Analytic density matrices in relativistic coupled cluster theory

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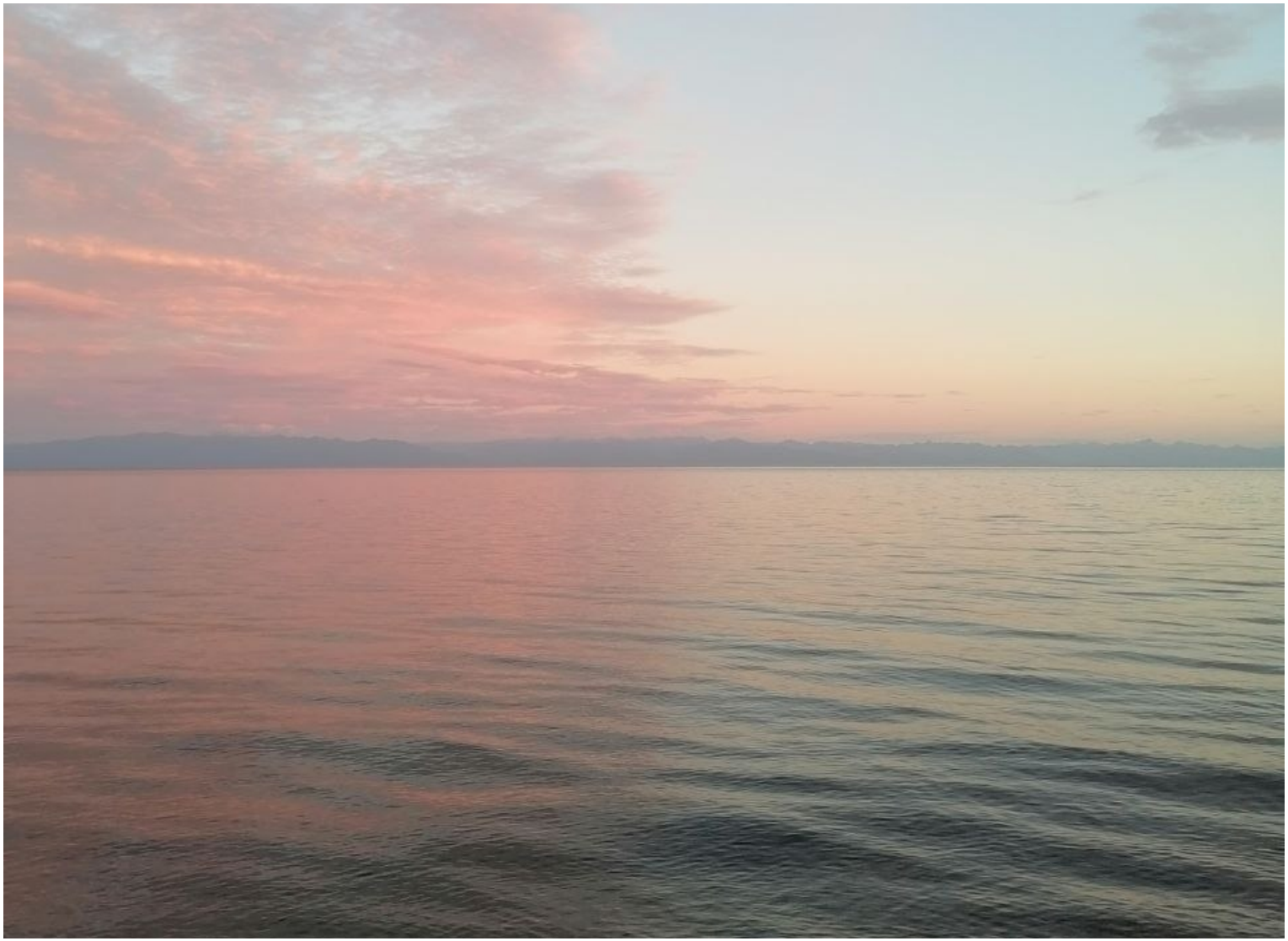

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Calculation of properties

- one-electron property operator:

$$\hat{O} = \sum_{pq} O_{pq} a_p^\dagger a_q$$

- expectation value in the state Ψ:

$$\langle O \rangle = \langle \Psi | \hat{O} | \Psi \rangle$$

- property via numerical differentiation:

$$\hat{H}' = \hat{H} + \lambda \hat{O}$$

$$\langle O \rangle = \frac{dE}{d\lambda}$$

Density matrix

- one-particle density matrix of the N-electron system:

$$\gamma(\boldsymbol{r}, \boldsymbol{r}') = N \int \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N) \Psi^*(\boldsymbol{r}_1', \boldsymbol{r}_2, ..., \boldsymbol{r}_N) \; d\boldsymbol{r}_2 ... d\boldsymbol{r}_N$$

$$\gamma(\boldsymbol{r}, \boldsymbol{r}') = \sum_{pq} D_{pq} \; \psi_p^*(\boldsymbol{r}') \psi_q(\boldsymbol{r})$$

- matrix elements D_{pq}:

$$D_{pq} = \langle \Psi | a_p^\dagger a_q | \Psi \rangle$$

in the basis of molecular spinors $\{\psi_p(\boldsymbol{r})\}_1^N$
square $N \times N$ matrix

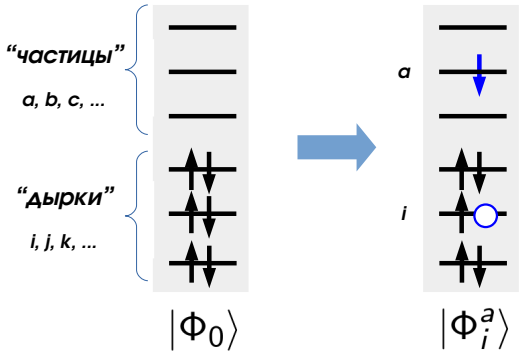
- formula for expectation values:

$$\langle O \rangle = \int O(\boldsymbol{r}) \gamma(\boldsymbol{r}, \boldsymbol{r}) d\boldsymbol{r} = \sum_{pq} D_{pq} O_{pq}$$

Coupled cluster theory

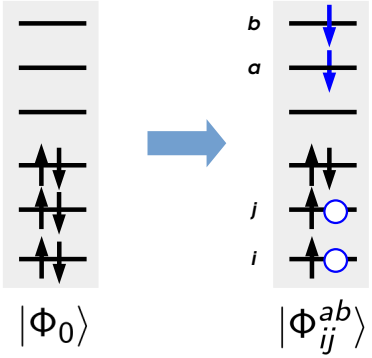
Cluster operator

Single excitations:

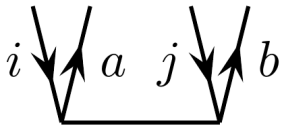


$$T_1 = \sum_{ia} t_i^a \{a_a^\dagger a_i\}$$

Double excitations:



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



Coupled cluster theory

Energy and CC amplitude equations

- Exact wavefunction:

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

- 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 diagrams
$E = E_{HF} + E_{corr}$

- Projection onto $\langle\Phi_0|$ $\Rightarrow$ expression for 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):

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

CC energy functional

Problem:
CC theory isn't variational $\Rightarrow$ Hellmann-Feynman theorem doesn't work

$$\langle O \rangle = \frac{dE}{d\lambda} \quad \neq \quad \langle \Psi | \frac{dH}{d\lambda} | \Psi \rangle$$

how to avoid differentiation of t amplitudes?

Solution: Lagrange method

$$\mathcal{L} = \underbrace{\langle \Phi_0 | (He^T)_c | \Phi_0 \rangle}_{E_{corr}} + \sum_I \lambda_I \underbrace{\langle \Phi_I | (He^T)_c | \Phi_0 \rangle}_{\text{amplitude eqn-s}}$$

λ_I – Lagrange multipliers, $I = ij...ab...$
conditions: amplitude equations

De-excitation operator Λ

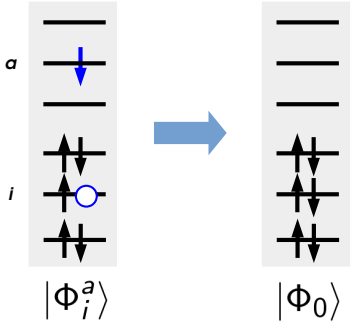
Rewrite in a compact form:

$$\mathcal{L} = \langle \Phi_0 | (He^T)_c | \Phi_0 \rangle + \sum_I \lambda_I \langle \Phi_I | (He^T)_c | \Phi_0 \rangle$$

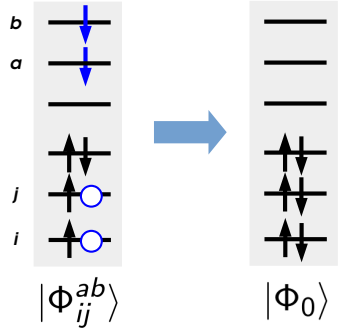
$$\Rightarrow$$

$$\mathcal{L} = \langle \Phi_0 | (1 + \Lambda)(He^T)_c | \Phi_0 \rangle$$

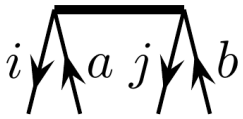
Within the CCSD model $\Lambda = \Lambda_1 + \Lambda_2$:



$$\Lambda_1 = \sum_{ia} \lambda_a^i \{a_i^\dagger a_a\}$$



$$\Lambda_2 = \frac{1}{4} \sum_{ijab} \lambda_{ab}^{ij} \{a_i^\dagger a_a a_j^\dagger a_b\}$$



Λ-equations for CCSD

$$\mathcal{L} = \langle \Phi_0 | (He^T)_c | \Phi_0 \rangle + \sum_I \lambda_I \langle \Phi_I | (He^T)_c | \Phi_0 \rangle$$

- differentiation wrt λ_I $\Rightarrow$ we obtain amplitude equations:

$$\langle \Phi_I | (He^T)_c | \Phi_0 \rangle = 0$$

- differentiation wrt t_I $\Rightarrow$ equations for λ_I (Λ-equations):

$$\langle \Phi_0 | (He^T)_c + \Lambda (He^T)_c - E_{corr} | \Phi_I \rangle = 0$$

- getting rid of E_{corr}:

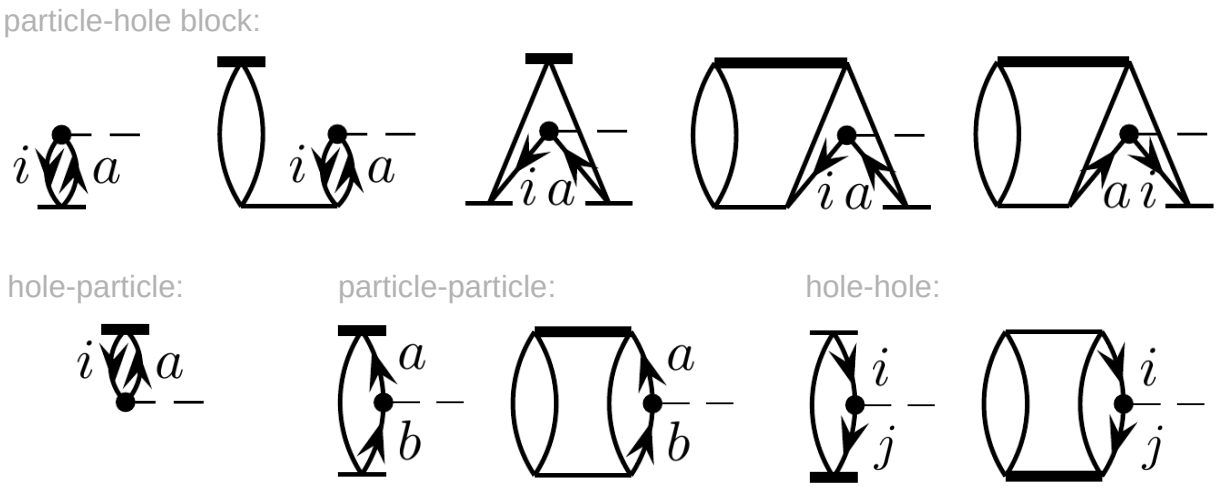
$$\langle \Phi_0 | (He^T)_c | \Phi_I \rangle + \langle \Phi_0 | (\Lambda (He^T)_c)_c | \Phi_I \rangle + \underbrace{\sum_K \langle \Phi_0 | (He^T)_c | \Phi_K \rangle \langle \Phi_K | \Lambda | \Phi_I \rangle}_{\text{disconnected diagrams}} = 0$$

- is linear in Λ, but the Jacobi method is more convenient to use
- number of floating-point operations: $O(N^6)$ for CCSD

Expression for density matrix elements (CCSD)

- Differentiation of $\mathcal{L}$ wrt the perturbation parameter λ
- Orbital relaxation is neglected $\Rightarrow \frac{dT}{d\lambda} = 0,\ \frac{d\Lambda}{d\lambda} = 0$
- DM matrix elements:

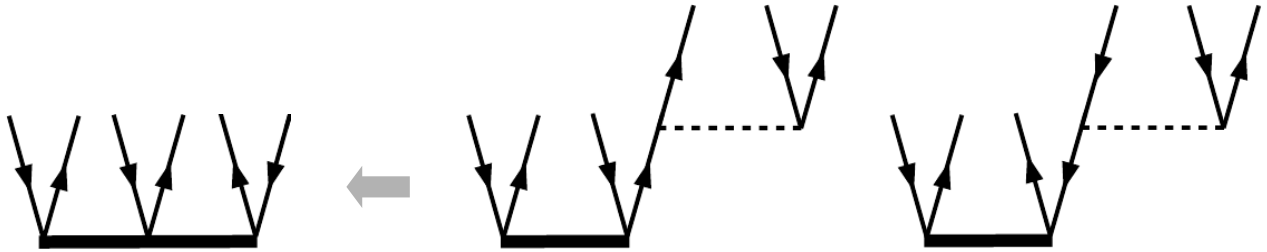
$$D_{pq} = \langle \Phi_0 | (1 + \Lambda)\ (\{a_p^\dagger a_q\} e^T)_c | \Phi_0 \rangle$$



- CC density matrix is non-hermitian!

The CCSD(T) model

Estimate of triple excitation amplitudes



- algebraic expression for the T_3 amplitudes:

$$\varepsilon_{ijk}^{abc} t_{ijk}^{abc} = P(k/ij)P(a/bc)\sum_d t_{ij}^{ad} \langle bc||dk\rangle - P(i/jk)P(c/ab)\sum_m t_{im}^{ab} \langle mc||jk\rangle$$

- energy denominators:

$$\varepsilon_{ijk}^{abc} = \varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c$$

- permutation operators:

$$P(i/jk) = 1 - P_{ij} - P_{ik}$$

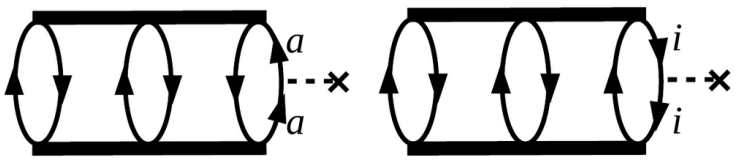
- $O(N^7)$ floating-poing operations, N – number of spinors

The CCSD(T) model

Perturbative energy correction

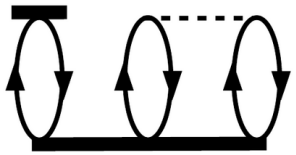
$$E_{CCSD(T)} = E_{CCSD} + \underbrace{E_T + E_{ST} + E_{DT}}_{\Delta E(T)}$$

- 4th order contribution of T_3 (using the energy formula $E = \langle \Phi_0 | (e^{T^\dagger} H e^T)_c | \Phi_0 \rangle$):



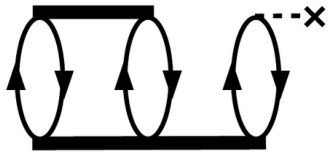
$$E_T = \frac{1}{36} \sum_{ijkabc} (t_{ijk}^{abc})^* t_{ijk}^{abc} \varepsilon_{ijk}^{abc}$$

- T_3 contributions to $T_1 \Rightarrow$ energy correction:



$$E_{ST} = \frac{1}{4} \sum_{ia} (t_i^a)^* \sum_{jkbc} \langle jk || bc \rangle \, t_{ijk}^{abc}$$

- T_3 contributions to $T_2 \Rightarrow$ energy correction:

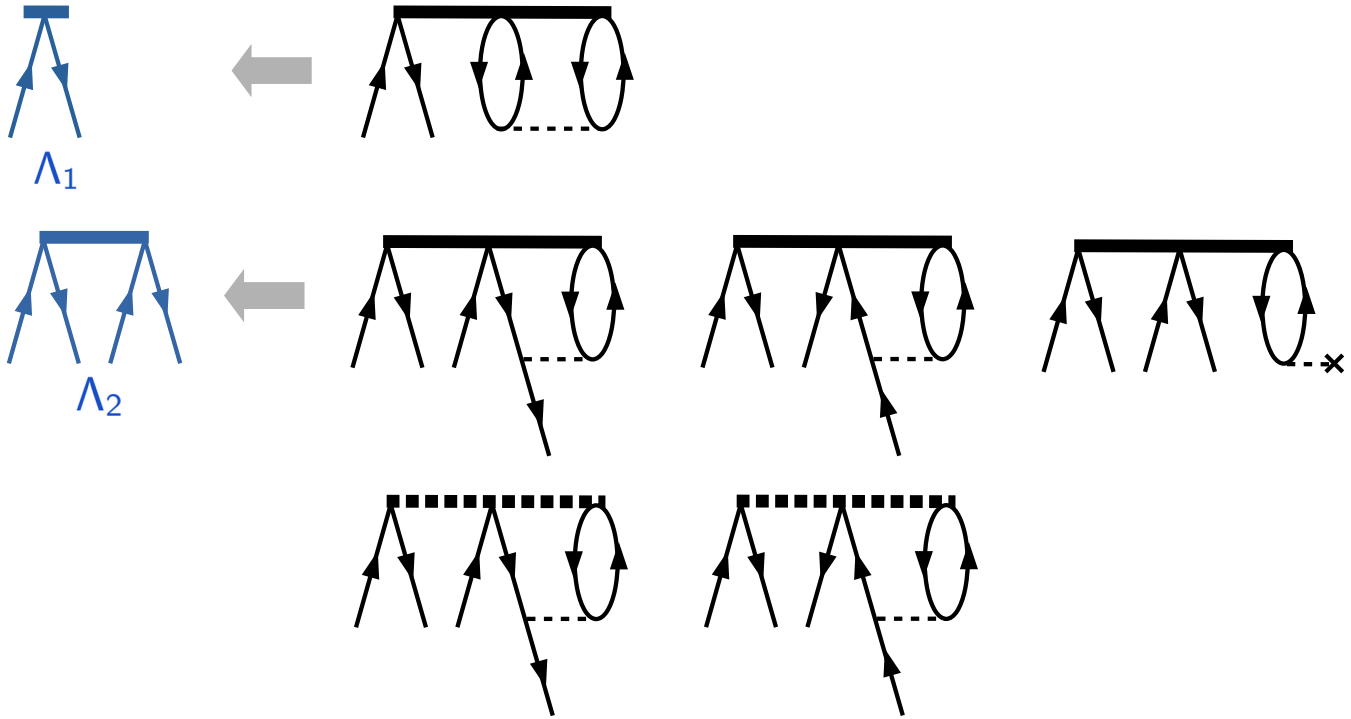


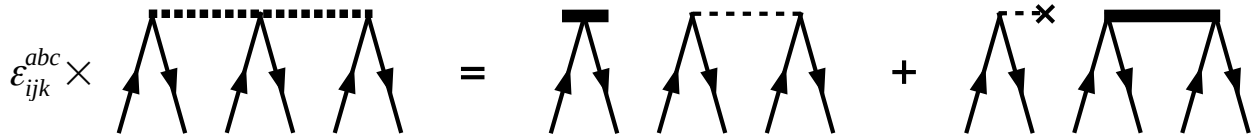
$$E_{DT} = \frac{1}{4} \sum_{ijab} (t_{ij}^{ab})^* \sum_{kc} f_{kc} t_{ijk}^{abc}$$

Λ equations for CCSD(T)

$$\mathcal{L} = E_{CCSD} + \underbrace{E_T + E_{ST} + E_{DT}}_{\Delta E(T)} + \sum_I \lambda_I \langle \Phi_I | (He^T)_c | \Phi_0 \rangle$$

Additional terms in CCSD Λ equations:

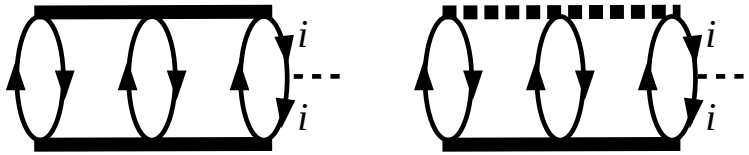




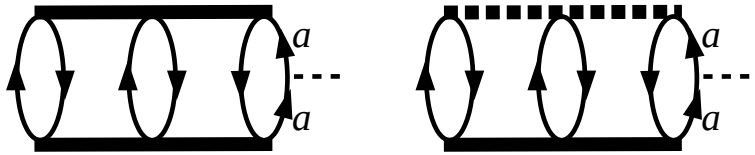
Expression for CCSD(T) density matrix elements

$$\mathcal{L} = E_{CCSD} + \underbrace{E_T + E_{ST} + E_{DT}}_{\Delta E(T)} + \sum_I \lambda_I \langle \Phi_I | (He^T)_c | \Phi_0 \rangle$$

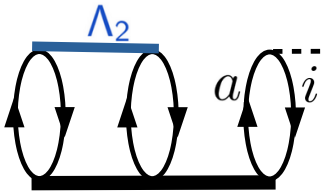
- contribution to diagonal "hole-hole" D_{ii}:



- contribution to diagonal "particle-particle" D_{aa}:



- contribution to off-diagonal "particle-hole" D_{ai}:



EXP-T program package

- open source project: `qchem.pnpi.spb.ru/expt`
- Kramers-unrestricted relativistic coupled cluster theory
- Fock-space MR-CC for open-shell problems
- CCSD, CCSD(T), CCSDT-1,2,3, CCSDT
- symmetry: D_{2h} and subgroups, $D_{\infty h}$, $C_{\infty v}$
- fast implementation of new models

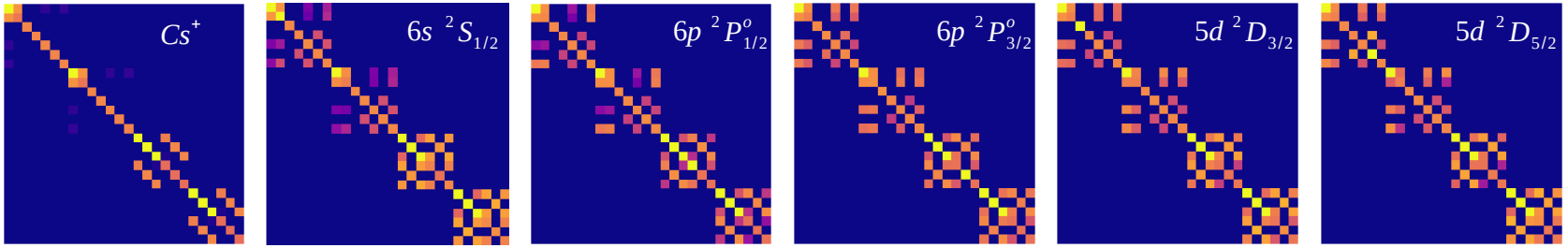
- analytic density matrix for single-reference CCSD and CCSD(T)
- CC natural orbitals

Pilot application 1: contracted basis sets

Atomic natural orbitals (ANO)

- many atomic states are single-reference
  $\Rightarrow$ CCSD, CCSD(T) work well
- averaging of density matrices for several electronic states
- diagonalization of DM $\Rightarrow$ natural orbitals (spinors)
- occupation number of ANO $\sim$ its significance in the basis set
- effective and compact contracted basis sets

Example: Cs atom, averaging over six DMs:



P.-O. Widmark, P.-Å. Malmqvist, B. O. Roos, Theor. Chim. Acta, 77, 291 (1990)

Pilot application 1: contracted basis sets

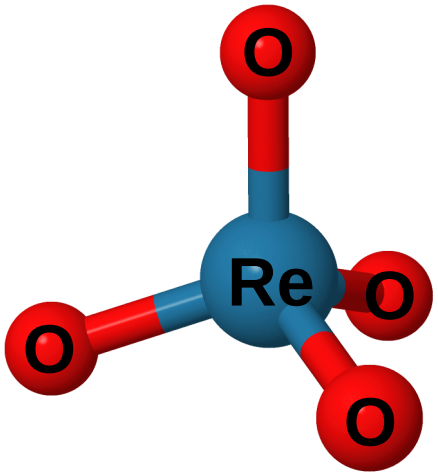
Basis for low-lying states of cesium

[cm^{-1}]	IP	$6p\ P^o_{1/2}$	$6p\ P^o_{3/2}$	$5d\ D^o_{3/2}$	$5d\ D^o_{5/2}$
uncontracted	31466	11237	11787	14572	14670
deviation from uncontracted basis:					
ANO, scal-rel CCSD	-80	-52	-57	-29	-30
ANO, rel CCSD	-62	-41	-44	-13	-14
ANO, rel CCSD(T)	-75	-44	-48	-1	-5
exptl	31406	11178	11732	14499	14597

All calculations are carried out using FS-CCSD
Semilocal pseudopotential, 28e in core, no effective QED potential
$4s$, $4p$, $4d$ shells were frozen
Uncontracted basis: $(14s14p10d6f5g5h3i)$
Contracted basis: $[7s8p7d4f3g2h1i]$

Pilot application 2: shielding constant on Re in ReO_4^-

L. V. Skripnikov, S. D. Prosnyak. **Refined nuclear magnetic dipole moment of rhenium: ^{187}Re and ^{187}Re.** *arXiv:2204.13015 [physics.atom-ph]*



- Shielding tensor can be formally defined as:

$$\sigma_{ij}^{\mathrm{Re}} = \frac{\partial^2 E}{\partial B_i \, \partial \mu_{\mathrm{Re},j}}$$

- Perturbation 1: interaction with an external magnetic field

$$H_B = \frac{1}{2} \boldsymbol{B} \cdot [(\boldsymbol{r} - \boldsymbol{R}_O) \times \boldsymbol{\alpha}]$$

($\boldsymbol{R}_O$ – origin of coordinates)

- Perturbation 2: magnetic dipole hyperfine interaction

$$H_{\mathrm{hf}} = \boldsymbol{\mu}_{\mathrm{Re}} \cdot \frac{[(\boldsymbol{r} - \boldsymbol{R}_{\mathrm{Re}}) \times \boldsymbol{\alpha}]}{|\boldsymbol{r} - \boldsymbol{R}_{\mathrm{Re}}|^3}$$

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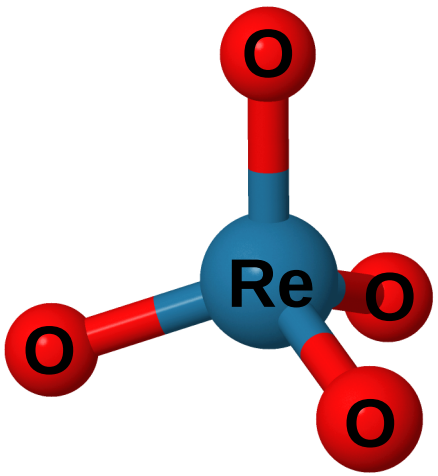

- Operators H_B, $H_{\rm hf}$ are T-odd
  $\Rightarrow$ analytic DMs in DIRAC cannot be used
- "paramagnetic" contribution to σ
  $\Rightarrow$ contribution from positive-energy spectrum
- CCSD model, 710 spinors
- numerical 2nd derivative (finite-diff method):

$$\sigma = 3678 \text{ ppm}$$

- analytic $\langle\Psi|H_B|\Psi\rangle$ + numerical 1st derivative

$$\sigma = 3675 \text{ ppm}$$

- finite-difference method: max 2nd derivatives
- analytic DM + numerical differentiation:
  3rd derivatives of energy $\Rightarrow$ hyperpolarizabilities, ...

Further plans

- code optimization
  ⇒ especially for CCSD(T)
- analytic density matrices for CCSDT
- analytic DMs for FS-RCC in non-trivial sectors
- basis sets for generalized relativistic pseudopotentials (GRPP)
  ⇒ GRPP will become the "golden standard" of high-precision modeling
- calculation of different properties defined as 2nd and 3rd derivatives of energy
  ⇒ shielding tensor, hyperpolarizability, P,T-odd properties, ...

- geometry gradients ⇒ optimization of defects in crystals
- GRPP analytic gradients