Recent advances in relativistic coupled cluster methods for open shell states

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Current challenges in chemical physics and theoretical chemistry – 2014
5th July, 2024

Why?

- 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...

Single-reference *vs* multi-reference approaches

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

- single-reference (SR): one leading Slater determinant
  + determinants excited wrt it

$$\psi_n = \Phi_0 + \sum_K C_K \Phi_K$$

- multi-reference (MR): several leading configurations (determinants)
  + determinants excited wrt them

$$\psi_n = \sum_\mu C_\mu \Phi_\mu + \sum_K C_K \Phi_K$$

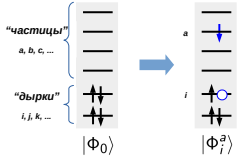
Review: D. I. Lyakh, M. Musial, V. F. Lotrich, *Chem. Rev.* 112(1), 182 (2012)

Single reference coupled cluster method

- exponential Ansatz for an electronic wavefunction:

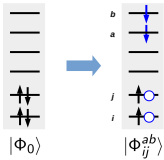
$$|\psi\rangle = e^{T}\,|\Phi_0\rangle$$

- single excitations:



$$T_1 = \sum_{ia} t_i^a \{a_a^\dagger a_i\}$$

- double excitations:



$$T_2 = \frac{1}{4}\sum_{ijab} t_{ij}^{ab} \{a_a^\dagger a_i a_b^\dagger a_j\}$$

objective: calculate amplitudes t_i^a, t_{ij}^{ab}, ...

Single reference coupled cluster method

Energy expression and amplitude equations

- wave function:

$$|\psi\rangle = e^T |\Phi_0\rangle$$

- Schrödinger equation $\Rightarrow$ Bloch equation:

$$H|\psi\rangle = E|\psi\rangle \quad \Rightarrow \quad (He^T)_c |\Phi_0\rangle = E_{corr} |\Phi_0\rangle$$

$(He^T)_c$ = only connected Brandow diagrams
$E = E_{HF} + E_{corr}$

- projection onto $\langle\Phi_0|$ $\Rightarrow$ expression for the correlation energy:

$$E_{corr} = \langle\Phi_0|(He^T)_c|\Phi_0\rangle$$

- projection onto $\langle\Phi_i^a|$, $\langle\Phi_{ij}^{ab}|$ $\Rightarrow$ amplitude equations (CCSD):

$$\begin{cases} \langle\Phi_i^a|(He^T)_c|\Phi_0\rangle = 0 & \textit{singles } (S) \\ \langle\Phi_{ij}^{ab}|(He^T)_c|\Phi_0\rangle = 0 & \textit{doubles } (D) \end{cases}$$

Fock-space multireference coupled cluster method

$$|\psi\rangle = \{e^T\} \sum_I C_I |\Phi_I\rangle$$

wave operator
no contractions between cluster operators

model vector
linear combination of Slater determinants

- wave operator $\Omega = \{e^T\} \Rightarrow$ dynamic correlation
- model vector $|\tilde{\psi}\rangle = \sum_\mu C_\mu |\Phi_\mu\rangle \Rightarrow$ multiconfigurational nature of a state

- effective Hamiltonian $\tilde{H}$ acts within a model space:

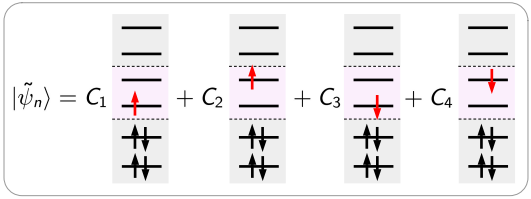
$$H|\psi_n\rangle = E_n|\psi_n\rangle \quad \Rightarrow \quad \tilde{H}|\tilde{\psi}_n\rangle = E_n|\tilde{\psi}_n\rangle$$

U. Kaldor, *Theor. Chim. Acta*, 80, 427, (1991)

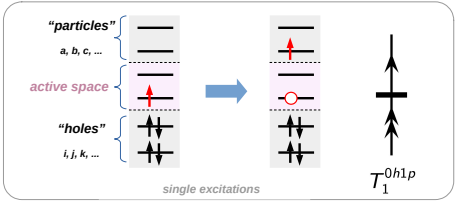
Fock-space multireference coupled cluster method

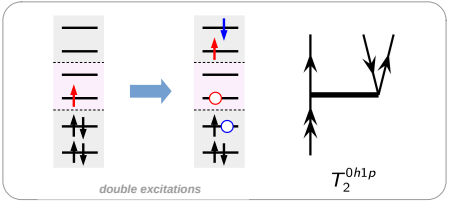
The $0h1p$ sector: one particle above the closed shell (CCSD model)

- model vector in the $0h1p$ sector:



- cluster operator $T = T^{0h0p} + T^{0h1p}$ (CCSD model):

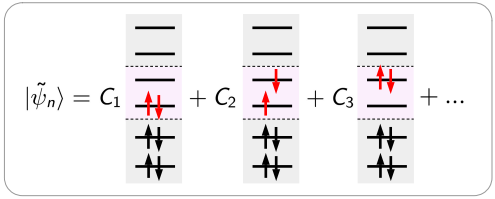




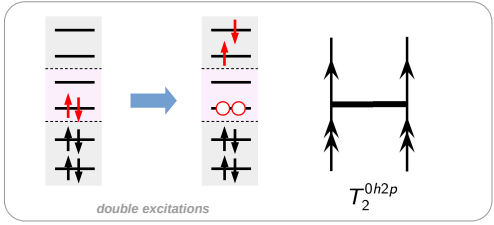
Fock-space multireference coupled cluster method

The $0h2p$ sector: two particles above the closed shell (CCSD model)

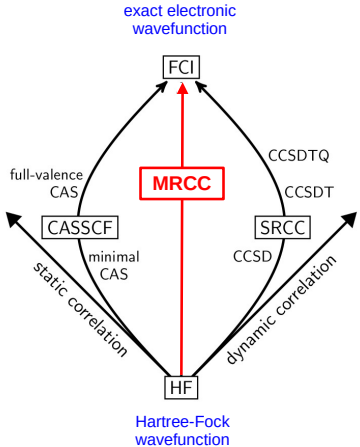
- model vector in the $0h2p$ sector:



- cluster operator $T = T^{0h0p} + T^{0h1p} + T^{0h2p}$ (CCSD model):



single-reference *vs* multi-reference



- multi-reference CC: well-balanced treatment of correlation effects of different nature

Fig. from: M. Hanauer, PhD thesis, 2013, http://doi.org/10.25358/openscience-2706

Hamiltonian: (generalized) relativistic pseudopotentials (GRPP)

- valence and outercore electrons are described by the two-component effective Hamiltonian:

$$\hat{H}^{RPP} = \sum_i \left(-\frac{\Delta_i}{2} + \sum_\alpha \left(-\frac{z_\alpha}{|\boldsymbol{R}_\alpha - \boldsymbol{r}_i|} + \hat{U}_\alpha(i) \right) \right) + \sum_{i>j} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

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

- pseudopotential $\hat{U}$ substitute inner core electrons and can effectively include:
  - scalar-relativistic effects ($\sim$ mass-velocity + Darwin)
  - spin-orbit interaction
  - Breit *e*-*e* interaction
  - finite nuclear charge distribution (Fermi model)
  - leading QED effects (model operator = self-energy + vacuum polarization)

- the most exact formulation: generalized relativistic pseudpotential (typical error of EEs < 50 cm^{-1})
- available in DIRAC and CP2K *via* the `LIBGRPP` library!

A. V. Titov, N. S. Mosyagin, *IJQC* 71, 359 (1999)

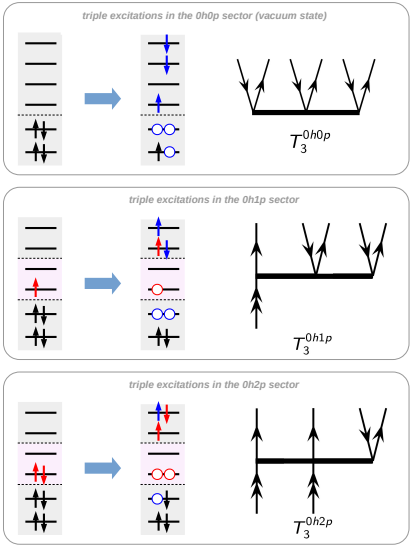
Challenges – 2017

- accounting for triples and three open shells
- transition moments and other off-diagonal properties
- density matrices
- impurity centers in crystals

also:

- intruder state problem $\Rightarrow$ amplitude equations typically fail to converge (A. V. Zaitsevskii)

Accounting for triples: the FS CCSDT model



- cluster operator:

$$T = T_1 + T_2 + T_3$$

- number of floating-point operations – $O(N^8)$

  N one-particle basis functions (spin-orbitals or spinors)

- correlation of "added" electrons in the $0h1p$ and $0h2p$ sectors

Pilot applications of the FS CCSDT model

Ionization potentials and excitation energies of the Tl and Pb atoms, cm^{-1}

A. Oleynichenko, A. Zaitsevskii, L. V. Skripnikov, E. Eliav, *Symmetry*, 12(7), 1101 (2020)

Table 1. Deviations of the calculated ionization potentials (IP) and excitation energies (EE) of neutral thallium and lead and lead cation (cm^{-1}) from the experimental values. FS-RCCSD/LB+T/SB stands for the combined scheme (8).

	State		Exptl [84]	IH-FS-RCCSD [47]	FS-RCCSD/LB	FS-RCCSD/LB + T/SB: SDT-1	SDT-1′	SDT-2	SDT-3	SDT
Tl, ground state $6s^26p\ {}^2P_{1/2}$										
IP			49,266		−56	−38	−38	−204	−151	−32
EE	$6s^26p$	$^2P_{3/2}$	7793		−112	23	23	1	9	−31
Pb^+, ground state $6s^26p\ {}^2P_{1/2}$										
IP			121,245	−168	−143	−28	−28	−190	−158	−59
EE	$6s^26p$	$^2P_{3/2}$	14,081	−196	−136	25	25	12	14	−42
Pb, ground state $6s^26p^2\ {}^3P_0$										
IP			59,819	−543	364				−336	7
EE	$6s^26p^2$	$^3P_1$	7819	−288	−302	76	5	−4	−3	−28
		$^3P_2$	10,650	−343	−235				−102	13
		$^1D_2$	21,458	−605	−394	215	158	158	167	5
		$^1S_0$	29,467	−208	414	170	248	291	302	173

CCSD → CCSDT

few meV accuracy achieved

the way towards the most precise atomic calculations ever?

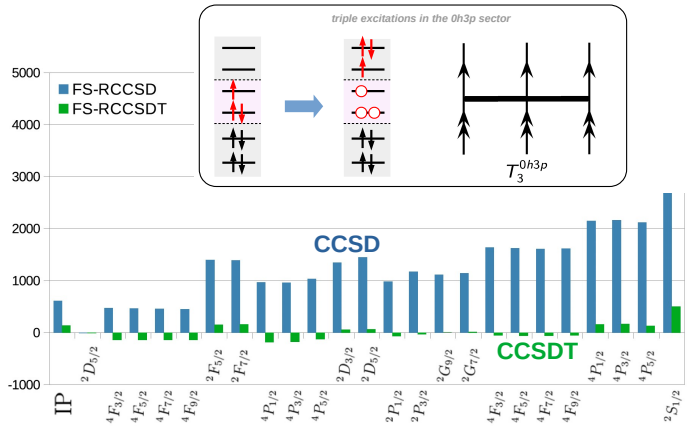
A. Landau, E. Eliav, Y. Ishikawa, U. Kaldor, J. Chem. Phys. 114, 2977 (2001)

J. E. Sansonetti, W. C. Martin, J. Phys. Chem. Ref. Data, 34, 1559 (2005)

Pilot applications of the FS CCSDT model

Lanthanum atom energy levels, configurations $6s^2 5d$, $6s^1 5d^2$, $5d^3$

Deviations of calculated excitation energies from experiment, cm^{-1}



$0h3p$ sector: refinement of the quadrupole moments of Bi isotopes

L. V. Skripnikov, A. V. Oleynichenko, A. V. Zaitsevskii, D. E. Maison, A. E. Barzakh, *Phys. Rev. C* 104(3), 034316 (2021)

- electromagnetic moments of heavy nuclei are known with a large uncertainty (up to 20%)!
- how to extract nuclear electric quadrupole moment Q from experimentally measured hyperfine constant B:

$$Q\ [\text{b}] = \frac{B\ [\text{MHz}]}{234.9648867 \cdot q\ [\text{a.u.}]}$$

B – electric quadrupole hyperfine-structure constant

q – electric field gradient on a nucleus

- $6p^3$ electronic states of the Bi atom are multiconfigurational (the $0h3p$ sector of the Fock space)

$0h3p$ sector: refinement of the quadrupole moments of Bi isotopes

L. V. Skripnikov, A. V. Oleynichenko, A. V. Zaitsevskii, D. E. Maison, A. E. Barzakh, *Phys. Rev. C* 104(3), 034316 (2021)

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TABLE I. The calculated values of the electric field gradient in a.u.($= E_H/a_B^2$) for the ground $^4S^o_{3/2}$ and excited $^2P^o_{3/2}$ electronic states of neutral bismuth and the deduced values of the NQM of ^{209}Bi.

	$6p^3\ ^4S^o_{3/2}$	$6p^3\ ^2P^o_{3/2}$
	EFG:	
FS-CCSD	2.983	−10.292
basis set correction	0.055	−0.050
FS-CCSDT − FS-CCSD	0.117	0.276
Breit contribution	−0.058	0.088
Total	3.097	−9.978
B, MHz [36]	−305.067(2)	978.638(10)
$Q(^{209}\mathrm{Bi})$, mb	−419	−417

Challenges – 2017

- accounting for triples and three open shells
- transition moments and other off-diagonal properties
- density matrices
- impurity centers in crystals

Effective operator of a property

A. V. Oleynichenko, A. V. Zaitsevskii, S. V. Kondratyev, E. Eliav, *Opt. Spectrosc.*, 131(11), 1471 (2023)

- basic idea: use truncated expression for the CC wavefunction:

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

- effective property operator $\tilde{O}$ in the 2$^{\text{nd}}$ order in T:

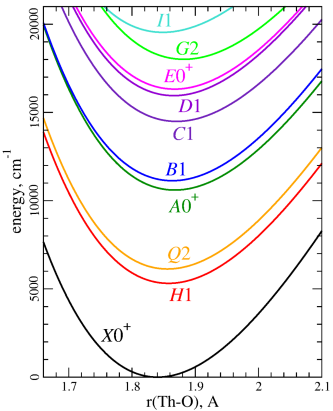
$$\tilde{O} \approx \left(O + T^\dagger O + OT + \frac{\{(T^\dagger)^2\}}{2}O + T^\dagger O T + O\frac{\{T^2\}}{2} - (T^\dagger T)_{cl} O\right)_{cl,conn}$$

- exact mutual cancellation of all disconnected diagrams
- intensities of absorption and emission $\sim |\langle\psi_n|\hat{d}|\psi_m\rangle|^2$
- one calculation $\Rightarrow$ matrix elements for all pairs of electronic states

See also: A. Zaitsevskii, A. V. Oleynichenko, E. Eliav. *Mol. Phys.* e2236246 (2023)

Application: excited states of the ThO molecule

Term energies T_e, cm^{-1} [A. Zaitsevskii, A. V. Oleynichenko, E. Eliav, *Mol. Phys.* e2236246 (2023)]



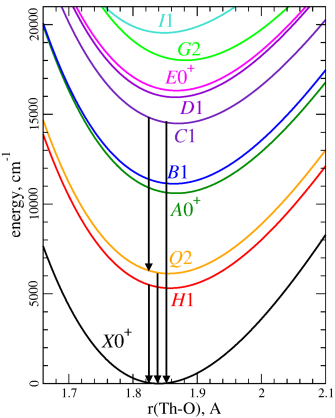
	exptl, cm^{-1}	deviation from experiment, cm^{-1} RPP/FS-CCSD 0h2p	DC/FS-CCSD 0h2p	DC/FS-CCSD 1h1p
H(i)1	5317	104	700	-149
Q(i)2	6128	97	738	-62
A(ii)0^+	10601	242	691	1098
B(ii)1	11129	302	927	–
C(iii)1	14490	424	1698	-39
D(iv)1	15946	440	1698	–
E(iii)0^+	16320	312	960	-1950
G(iv)2	18010	165	–	–
F(iv)0^+	18338	431	–	–
I(vi)1	19539	367	–	–
		[present work]		[Tecmer et al, *PCCP*, 2018]

Why ThO? One of the objects to search for electron electric dipole moment

ACME Collaboration, *Nature*, 562, 355 (2018)

Application: excited states of the ThO molecule

Lifetimes of excited states [A. Zaitsevskii, A. V. Oleynichenko, E. Eliav, *Mol. Phys.* e2236246 (2023)]

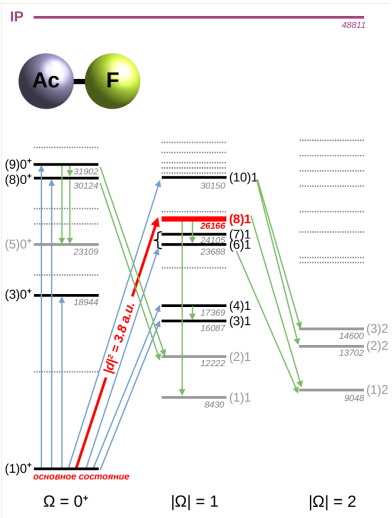


	exptl	theory
$H \to X$	4.2 ± 0.5 ms[a]	3.82 ms
$Q \to X$	> 62 ms[b]	177 ms
$C \to \ldots$	> 480 ns[c]	
	468 ± 30 ns[d]	400 ns
$C \to Q$	5.4 ± 1.3 ms[b]	5.49 μs

[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)

Spectroscopy of the AcF molecule

L. V. Skripnikov et al, *J. Chem. Phys.* 159, 124301 (2023)



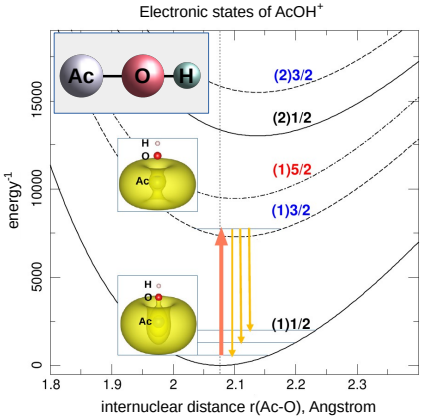
- promising object for the searches of the $\mathcal{T}$,$\mathcal{P}$-odd nuclear Schiff moment (^{225}Ac, ^{227}Ac)

  L. V. Skripnikov et al, *PCCP* 22, 18374 (2020)
- low-lying states: two electrons above the closed-shell vacuum AcF^{2+}
- $\sim$ 80 states below 43000 cm^{-1}
- the most intense transitions were predicted

  $\max \mid \langle \psi_i | \boldsymbol{d} | \psi_f \rangle \mid^2$
- the (8)1 state was studied experimentally at CRIS/ISOLDE (CERN)

the first experimental study of the AcF molecule was not possible without theoretical modeling!

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



a promising system for the new generation of experiments to search $\mathcal{T}, \mathcal{P}$-violation effects

$\Rightarrow$ physics beyond the Standard Model

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

Challenges – 2017

- accounting for triples and three open shells
- transition moments and other off-diagonal properties
- density matrices
- impurity centers in crystals

Approximate method to calculate FS CC density matrices

- exact expression:

$$(\gamma_N)_{qp} = \frac{N_i}{N_f} \langle \tilde{\psi}_i^{\perp\perp} | (\Omega^\dagger \Omega)^{-1} \; \Omega^\dagger \{ a_p^\dagger a_q \} \Omega | \tilde{\psi}_f \rangle \qquad N_i = \langle \tilde{\psi}_i | \Omega^\dagger \Omega | \tilde{\psi}_f \rangle^{1/2}$$

$$\Omega = \{ e^T \} = \{ 1 + T + \frac{TT}{2} + \frac{TTT}{6} + ... \}$$

- use the Taylor expansion to express the inverse metric operator:
  only for the Fock space sectors $0hPp$ and $Hh0p$!

$$(\Omega^\dagger \Omega)^{-1} \approx 1 - \Omega^\dagger \Omega + ...$$

- we retain only terms linear and quadratic in T:

$$(\Omega^\dagger \Omega)^{-1} \; \Omega^\dagger \{ a_p^\dagger a_q \} \Omega \;\approx\; \boxed{\Omega^\dagger \{ a_p^\dagger a_q \} \Omega - (T^\dagger T)_{cl} \{ a_p^\dagger a_q \}}$$

- exact mutual cancellation of disconnected diagrams
- very low computational cost!

How to use density matrices and natural spinors?

not density matrices themselves, but natural [transition] spinors are of primary interest

- contracted relativstic ANO-type basis sets for excited state calculations
  - ⇒ before: scalar-relativistic CCSD/CCSD(T) density matrices to construct ANOs (`CFOUR`)
  - ⇒ now: fully relativistic CCSD DMs (`DIRAC+EXP-T`)
  - ⇒ future: basis sets with nearly the same contraction error for all target electronic states?
- natural spinors as a basis for FS CCSDT calculations?
- visualization of excited states and electronic transitions?

Challenges – 2017

- accounting for triples and three open shells
- transition moments and other off-diagonal properties
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- impurity centers in crystals

Localized excitations on f-element ions Ce^{3+}, Th^{3+} in xenotime YPO_4 crystals (Y. V. Lomachuk)

- 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 et al, *Phys. Rev. A* 109, 042806 (2024)

Xenotime crystal

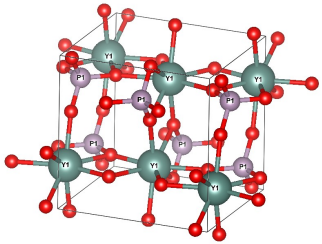
Locality: Novo Horizonte, Brazil

https://en.wikipedia.org/wiki/Xenotime

Minimal cluster model of an impurity center

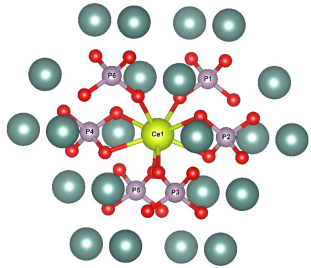
periodic model (crystal)

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



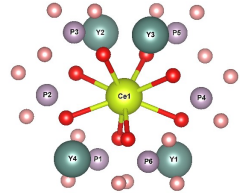
extended cluster model with impurity ion

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



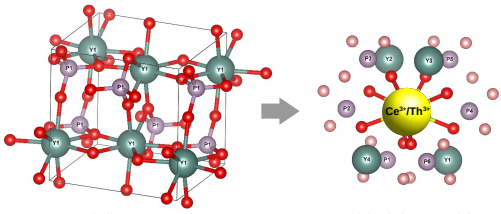
minimal cluster model with impurity ion

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

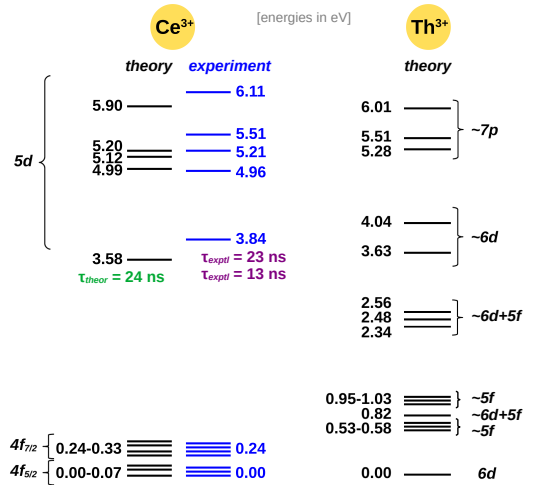


CTEP = Compound-Tunable Effective Potential

Excitation energies and radiative lifetimes of excited states in crystal



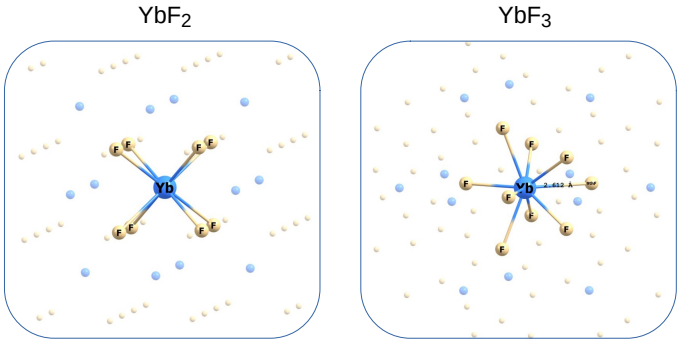
- errors of order 0.2 – 0.3 eV
- ground state of Th^{3+} in crystal – $6d^1$
- minimal cluster model calculations: FS RCCSD
- correction for the cluster model size: TD-DFT☹
- the interplay of the crystal field and spin-orbit interaction



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

Coming soon: relativistic CC to calculate X-ray emission shifts in solids

(**P. A. Khadeeva**, V. M. Shakhova, A. V. Titov)



- X-ray emission shift: direct probe of the state of an Atom-in-Compound (AiC)
- compound-tunable embedding potential
- configurations f^{14} (Yb^{2+}) and f^{13} (Yb^{3+}) $\Rightarrow$ Kramers-unrestricted CCSD(T) works well

Fig. from: V. M. Shakhova et al, *Phys. Chem. Chem. Phys.* 24, 19333 (2022)

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
- written from scratch in C
- molecular integrals are imported from the DIRAC package
  relativistic Hamiltonians: Schrödinger, Dirac-Coulomb(-Gaunt) DC(G), **(generalized) pseudopotentials**
- parallelization: OpenMP
- 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

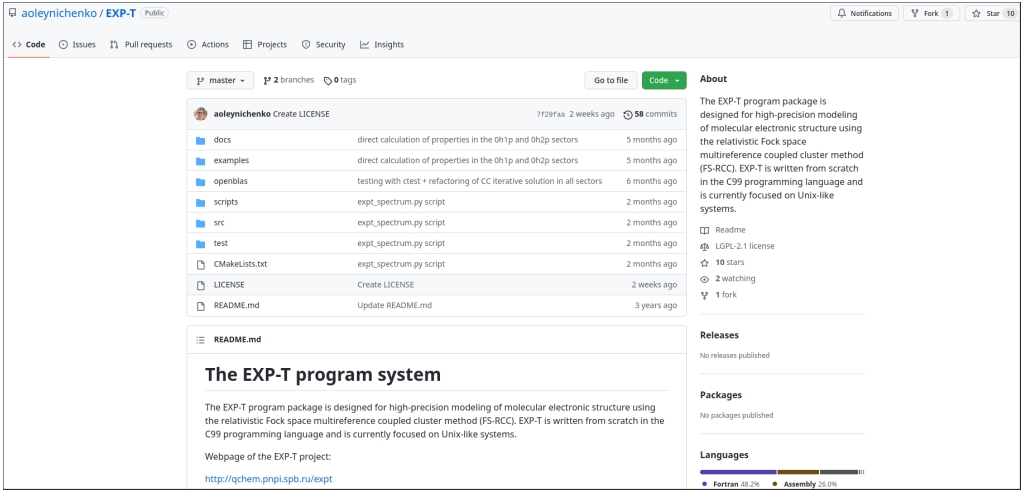
Implemented models and other features:

- Kramers-unrestricted relativistic coupled cluster theory
- open shells: Fock-space multireference coupled cluster
  $\Rightarrow$ up to $3h0p$, $2h1p$, $1h2p$, $0h3p$
- CCSD, CCSD(T), CCSDT-1,2,3, CCSDT models
- analytic density matrices for single-reference relativistic CCSD and CCSD(T)
- approximate [transition] density matrices for FS CCSD
- property calculations
  $\Rightarrow$ transition moments: lifetimes and intensities in spectra
  $\Rightarrow$ hyperfine structure

* unique features

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

Summary

breakthrough in accuracy = basis + CCSDT + GRPP + QED

but...

- max 3 unpaired electrons...
  ⇒ multi-partitioning multireference PT (A. V. Zaitsevskii)
  ⇒ other MRCC Ansatze
- extremely high computational cost
  ⇒ localization techniques, DLPNO?
  ⇒ tensor trains
- relaxed densities and nuclear gradients
- non-adiabatic couplings $\langle \psi_i | \nabla_{\boldsymbol{R}} | \psi_f \rangle$

Some other MRCC formulations

- Jeziorski-Monkhorst SU-MRCC

$$|\psi_n\rangle = \sum_\mu e^{T(\mu)} |\Phi_\mu\rangle \langle\Phi_\mu| \cdot |\tilde{\psi}_n\rangle$$

  $\Rightarrow$ intruder-state problem
  $\Rightarrow$ state-universal method (spectroscopy)
  $\Rightarrow$ multi-vacuum = very costly ☹

- internally-contracted (ic) MRCC

$$|\psi_n\rangle = e^T \cdot |\tilde{\psi}_n\rangle$$

  $\Rightarrow$ state-specific or state-selective
  $\Rightarrow$ extremely complicated equations
  $\Rightarrow$ automated generation of diagrams is needed
  $\Rightarrow$ acceptable cost?
  $\Rightarrow$ an open-source non-relativistic implementation exists (GeCCo)

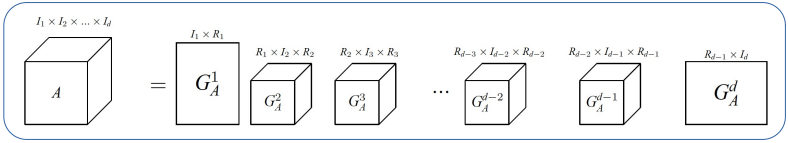
D. I. Lyakh, M. Musial, V. F. Lotrich, *Chem. Rev.* 112(1), 182 (2012)
M. Hanauer, PhD thesis, 2013
https://github.com/ak-ustutt/GeCCo-public

Coming soon: tensor trains in coupled cluster theory (A. S. Rumyantsev)

- all molecular integrals and amplitudes are stored as multidimensional arrays – "tensors"

$$\langle ij||ab\rangle \qquad t_{ij}^{ab} \qquad t_{ijk}^{abc}$$

- tensor train decomposition [I. V. Oseledets, *SIAM J. Sci. Comput.*, 33, 2295 (2011)]:
  = matrix product state



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

- very efficient tensor contractions
- still issues with the decomposition algorithm
- a new library was written in Rust from scratch (contractions, transpositions, sparse arithmetics...)
- first implementation of single-reference CCSD using tensor trains

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

questions?

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