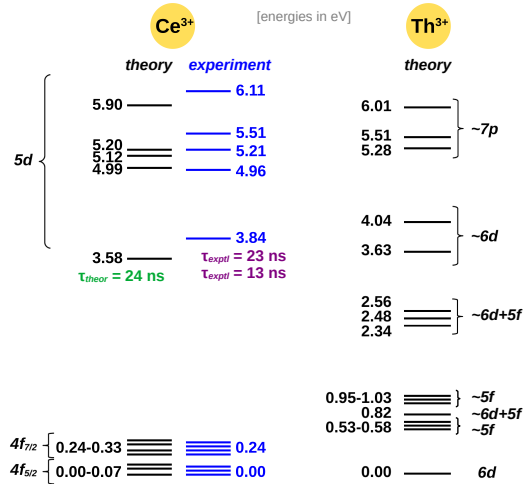


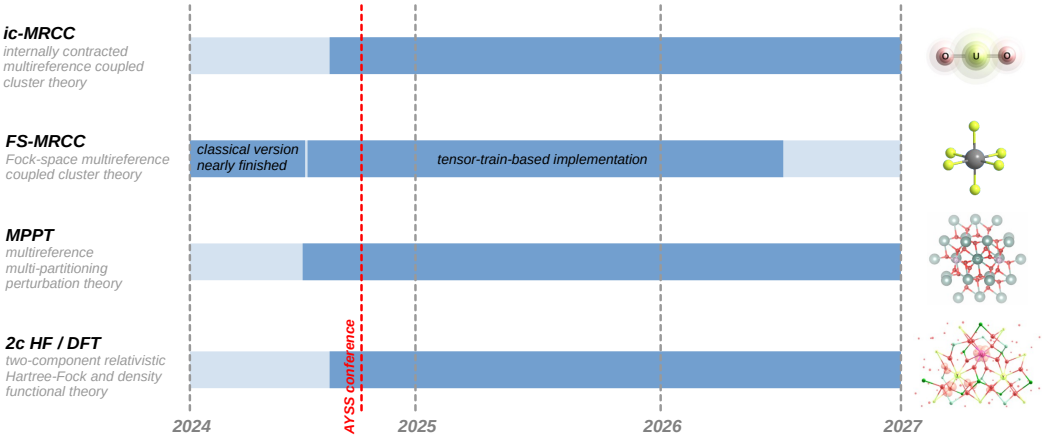
minimal cluster model



- 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] A. V. Oleynichenko, Y. V. Lomachuk, D. A. Maltsev, N. S. Mosyagin, V. M. Shakhova, A. Zaitsevskii, A. V. Titov, *PRB* 109, 125106 (2024)

When?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AYSS conference
2024
2025
2026
2027

Related reports at AYSS-2024

- Artem Rumiantsev (NRC "Kurchatov Institute" – PNPI)
  Solving coupled cluster equations using tensor train decomposition
- Polina Khadeeva (NRC "Kurchatov Institute" – PNPI)
  Ab initio study of chemical shifts of X-ray emission spectra in ytterbium halides by the coupled cluster method
- Yuri Kashpurovich (JIHT RAS)
  First steps in implementing the RI-HF algorithm for electronic structure calculations

Summary

- a large software package for multi-scale electronic structure simulations is under development
- lanthanides, actinides, superheavy elements
- relativistic effects + QED + multireference wave functions
- from atoms to solids
- many models are already available for use!

any collaborations is welcome!!!

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

https://atom.mipt.ru

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  A. Zaitsevskii, J.-P. Malrieu
  Chem. Phys. Lett., 233, 597 (1995)

- Towards high performance relativistic electronic structure modelling: the EXP-T program package
  A. V. Oleynichenko, A. Zaitsevskii, E. Eliav
  Commun. Comput. Inf. Sci. 1331, 375 (2020)

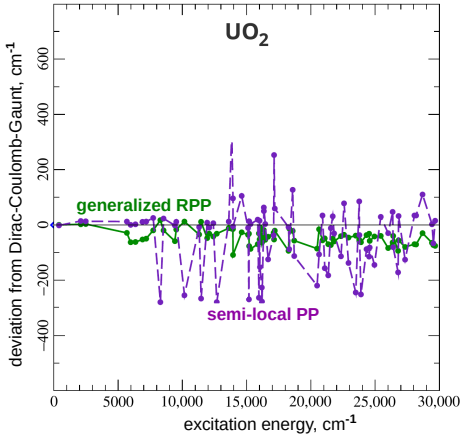
- Relativistic Fock space coupled cluster method for many-electron systems: non-perturbative account for connected triple excitations
  A. V. Oleynichenko, A. Zaitsevskii, L. V. Skripnikov, E. Eliav
  Symmetry, 12(7), 1101 (2020)

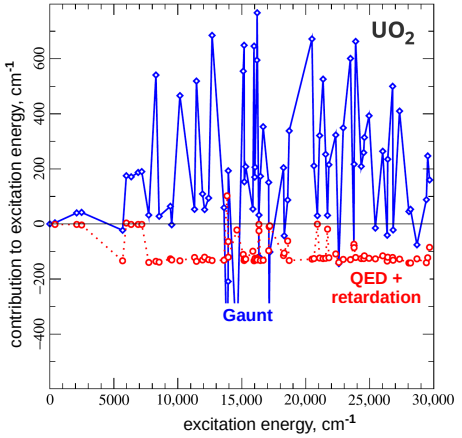
- LIBGRPP: a library for the evaluation of molecular integrals of the generalized relativistic pseudopotential operator over Gaussian functions
  A. V. Oleynichenko, A. V. Zaitsevskii, N. S. Mosyagin, A. N. Petrov, E. Eliav, A. V. Titov
  Symmetry 15(1), 197 (2023)

appendix

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)