High-sector FSCC for atomic systems: towards implementation

Martijn Reitsma

Yuly Andrea Chamorro Mena
Anastasia Borschevsky, Ephraim Eliav

rijksuniversiteit
groningen

Van Swinderen Institute for Particle Physics and Gravity
University of Groningen, The Netherlands

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Overview

1. Coupled cluster diagrams
   - Graphical method to generate amplitudes
   - Singles, doubles, triples amplitudes
   - Antisymmetrization in atomic symmetry
   - Angular reduction
2. Existing codes
   - TRAFS-3C: Atomic, Dirac-Coulomb(-Breit), FS-CCSD, up to 0h2p, 2h0p
   - EXP-T: Molecular, integrals from DIRAC, FS-CCSDT up to 0h3p, 3h0p
   - AMC: Automatic angular reduction
3. Implementation
   - Schematic of programs
   - Considerations: interfaces, antisymmetrization, radial & angular separation
4. Applications of current implementations
   - Comparing current atomic and molecular implementations
   - (bonus) Energies, hyperfine structure, isotope shift $\rightarrow$ nuclear properties

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Antisymmetric CCSD equations

- Molecular implementations: based on antisymmetric (Hamiltonian and amplitude) matrix elements
- Atomic: never fully antisymmetric due to radial and angular separation
- Possible solution: recoupling angular parts of two-body tensor

Antisymmetric CCSD equations

Regular atomic two-body Coulomb matrix element:

$$g_{abcd} = \sum_{L_1} \; a \; b \; - L_1 + \; c \; d \; X^{L_1}_{abcd}$$

Antisymmetric CCSD equations

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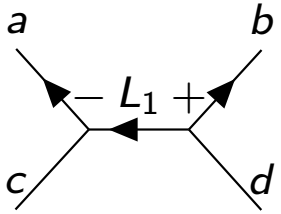
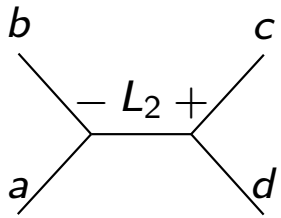
$$g_{abcd} = \sum_{L_1} \quad X^{L_1}_{abcd}$$



Recoupled angular momentum

$$g_{abcd} = \sum_{L_2} \quad \hat{L}_2^2 \sum_{L_1} (-1)^{L_1+L_2+j_a+j_d} \begin{Bmatrix} j_b & L_1 & j_d \\ j_c & L_2 & j_a \end{Bmatrix} X^{L_1}_{abcd}$$



Antisymmetric CCSD equations

Recoupled angular momentum

$$g_{abcd} = \sum_{L_2} \; b \; c \; - L_2 + \; a \; d \; \hat{L}_2^2 \sum_{L_1} (-1)^{L_1+L_2+j_a+j_d} \begin{Bmatrix} j_b & L_1 & j_d \\ j_c & L_2 & j_a \end{Bmatrix} X^{L_1}_{abcd}$$

Antisymmetric CCSD equations

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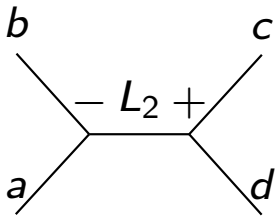
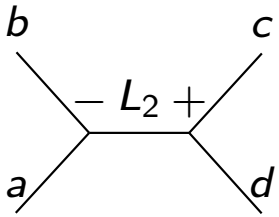


$$\hat{L}_2^2 \sum_{L_1} (-1)^{L_1+L_2+j_a+j_d} \begin{Bmatrix} j_b & L_1 & j_d \\ j_c & L_2 & j_a \end{Bmatrix} X^{L_1}_{abcd}$$

Redefining "radial" X to X' gives us

$$g_{abcd} = \sum_{L_2}$$



$$X'^{L_2}_{abcd}$$

Antisymmetric CCSD equations

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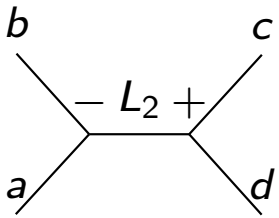

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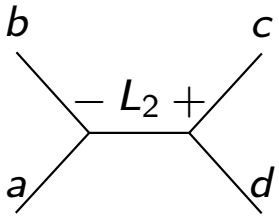

$$X'^{L_2}_{abcd}$$

where

$$X'^{L_2}_{abcd} = \hat{L}_2^2 \sum_{L_1} (-1)^{L_1+L_2+j_a+j_d} \begin{Bmatrix} j_b & L_1 & j_d \\ j_c & L_2 & j_a \end{Bmatrix} X^{L_1}_{abcd}$$

Antisymmetric CCSD equations

So we have

$$g_{abcd} = \sum_{L_2} \; b \; c \; - L_2 + \; a \; d \; X'^{L_2}_{abcd}$$

instead of

$$g_{abcd} = \sum_{L_1} \; a \; b \; - L_1 + \; c \; d \; X^{L_1}_{abcd}$$

Antisymmetric CCSD equations

So we have

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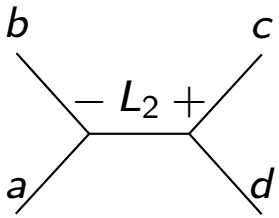
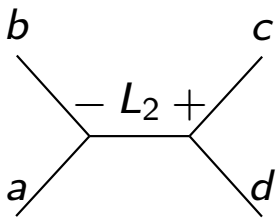


$$X'^{L_2}_{abcd}$$

now we can write the fully antisymmetrized element as

$$\overline{g}_{abcd} = \sum_{L_2}$$



$$\{X'^{L_2}_{abcd} - X'^{L_2}_{bacd}(-1)^{j_a+j_b+L_2} + X'^{L_2}_{badc}(-1)^{j_a+j_b+L_2}(-1)^{j_c+j_d+L_2} - X'^{L_2}_{abdc}(-1)^{ja_c+j_d+L_2}\}$$

Antisymmetric CCSD equations

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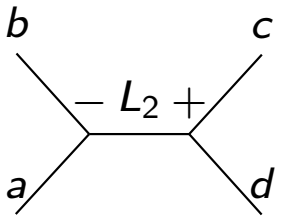
$$g_{abcd} = \sum_{L_2}$$ 

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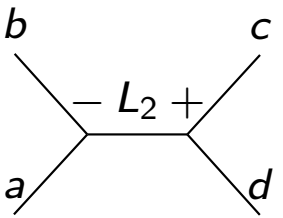
$$\overline{g}_{abcd} = \sum_{L_2}$$ 

$$\overline{X'}^{L_2}_{abcd}$$

Antisymmetric CCSD equations

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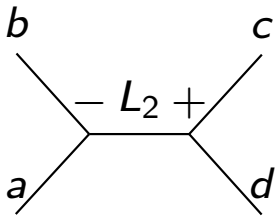

$$X'^{L_2}_{abcd}$$

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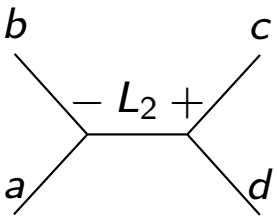


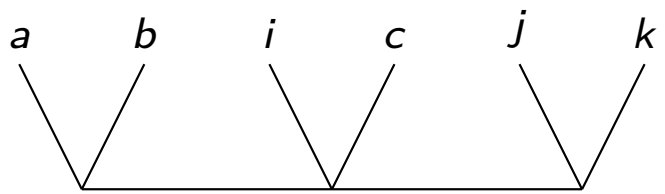
$$\overline{X'}^{L_2}_{abcd}$$

Note that the t_2 amplitudes are equal to this expression on first iteration.

Anti-symmetrized three-body tensor T3

Now we can derive the $\bar{t}_3$ tensor from $\bar{t}_2$, as an antisymmetric Goldstone diagram:

$$\overline{t_3}^{ijk}_{abc} = \sum_h \overline{t_2}^{ih}_{ab} \overline{t_2}^{jk}_{hc}:$$



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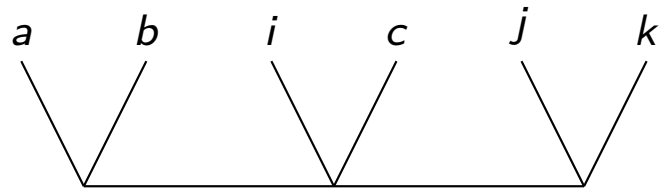
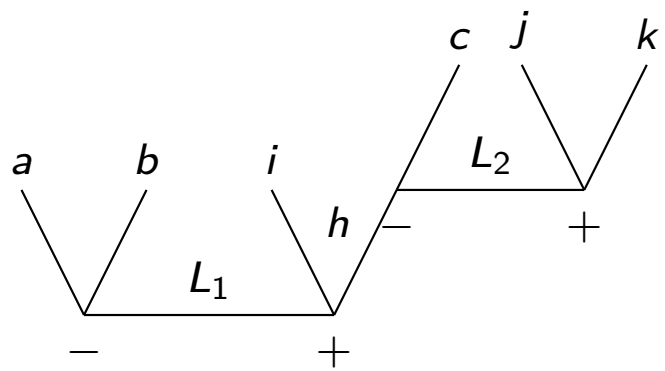


With the corresponding angular coupling diagram:



Next: Antisymmetrized amplitude equations

- We now have antisymmetric expressions for the Coulomb (g_{abcd}) and excitation amplitude tensors $t_{1,2,3}$
- Now we can write all terms in the coupled cluster iteration
- Next slides: sector 0h0p amplitude equations

Graphical derivation: Goldstone diagrams

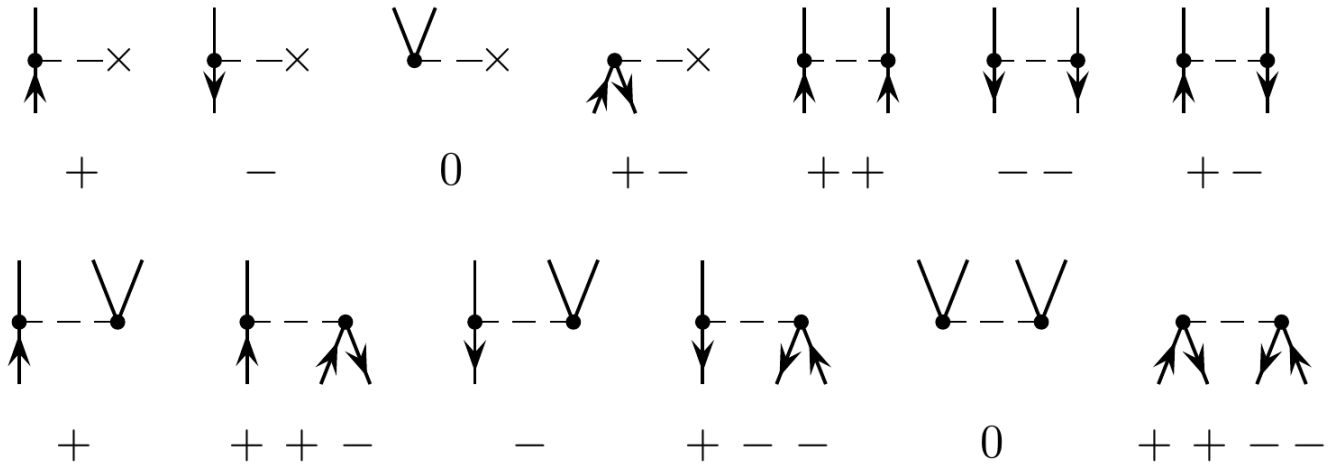


Figure: Hamiltonian one- and two-body operators

Figures: I. Shavitt, R. J. Bartlett, Many-Body Methods in Chemistry and Physics, 2009

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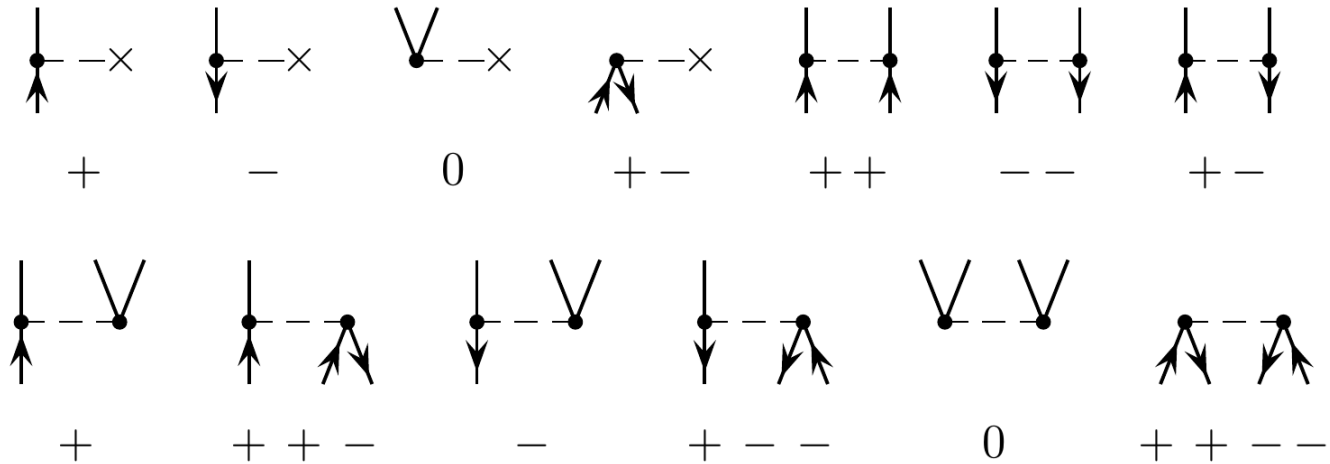


Figure: Hamiltonian one- and two-body operators

Figure: One-, two- and three-body excitation operators

Figures: I. Shavitt, R. J. Bartlett, Many-Body Methods in Chemistry and Physics, 2009

Diagrams contributing to singles equations

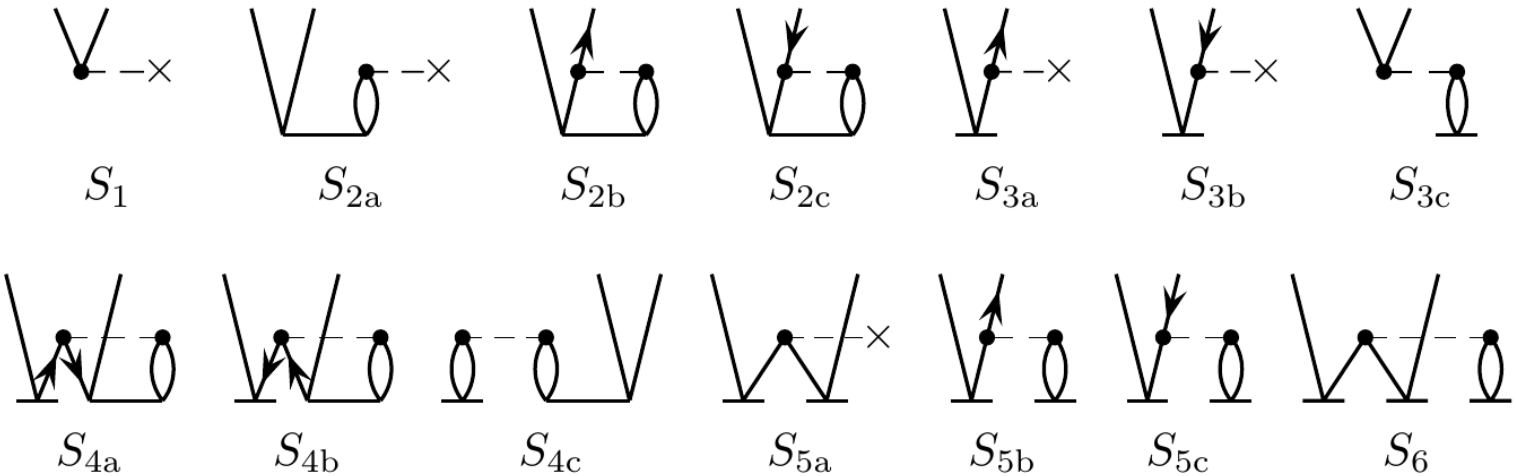


Figure: CCSD contributions to the T1 equation.

Diagrams contributing to singles equations

$$
\begin{aligned}
& f_{ai} + \sum_{kc} f_{kc} t_{ik}^{ac} + \tfrac{1}{2} \sum_{kcd} \langle ak \| cd \rangle t_{ik}^{cd} - \tfrac{1}{2} \sum_{klc} \langle kl \| ic \rangle t_{kl}^{ac} + \sum_{c} f_{ac} t_{i}^{c} \\
& - \sum_{k} f_{ki} t_{k}^{a} + \sum_{kc} \langle ak \| ic \rangle t_{k}^{c} - \tfrac{1}{2} \sum_{klcd} \langle kl \| cd \rangle t_{i}^{c} t_{kl}^{ad} - \tfrac{1}{2} \sum_{klcd} \langle kl \| cd \rangle t_{k}^{a} t_{il}^{cd} \\
& + \sum_{klcd} \langle kl \| cd \rangle t_{k}^{c} t_{li}^{da} - \sum_{kc} f_{kc} t_{i}^{c} t_{k}^{a} + \sum_{kcd} \langle ak \| cd \rangle t_{i}^{c} t_{k}^{d} \\
& - \sum_{klc} \langle kl \| ic \rangle t_{k}^{a} t_{l}^{c} - \sum_{klcd} \langle kl \| cd \rangle t_{i}^{c} t_{k}^{a} t_{l}^{d} = 0 \qquad \text{(for all } i, a\text{)}.
\end{aligned}
$$

Figure: CCSD contributions to the T1 equation.

Diagrams contributing to doubles equations

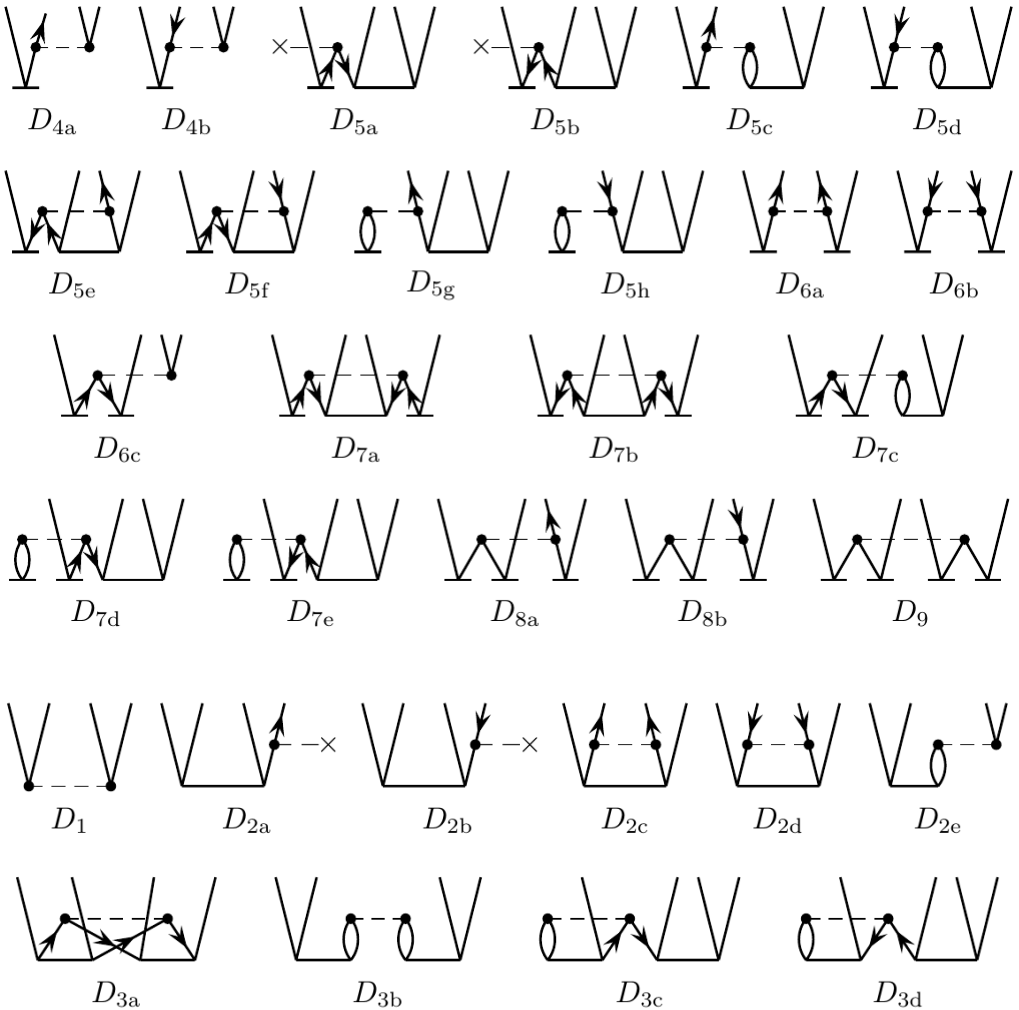


Figure: CCSD contributions to the T2 equation.

Triples contributions to T1 and T2 equations

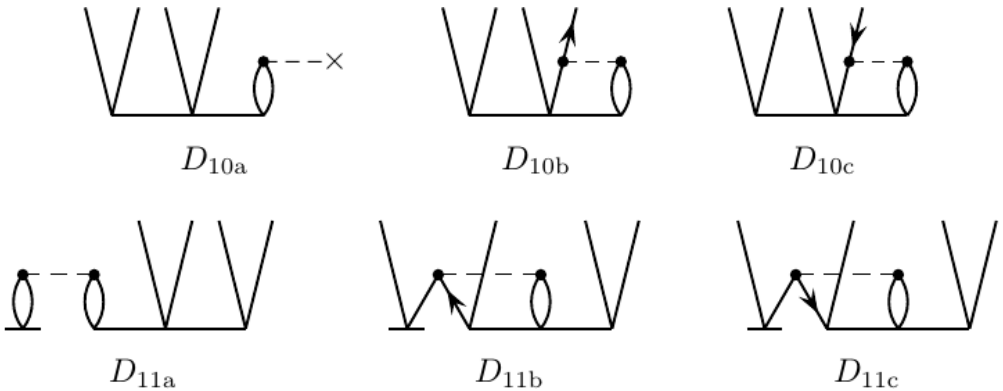


Figure: Triples contributions to the T2 equation.

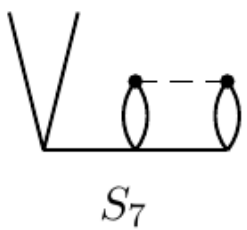


Figure: Triples contributions to the T1 equation.

Diagrams contributing to triples equations

TRAFS-3C: Atomic FSCC code

- Ephraim Eliav
- Relativistic FSCC code by E. Eliav, U. Kaldor, and Y. Ishikawa
- Hartree-Fock: Dirac-Coulomb or Dirac-Coulomb-Breit Hamiltonians
- FSCC code up to CCSD level and 2h0p, 1h0p, 1h1p, 0h1p, 0h2p sectors
  - Atomic symmetry: efficient and fast
  - But: Includes up to singles and doubles, 2 valence h/p; sequential code
- Goals: include CCSDT; 3 valence particle/hole sectors; parallelization

E. Eliav, U. Kaldor, and Y. Ishikawa, Tel-Aviv Relativistic Atomic Fock Space coupled cluster code (TRAFS-3C), available on request.

EXP-T: Molecular FSCC code

- Alexander Oleynichenko
- FSCC algorithm written in C99
- single-point energy calculations with any point groups and (nearly) all Hamiltonians, implemented in DIRAC (4c-DC, X2Cmmf, 2c-ECP, non-relativistic)
- ground state energy calculations: CCSD, CCSD(T), CCSDT-n (n=1,2,3), CCSDT models
- FSCC (CCSD, CCSDT-1,2,3, CCSDT) for excited states is implemented for the 0h1p, 1h0p, 1h1p, 0h2p, 2h0p, 0h3p sectors

A. V. Oleynichenko, A. Zaitsevskii, E. Eliav, Towards High Performance Relativistic Electronic Structure Modelling: The EXP-T Program Package. Commun. Comput. Inf. Sci., 1331, 375-386 (2020) doi: 10.1007/978-3-030-64616-5_33, https://github.com/aoleynichenko/EXP-T

DIRAC, a relativistic ab initio electronic structure program, doi: 10.5281/zenodo.7670749, https://diracprogram.org/

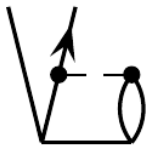
AMC: Symmetry reduction of tensor networks in many-body theory

- Alexander Tichai, Thomas Duguet
- Symmetry reduction of tensor networks, originating from nuclear CC theory
- Based on python: **pip install amc** - easy to use!
- Some changes needed to match our theory and conventions

A. Tichai, R. Wirth, J. Ripoche, T. Duguet, Symmetry reduction of tensor networks in many-body theory, Eur. Phys. J. A (2020) 56:272, https://github.com/radnut/amc

Angular momentum diagrams

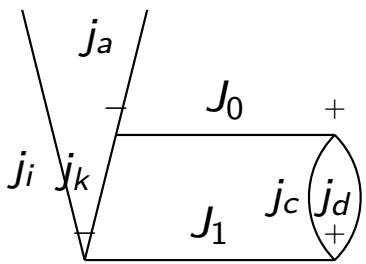
Performing angular reduction, derived by hand compared to AMC. Diagram S2b:



S_{2b}

$$\frac{1}{2}\sum_{kcd}\langle ak||cd\rangle\, t_{ik}^{cd} \qquad (1)$$

Containing the radial integral and the following angular coupling factor:



$$\rightarrow \sum_{J_0} \delta(j_a, j_i)\hat{j}_a^{-2}\hat{J}_0^{-2}$$

Angular momentum diagrams

AMC code for diagram S2b:

```
declare S {
    mode=2,
    latex="S",
    scalar=true,
}

declare T2 {
    mode=4,
    latex="T2",
}

declare X2 {
    mode=4,
    latex="X",
    scalar=true,
}

S_ia = sum_kcd(X2_akcd * T2_cdik);
```

Angular momentum diagrams

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```

$$S^0_{ia} = \delta_{j_i,j_a} \hat{j_a^{-2}} \sum_{cdkJ_0} \hat{J_0^2} X^{J_0 J_0 0}_{akcd} T2^{J_0 J_0 0}_{cdik}$$

Angular momentum diagrams

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$$S^0_{ia} = \delta_{j_i,j_a} \hat{j_a^{-2}} \sum_{cdkJ_0} \hat{J}_0^2 X^{J_0 J_0 0}_{akcd} T2^{J_0 J_0 0}_{cdik}$$

Not a perfect match (yet):

$$\sum_{J_0} \delta(j_a, j_i) \hat{j}_a^{-2} \hat{J}_0^{-2}$$

Towards implementing atomic FSCC

- Use TRAFS-3C DC/DCB integrals as input for atomic EXP-T
- Interface for TAU integrals to (matrix) format used in EXP-T
  - Antisymmetrize
  - Integral sorting, symmetry blocks
- Exploit efficient matrix multiplication of exp-t for amplitude equations
  - Efficient mult algorithms
- Angular factors for each diagram
  - Interface AMC
    - Calculate reduced factors during compilation or runtime?
    - Store angular factors for each set of indices or calculate on the fly?

Considerations

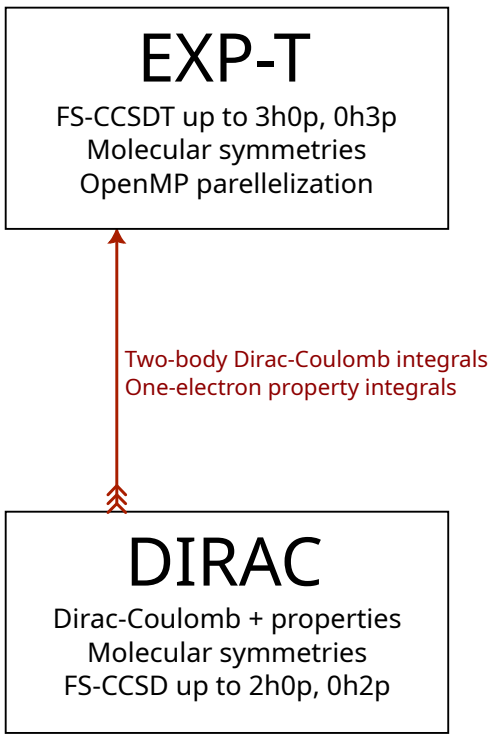
- Writing an interface TRAFS-3C to EXP-T
- Antisymmetrize the two-body matrix elements
- Where and how to implement radial, angular factorization

Connecting the programs

EXP-T

FS-CCSDT up to 3h0p, 0h3p
Molecular symmetries
OpenMP parellelization

Connecting the programs



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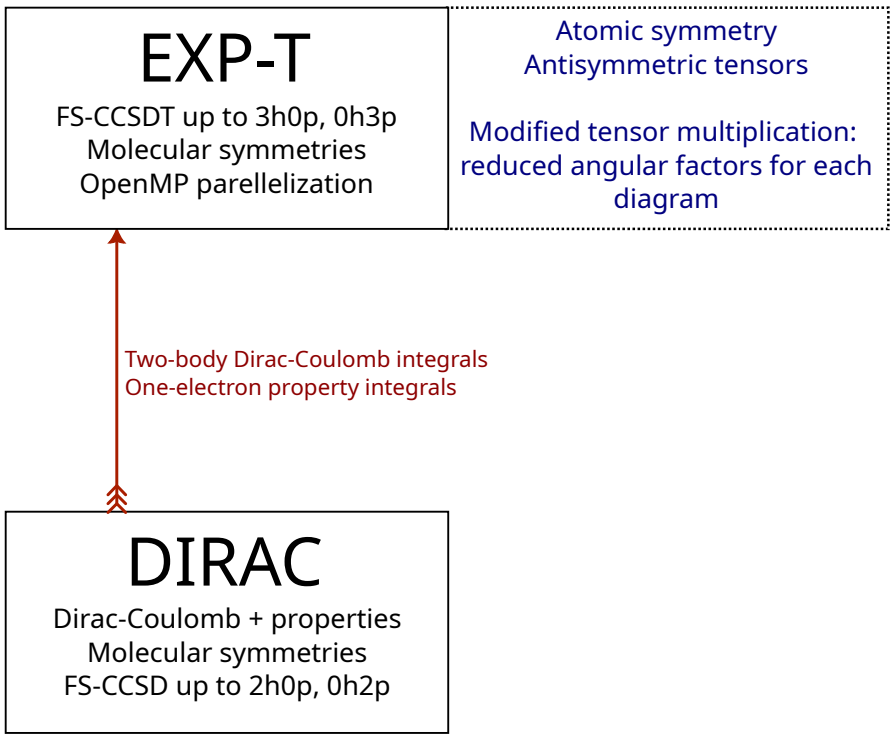

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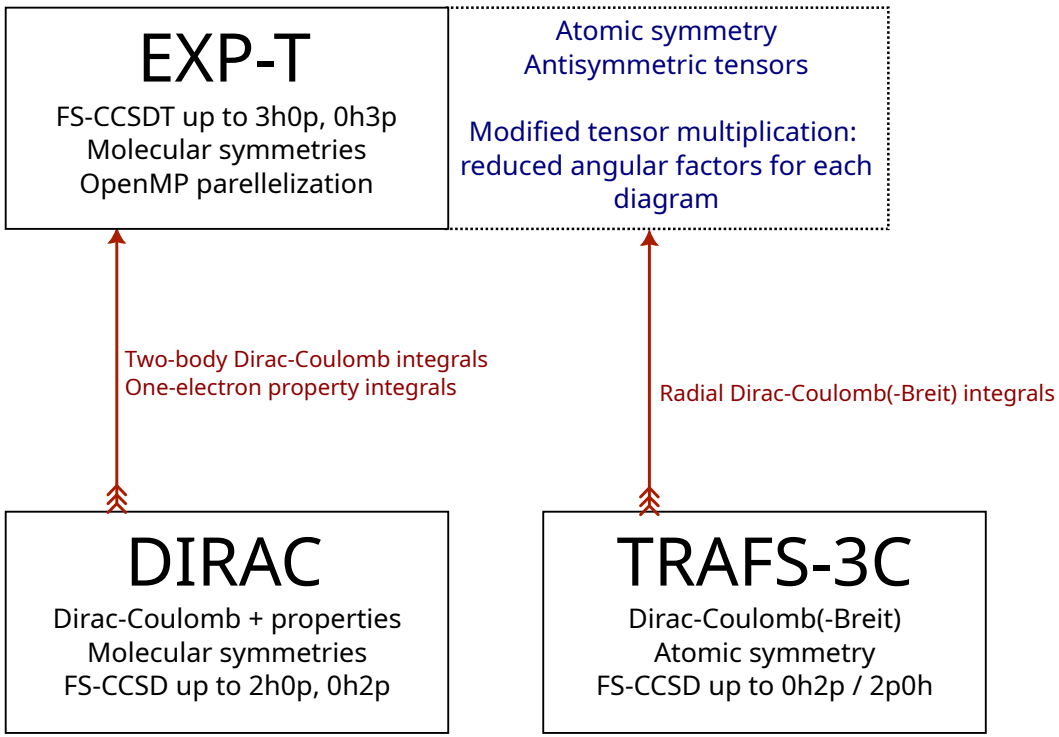
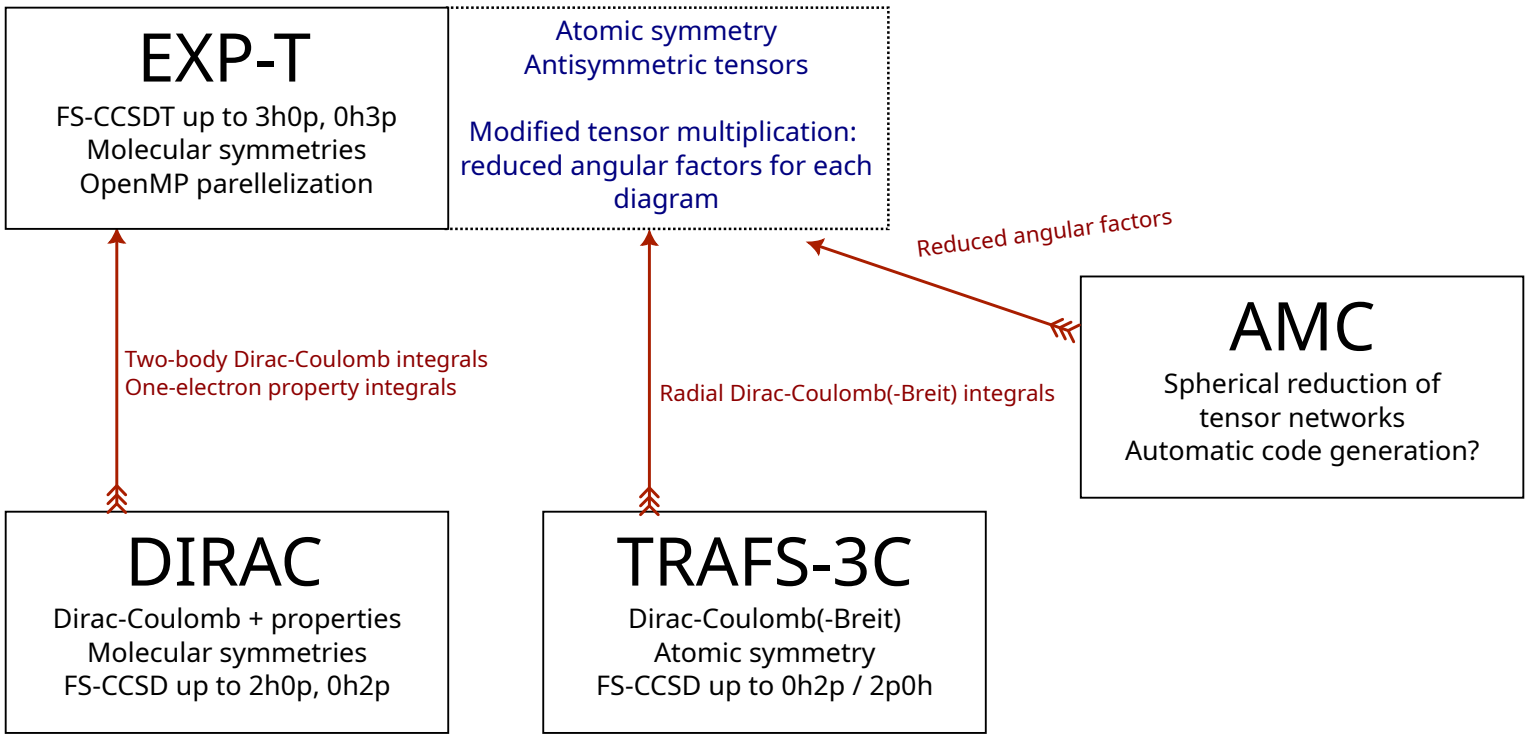


Connecting the programs



Applications / tests

So far:

- Two-body Dirac-Coulomb(-Breit) tensor, single-, double- and triple-excitation operators
- Separation of radial and angular integration
- Antisymmetrization

Finally, applying current implementations:

- Excited state energies
- Atomic (TRAFS-3C) compared to molecular (EXP-T) code performance

Atomic versus molecular calculations: some small tests

- Lutetium calculation of ($6s^2$) 5d, 6p and 7s excited states in sector 0h1p.

	TRAFS-3C	EXP-T
$6s^2 5d_{3/2}$	0	0
$6s^2 5d_{5/2}$	1940	1949
$6s^2 6p_{1/2}$	3609	3598
$6s^2 6p_{3/2}$	6916	6910
$6s^2 7s_{1/2}$	24990	24985
Time/iteration	3.6s	21.0s

Table: Atomic v.s. molecular calculation with dyall.cv3z basis, frozen core $\leq$ 3s 3p 3d and virtual cutoff +30 a.u., 1 cpu core.

Atomic versus molecular calculations: some small tests

- Cf^{16+} FS-CCSD and FS-CCSDT calculations with molecular EXP-T code.

Config.	J	FS-CCSD	FS-CCSDT	Difference
$6p^2$	0	0	0	0
$5f6p$	3	2101	1707	-393
$5f6p$	2	8973	8515	-458
$5f^2$	4	19506	18644	-863
$5f6p$	4	28914	28369	-545
$5f^2$	2	33070	32125	-944
$5f6p$	3	26749	26330	-419
$5f^2$	5	39784	38859	-925
$5f^2$	3	46585	45649	-936
Sector		time/it.	time/it	
0h1p		2.7s	2950.2s	
0h2p		0.8s	1804.6s	

Table: FS-CCSD v.s. FS-CCSDT with dyall.ae3z basis, frozen core $\leq$ 4s4p4d4f frozen and -5 a.u. virtual cutoff (102 spinors).

Conclusions

Summary:

- TRAFS-3C provides DC or DCB integrals to be antisymmetrized and sorted for use in FSCC
- The AMC code can provide angular factors for atomic CC diagrams
- Higher sectors will enable the calculation of more than 2 valence electrons or holes, while including higher order excitations improves accuracy of lower sectors.

Outlook:

- Determine the best way to implement the radial and angular separation in EXP-T,
- The discrepancy between angular factors provided by AMC and our conventions needs to be resolved,
- Implementation and testing of atomic FSCC code for existing and higher sectors.

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Atomic high-sector FSCC
Martijn Reitsma
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AMC
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Thomas Duguet

EXP-T
Alexander Oleynichenko

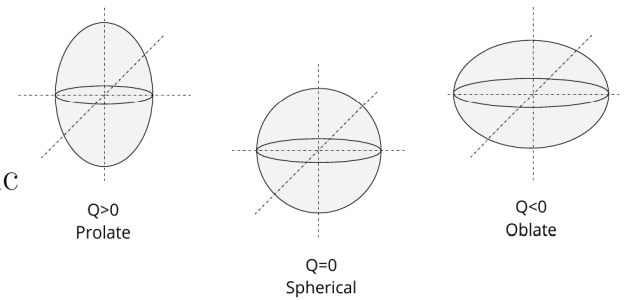
Thank you for your attention!

Applications: HFS, isotope shift and nuclear properties

Hyperfine structure to extract nuclear moments from experiment and theory:

$$A = A_0 \cdot \mu \; / \; I$$
$$Q = - \; B \; / \; q$$

- μ, Q: nuclear dipole and quadrupole moments;
- A, B: measured hyperfine structure parameters;
- A_0, q: calculated magnetic hyperfine field and electric field gradient.



Isotope shift factors to extract changes in nuclear charge radii:

$$\delta\langle r^2\rangle^{A,A'} = \frac{1}{F} \left(\delta\nu^{A,A'} - \mu^{A,A'} \, k_{MS} \right)$$

- F, k_{MS}: field and mass shift factors;
- $\delta\nu^{A,A'}$: measured isotope shift between isotopes A and A';
- $\delta\langle r^2\rangle^{A,A'}$: change in nuclear charge radius between isotopes A and A'.

Applications: germanium and tin

A	N	I^π	$\mu^{lit}(\mu_N)$	$\mu^{expt}(\mu_N)$	Q^{lit}	$Q^{expt}(b)$
69	37	$5/2^-$	+0.735(7)	**+0.920(5)**	+0.027(5)	**+0.114(7)**
71	39	$1/2^-$	+0.54606(7)	+0.547(5)		
73	41	$9/2^+$	-0.87824(5)	-0.904(21)	-0.196(1)	-0.198(4)

Table: Germanium nuclear moments

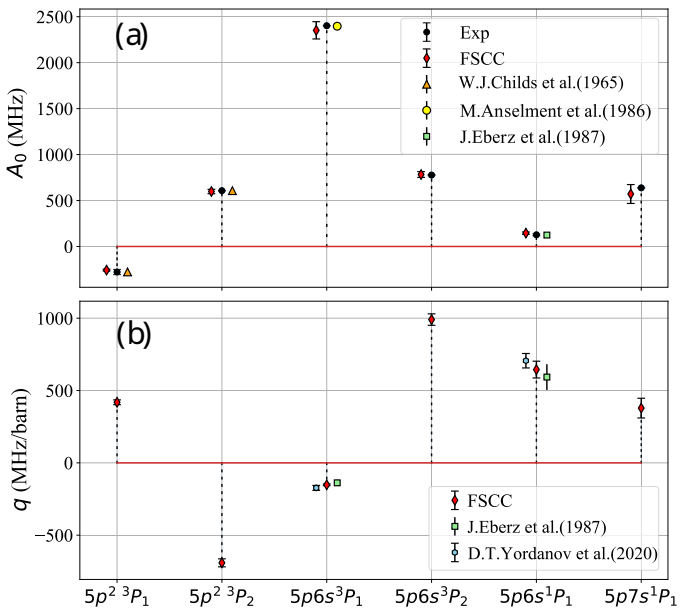


Figure: Sn HFS parameters

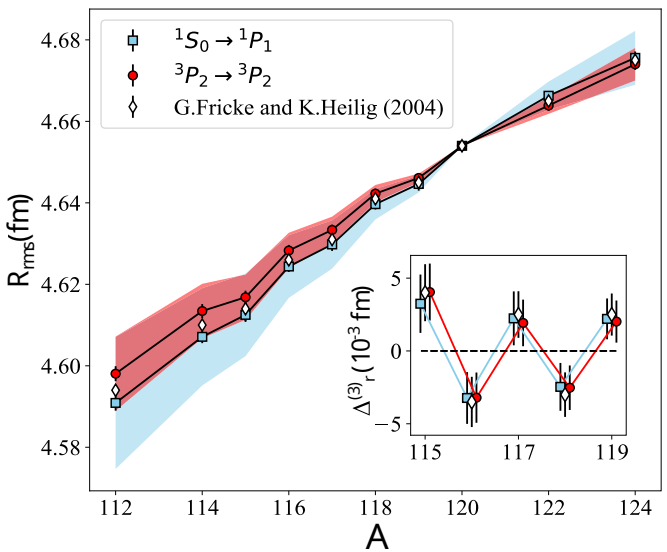


Figure: Sn nuclear charge radii

A. Kanellakopoulos, .., M. L. Reitsma et al., Nuclear moments of germanium isotopes near N=40, Phys. Rev. C 102, 054331 (2020)

F. P. Gustafsson, .., M. L. Reitsma et al., Tin resonance-ionization schemes for atomic- and nuclear-structure studies, Phys. Rev. A 102, 052812, 2020