Spin Adaption in Coupled Cluster, ESNT

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Contents

Spin Independent Hamiltonian, CSFs

- fundamental property in QM

$$[\hat{H}, \hat{O}] = 0$$

$\Rightarrow$

  - implies common eigensystems
  - blocking of representations
  - governs term symbols, e.g., ${}^3\Sigma_g^-$

- in the spin independent picture it is

$$[\hat{H}, \hat{S}_z] = 0 \qquad \rightarrow \text{easy}$$
$$[\hat{H}, \hat{S}^2] = 0 \qquad \rightarrow \text{not so easy}$$

- eigenequations for spin

$$\hat{S}_z|\Psi\rangle = S_z|\Psi\rangle$$
$$\hat{S}^2|\Psi\rangle = S(S+1)|\Psi\rangle$$

[a] in the following we use $S_z = M$

Symmetric Group Approach (SGA)[a] (1)

Ansatz

- idea:

$$\Phi_n^{\mathrm{SGA}} = |\lambda, S, M, k\rangle, = \hat{A} \prod_{j=1}^{N} \phi_{n(j)}^{\mathrm{MO}}(\vec{r}_j) \cdot \Theta_k^{S,M}(\omega_1, \ldots, \omega_n) \tag{1}$$

  with spin eigenfunctions $\Theta_k^{S,M}$, k degeneracy index

- degree of degeneracy with ν open shells

$$f_{S,\nu}^{\mathrm{SGA}} = \binom{\nu}{\frac{1}{2}\nu - S} - \binom{\nu}{\frac{1}{2}\nu - S - 1}. \tag{2}$$

- expansion of spin eigenfunctions into primitive strings of α and β [**?**]:

$$\Theta_k^{S,M} = \sum_i \gamma_i \prod_j \Omega_{ij}(\omega_j). \tag{3}$$

[a] R. Pauncz, "Spin Eingenfunctions, Construction an Use", Plenum Press, New York, 1979

- matrix elements between two CSFs[a]:

$$\langle \Phi_n^{\mathrm{SGA}} | \hat{H} | \Phi_m^{\mathrm{SGA}} \rangle =$$

$$\frac{1}{N!} \sum_{\hat{P} \in \mathrm{S}_n} (-1)^P \underbrace{\left\langle \prod_{j=1}^{n} \phi_{n(j)}^{\mathrm{MO}}(\vec{r}_j) \middle| \hat{H}\hat{P} \middle| \prod_{j=1}^{N} \phi_{m(j)}^{\mathrm{MO}}(\vec{r}_j) \right\rangle}_{\text{spatial part}} \cdot \underbrace{\langle \Theta_l^{S,M}(\omega_1, \ldots, \omega_N) \ | \hat{P} | \langle \Theta_k^{S,M}(\omega_1, \ldots, \omega_N) \rangle}_{\text{spin part } (\underline{\underline{U}})_{kl}} \tag{4}$$

- $\underline{\underline{U}}$: representation of $\hat{P}$ in basis of spin eigenfunctions
  to allows for generation of a whole block of matrix elements for one spatial interaction
- (4) may be reformulated into interaction cases ($\rightarrow$ lineup permutations), discrimination by orbital interaction cases (similar to Slater-Condon rules)
- direct calculation of representations possible using Young-Tableaus

[a] W. Duch und J. Karwowski, Comp. Phys. Rep. **2** (1985) 93, Int. J. Quantum Chem. **22** (1982) 783, "Symmetric Group Approach to Configuration Interaction Methods", North-Holland - Amsterdam, 1985

- linear combination of Slater determinants of same spatial part

$$\Phi_i^{S,M} = \sum_j \kappa_{ij}^{S,M} \hat{A} \prod_{k=1}^{n} \phi_{\eta_i(k)}^{\mathrm{MO}}(\vec{r}_k) \cdot \Omega_{\tilde{\eta}_{ij}(k)}(\omega_k) \tag{5}$$

- a configuration with ν open shells at multiplicty of $2S+1$ corresponds to

$$f_{S,\nu}^{\mathrm{Slater}} = \binom{\nu}{\frac{1}{2}\nu - S} \tag{6}$$

  Slater determinants.

  $\Rightarrow$ great savings from CSFs, particularly for many open shells

- achievement of spin adaption:
  - Slater determinants: first anti-symmetrize then linearly combineto spin eigenfunctions
  - Symmetric group approach: first linearly combine to spin eigenfunctions then anti-symmetrize

Spin Adaption and Spin Completeness

- spin adaption

$$\hat{S}^2|\Psi\rangle = S(S+1)|\Psi\rangle$$

- spin completeness (for one configuration)

$$V_N^{S,M} = \operatorname{ls}_k \Theta_k^{S,M}(\omega_1, \ldots, \omega_N)$$

- application of SGA to
  - CI theory is straight forward
  - CC theory is not possible (no way to define reasonable product, since spin degeneracy increases with number of open shells)

Relevance of Spin Symmetry (Spin Adaption)

- governs total energy (also for non-spin dependent H) by anti-symmetry
- spin contaminated WFs deliver energies from mixed multiplicities
  $\rightarrow$ error depends on distance of spin states
- spin related properties expected to be sensitive
- targeting states selectively (particularly in case of many open shells)
- $\rightarrow$ illustration

Spin Projection Errors in SO-Based MRCI and MRCC

- given an expansion into determinants $|i\rangle$

$$|\Psi_{\mathrm{det}}\rangle = \sum_i c_i |i\rangle \qquad \text{assuming} \qquad \langle\Psi_{\mathrm{det}}|\Psi_{\mathrm{det}}\rangle = 1$$

- introduce projector onto a CSF basis

$$\hat{P}^{S,S_z}_{\mathrm{CSF}} = \sum_{i'} |i'\rangle\langle i'| \qquad \text{with } |i'\rangle \text{ a CSF according to} \qquad |i'\rangle = \xi_{\eta_{i'}} \hat{A}|\eta_{i'}\rangle|S, S_z, \nu_{i'}\rangle$$

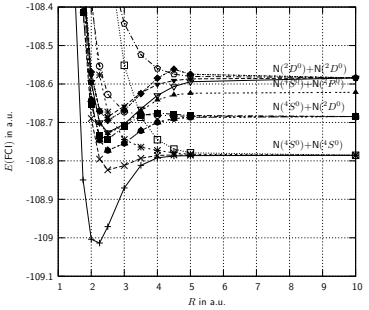
  - η a configuration (spatial orbital occupation pattern),
  - $\hat{A}$ the antisymmetrizer,
  - ξ_η a normalization constant
  - $|S, S_z, \nu\rangle$ a spin eigenfunction with total spin S, z projection S_z
  - degeneracy index ν
  - ξ_η and the valid values for ν depend on the number of open shells and the total spin S

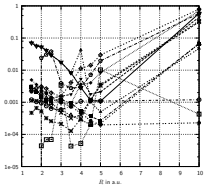
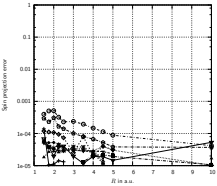
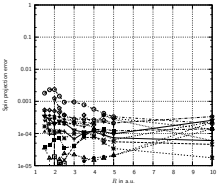
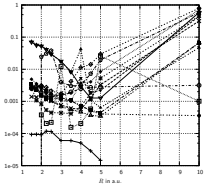
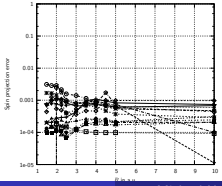
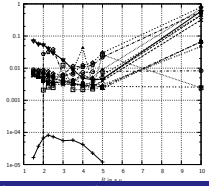
- spin projection error

$$\varepsilon = \sqrt{1 - \langle \hat{P}^{S,S_z}_{\mathrm{CSF}} \Psi_{\mathrm{det}} | \hat{P}^{S,S_z}_{\mathrm{CSF}} \Psi_{\mathrm{det}} \rangle}$$

$\rightarrow$ is stronger than the evaluation of the $\hat{S}^2$ expectation value

Spin Projection Errors in SO-Based MRCI and MRCC: Results on N_2[a]



Space	SOMRCI	MRexpT	SRMRCC
Ref.[a]	exact	exact	
MRSD[a]			
exp[a]	—		

[a] A. Engels-Putzka, M. Hanrath, Mol. Phys., **107** 143 (2009)

Contents

Aproaches From Literature

- spin projected [1, 2]
- spin restricted [3, 4, 5, 6, 7, 8, 9, 10, 11, 12]
- UGA
  - orthogonal [13, 14, 15, 16, 17, 18, 19, 20, 21]
  - non-orthogonal [22, 23]
- normal ordered exponential
  - without $\hat{T}$ contractions [24, 25, 26, 27]
  - with $\hat{T}$ contractions (COSCC) [28, 29, 30, 31, 32, 33, 34]

$\rightarrow$ no high spin state high substitution rank implementations reported

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Spin Orbital vs. Spin Free Formalism

	Spin Orbital	Spin Independent
Substitution Operators	$\hat{\tau}^{p_1\cdots p_n}_{q_1\cdots q_n} = \prod_{\nu=1}^{n}\sum_{\mu=1}^{N} \lvert\chi_{p_\nu}(\vec{x}_\mu)\rangle\langle\chi_{q_\nu}(\vec{x}_\mu)\rvert = \prod_{\nu=1}^{n} a^\dagger_{p_\nu} a_{q_\nu}$	$\hat{E}^{\bar{p}_1\cdots\bar{p}_n}_{\bar{q}_1\cdots\bar{q}_n} = \prod_{\nu=1}^{n}\sum_{\mu=1}^{N} \lvert\phi_{\bar{p}_\nu}(\vec{r}_\mu)\rangle\langle\phi_{\bar{q}_\nu}(\vec{r}_\mu)\rvert = \prod_{\nu=1}^{n} (a^\dagger_{\bar{p}_\nu\uparrow} a_{\bar{q}_\nu\uparrow} + a^\dagger_{\bar{p}_\nu\downarrow} a_{\bar{q}_\nu\downarrow})$
Cluster Operators	$\hat{T}_\nu = \underbrace{\sum_{\substack{i<j<\dots \\ a<b<\dots}}}_{\nu \text{ times}} t^{ab\dots}_{ij\dots}\ \hat{\tau}^{ab\dots}_{ij\dots}$	$\hat{T}_\nu = \underbrace{\sum_{\substack{\bar{i}\leq\bar{j}\leq\dots \\ \bar{a}\,,\,\bar{b}\,,\,\dots}}}_{\nu \text{ times}} t^{\bar{a}\bar{b}\dots}_{\bar{i}\bar{j}\dots}\ \hat{E}^{\bar{a}\bar{b}\dots}_{\bar{i}\bar{j}\dots}$
Symmetries	$\hat{\tau}^{\hat{P}\,pq\dots}_{\hat{Q}\,rs\dots} = (-1)^{P(\hat{P})}(-1)^{P(\hat{Q})}\hat{\tau}^{pq\dots}_{rs\dots}$ $t^{\hat{P}\,pq\dots}_{\hat{Q}\,rs\dots} = (-1)^{P(\hat{P})}(-1)^{P(\hat{Q})} t^{pq\dots}_{rs\dots}$	$\hat{E}^{\hat{P}\bar{a}\bar{b}\dots}_{\hat{P}\bar{i}\bar{j}\dots} = \hat{E}^{\bar{a}\bar{b}\dots}_{\bar{i}\bar{j}\dots}$ $t^{\hat{P}\bar{a}\bar{b}\dots}_{\hat{P}\bar{i}\bar{j}\dots} = t^{\bar{a}\bar{b}\dots}_{\bar{i}\bar{j}\dots}$

$\hat{T}$ vs. $\hat{E}$ Operators: Pros and Cons

- $\hat{T}$
  - $[\hat{T}, \hat{S}^2] \neq 0$
  - non-minimal parametrization
  - \+ $[\hat{T}, \hat{T}'] = 0$ (for standard CC)
- $\hat{E}$
  - \+ $[\hat{E}, \hat{S}^2] = 0$
  - \+ potentially minimal parametrization
  - $[\hat{E}, \hat{E}'] \neq 0$
  - spin completeness not automatically guaranteed
  - possibly linearly dependent
  - spectator orbitals

ν	$\eta_\nu^{\hat{T}}$	$\nu!$	$\eta_\nu^{\hat{\sigma}}$
1	2	1	1
2	6	2	2
3	20	6	5
4	70	24	14
5	252	120	42
6	924	720	132
7	3432	5040	429
8	12870	40320	1430
9	48620	362880	4862
10	184756	3628800	16796

- ν: substitution level
- $\eta_\nu^{\hat{T}}$; # S_z conserving spin-orbital substitutions
- $\nu!$: # spatial orbital permutations
- $\eta_\nu^{\hat{E}}$: # linearly independent substitutions (for singlet, closed shell reference)

Previous Attempts

- based on
  - SGA (initially, 1999): fail, no reasonable product at hand
  - commutators of $\hat{E}$ operators (2012): partial success, too expensive, not implemented
  - spin integration of spin orbital equations (2014): success, not implemented
  - permutation operators and Löwdin projectors (2020): success, implemented

Contents

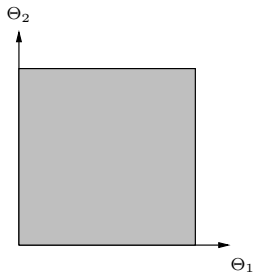
CC and Spin

- Two major problems with CC and spin
  - Spin adaption
  - Eigenfunction spanning

- Illustration

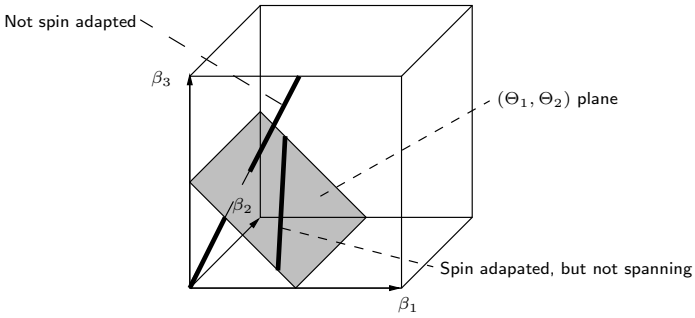
Spin eigenfunction space

$\Psi_{\text{spin}} = a_1\Theta_1 + a_2\Theta_2$



Determinantal space

$\Psi = b_1\beta_1 + b_2\beta_2 + b_3\beta_3$



$\hat{E}$ Spanning Spin space: Closed shell case

- Closed shell case, single excitation:

$$\begin{aligned}\hat{E}_{3\leftarrow 1}|1\bar{1}2\bar{2}\rangle &= |3\bar{1}2\bar{2}\rangle + |1\bar{3}2\bar{2}\rangle \\ &= -|\bar{1}2\bar{2}3\rangle + |12\bar{2}\bar{3}\rangle\end{aligned}$$

  2 open shells, singlet $\Rightarrow$ 1 spin eigenfunctions, 1 independent Amplitude $t_{3\leftarrow 1}$ $\Rightarrow$ spin space complete

- Closed shell case, double excitation:

$$\begin{aligned}\hat{E}_{43\leftarrow 21}|1\bar{1}2\bar{2}\rangle &= \\ \hat{E}_{4\leftarrow 2}\hat{E}_{3\leftarrow 1}|1\bar{1}2\bar{2}\rangle &= \hat{E}_{4\leftarrow 2}[|3\bar{1}2\bar{2}\rangle + |1\bar{3}2\bar{2}\rangle] \\ &= \quad |3\bar{1}4\bar{2}\rangle + |1\bar{3}4\bar{2}\rangle + |3\bar{1}2\bar{4}\rangle + |1\bar{3}2\bar{4}\rangle \\ &= -|\bar{1}\bar{2}34\rangle + |1\bar{2}\bar{3}4\rangle + |\bar{1}23\bar{4}\rangle - |12\bar{3}\bar{4}\rangle \\ \hat{E}_{34\leftarrow 21}|1\bar{1}2\bar{2}\rangle &= \\ \hat{E}_{3\leftarrow 2}\hat{E}_{4\leftarrow 1}|1\bar{1}2\bar{2}\rangle &= \hat{E}_{3\leftarrow 2}[|4\bar{1}2\bar{2}\rangle + |1\bar{4}2\bar{2}\rangle] \\ &= \quad |4\bar{1}3\bar{2}\rangle + |1\bar{4}3\bar{2}\rangle + |4\bar{1}2\bar{3}\rangle + |1\bar{4}2\bar{3}\rangle \\ &= +|\bar{1}\bar{2}34\rangle - |1\bar{2}\bar{3}4\rangle - |\bar{1}2\bar{3}4\rangle + |12\bar{3}\bar{4}\rangle\end{aligned}$$

  4 open shells, singlet $\Rightarrow$ 2 spin eigenfunctions, 2 independent Amplitudes $t_{43\leftarrow 21}$ and $t_{34\leftarrow 21}$ $\Rightarrow$ spin space complete

$\hat{E}$ Spanning Spin space: Open shell case

- Open shell case, single excitation:

$$\begin{aligned}\hat{E}_{3\leftarrow 1}|1\bar{1}2\rangle &= |3\bar{1}2\rangle + |1\bar{3}2\rangle \\ &= |\bar{1}23\rangle - |12\bar{3}\rangle\end{aligned}$$

3 open shells, doublet $\Rightarrow$ 2 spin eigenfunctions, 1 independent Amplitude $t_{3\leftarrow 1}$ $\Rightarrow$ spin space **incomplete**
Furthermore: What about $|1\bar{2}3\rangle$? It is missing!!!

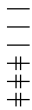
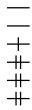
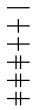
- Open shell case, double excitation:

$$\begin{aligned}\hat{E}_{43\leftarrow 21}|1\bar{1}2\bar{2}5\rangle &= \\ \hat{E}_{4\leftarrow 2}\hat{E}_{3\leftarrow 1}|1\bar{1}2\bar{2}5\rangle &= \\ &\vdots\end{aligned}$$

5 open shells, doublet
$\Rightarrow$ 5 spin eigenfunctions, 2 independent Amplitudes $t_{43\leftarrow 21}$ and $t_{34\leftarrow 21}$
$\Rightarrow$ spin space **incomplete**

Spin Degeneracy vs. Spatial Orbital Permutations

Open Shells Created From Substitutions

Reference		Substitution rank $\nu = 1$	$\nu = 2$	$\nu = 3$
$S = 0$		$f^{\mathsf{a}}(2,0) = \mathbf{1}$	$f(4,0) = \mathbf{2}$	$f(6,0) = \mathbf{5}$
$S = \frac{1}{2}$		$f(3,\frac{1}{2}) = \mathbf{2}$	$f(5,\frac{1}{2}) = \mathbf{5}$	$f(7,\frac{1}{2}) = \mathbf{14}$
$S = 1$		$f(4,1) = \mathbf{3}$	$f(6,1) = \mathbf{9}$	$f(8,1) = \mathbf{28}$

$$f(o,S) = \binom{o}{\frac{o}{2} - S} - \binom{o}{\frac{o}{2} - S - 1}$$

Löwdin's Projector Operator Method and Particle Permutations

- Löwdin projection operator method[a]

$$\Theta^{S,S_z}(\omega_1,\ldots,\omega_N) = \underbrace{\prod_{K\neq S} \frac{\hat{S}^2 - K(K+1)}{S(S+1) - K(K+1)}}_{\hat{O}_S} \Theta^{S_z}(\omega_1,\ldots,\omega_N)$$

- it is

$$[\hat{O}_S, \hat{P}] = 0$$

- complete (non-orthogonal) set of spin eigenfunctions $\{\Theta_k^{S,S_z}\}$, $k \in [1 \ldots f(o,S)]$ may be generated from

$$\Theta_k^{S,S_z} = \hat{P}_{0\to k}\Theta_0^{S,S_z}$$

[a] P.-O. Löwdin *Phys. Rev.* **97**, 1509, (1955), *Rev. Mod. Phys.* **36**, 966, (1964)

Finding Suitable Spatial Permutations on $\hat{E}^{\cdots}_{\cdots}$ (1)

- recall the SGA approach

$$|\Psi_{\Phi,0}\rangle = \mathcal{A}\left[\Phi(\vec{r}_1,\ldots,\vec{r}_N)\cdot\Theta_0^{S,S_z}(\omega_1,\ldots,\omega_N)\right]$$

apply spatial substitution

$$|\Psi_{\Phi',0}\rangle = \mathcal{A}\left[\left(\hat{E}^{q_1\ldots q_\nu}_{p_1\ldots p_\nu}\Phi(\vec{r}_1,\ldots,\vec{r}_N)\right)\cdot\Theta_0^{S,S_z}(\omega_1,\ldots,\omega_N)\right]$$

- introduce spin permutations and propagate to spatial permutations

$$\begin{aligned}
|\Psi_{\Phi',k}\rangle &= \mathcal{A}\left[\left(\hat{E}^{q_1\ldots q_\nu}_{p_1\ldots p_\nu}\Phi\right)\cdot\hat{P}^{\Theta}_{0\to k}\Theta_0^{S,S_z}\right]\\
&= \mathcal{A}\hat{P}_{0\to k}\hat{P}_{k\to 0}\left[\left(\hat{E}^{q_1\ldots q_\nu}_{p_1\ldots p_\nu}\Phi\right)\cdot\hat{P}^{\Theta}_{0\to k}\Theta_0^{S,S_z}\right]\\
&= \mathcal{A}\hat{P}_{0\to k}\left[\left(\hat{P}^{\Phi}_{k\to 0}\hat{E}^{q_1\ldots q_\nu}_{p_1\ldots p_\nu}\Phi\right)\cdot\hat{P}^{\Theta}_{k\to 0}\hat{P}^{\Theta}_{0\to k}\Theta_0^{S,S_z}\right]\\
&= (-1)^{p(\hat{P}_{0\to k})}\mathcal{A}\left[\left(\hat{P}^{\Phi}_{k\to 0}\hat{E}^{q_1\ldots q_\nu}_{p_1\ldots p_\nu}\Phi\right)\cdot\Theta_0^{S,S_z}\right]
\end{aligned}$$

Finding Suitable Spatial Permutations on $\hat{E}^{\cdots}_{\cdots}$ (2)

- further steps
  - back mapping of spin permutations to spatial permutations
    $\rightarrow$ not bijective due to doubly occupied spatial orbitals
  - introduce prototypes, e.g., $\hat{E}^{abcc}_{iijk}$ or $\hat{E}^{abccv}_{iijkv}$ to cover full spin space

$\Rightarrow$ non-orthogonal but simple setup of complete spin space in terms of $\hat{E}^{\cdots}_{\cdots}$

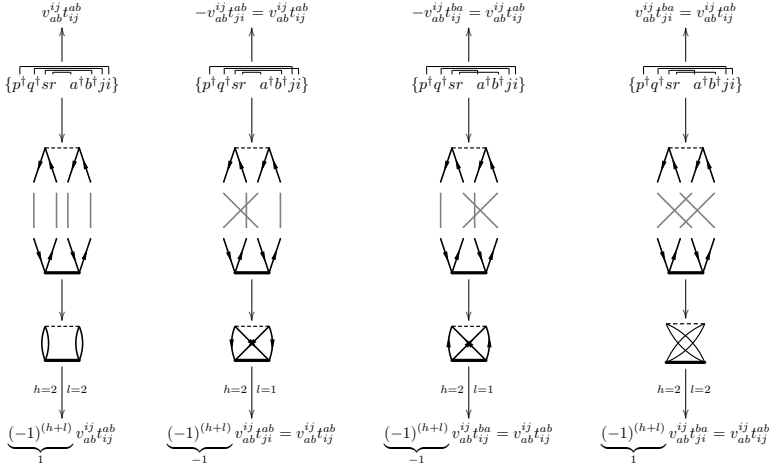
Diagrammatic vs. Algebraic Equivalence: Spin Orbital Picture

The Battle For Storing No Irrelevant But Also Sufficient Information In Diagrams

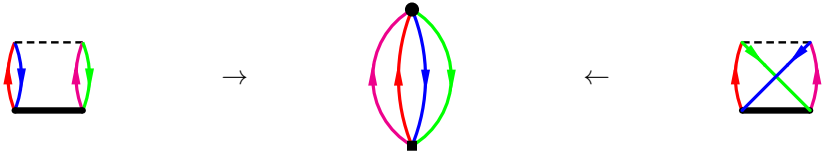
- symmetry

$$\hat{\tau}^{\hat{P}\,pq\ldots}_{\hat{Q}\,rs\ldots} = (-1)^{P(\hat{P})}(-1)^{P(\hat{Q})}\hat{\tau}^{pq\ldots}_{rs\ldots}$$

- it is



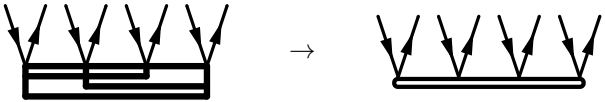
Diagrammatic vs. Algebraic Equivalence Hugenholtz: Spin Orbital Picture



- symmetry

$$\hat{E}^{\hat{P}ab\ldots}_{\hat{P}ij\ldots} = \hat{E}^{ab\ldots}_{ij\ldots}$$

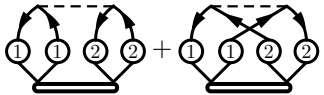
- introduce anonymous cluster line



- it is, e.g.,

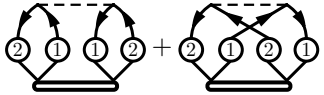
- however: too much information lost, fix by enumerating lines on anonymous cluster line[a]

$$\sum_{i<j,a<b} \langle \Psi_0 | \hat{V}_N t_{ij}^{ab} \hat{E}_{ij}^{ab} \Psi_0 \rangle \rightarrow$$



$$= \sum_{i<j,a<b} \left(4o_{ab}^{ij} - 2o_{ba}^{ij} \right) t_{ij}^{ab}$$

$$\sum_{i<j,a<b} \langle \Psi_0 | \hat{V}_N t_{ji}^{ab} \hat{E}_{ji}^{ab} \Psi_0 \rangle \rightarrow$$



$$= \sum_{i<j,a<b} \left(-2o_{ab}^{ij} + 4o_{ba}^{ij} \right) t_{ji}^{ab}$$

$\rightarrow$ restores missing information

- note: indices are local to anonymous cluster line

[a] o_{ab}^{ij}: spatial integrals (not anti-symmetric)

Implementation Stages

1. operator representation in FCI basis ("foolproof", hopefully), just matrix-matrix multiplications

   $\rightarrow$ "determinant approach"

2. tensor contractions, not correctly scaling

   $\rightarrow$ "algebraic/diagrammatic approach"

3. tensor contractions, correctly scaling, term at a time

4. currently missing (for spin free implementation): global optimization

Results

Molecule	$S = S_z$	E_{corr} (SASC CC)[a] SD	% FCI	E_{corr} (spin orbital CC) [b] SD	% FCI
OH	1/2	−0.169 503 9	98.80%	−0.169 317 6	98.70%
	3/2	−0.137 953 2	99.07%	−0.137 626 0	98.83%
	5/2	−0.102 096 6	99.14%	−0.101 896 8	98.95%
	7/2	−0.026 192 9	99.65%	−0.026 191 8	99.64%
	9/2	−0.018 330 0	99.85%	−0.018 330 0	99.85%
BH_2	1/2	−0.088 862 6	98.40%	−0.088 739 8	98.26%
	3/2	−0.089 152 4	98.11%	−0.088 266 3	97.13%
	5/2	−0.029 326 7	99.06%	−0.029 325 2	99.05%
	7/2	−0.021 532 5	99.15%	−0.021 532 5	99.15%
CH_2	0	−0.138 223 7	96.34%	−0.138 223 7	96.34%
	1	−0.120 937 9	98.44%	−0.120 576 8	98.14%
	2	−0.114 401 0	97.40%	−0.113 109 0	96.30%
	3	−0.036 432 9	99.24%	−0.036 430 9	99.24%

[a] N. Herrmann and M. Hanrath *J. Chem. Phys.* **156**, 504111 (2022)

[b] Q. Sun, *J. Comput. Chem.* **30**, 1664 (2015), Q. Sun, T. C. Berkelbach et. al. *WIREs Comput. Mol. Sci.* **8**, e1340, (2018)

Number of Diagrams

Comparison: number of generated diagrams spin orbital vs SASC CC

CC method		BCH truncation 0	1	2	3	4	$\sum$
Spin orbital	S	1	4	4	1	–	10
	SD	2	15	22	8	1	48
SASC	S	7	92	401	735	432	1 667
	SD	42	12 913	628 378	2 660 888	2 866 668	6 168 889

Current Limitations

- creation of redundant terms by Wick contractions

  $\rightarrow$ filtered out by diagrammatic analysis

- annihilator and creator index coupling

  $\rightarrow$ more difficult non-redundant tensor addressing

- factorization: term at a time, global optimization currently missing (in spin free implementation)

- code generated: code blow

  - large executables (filesize >2 GByte, linkage trouble)

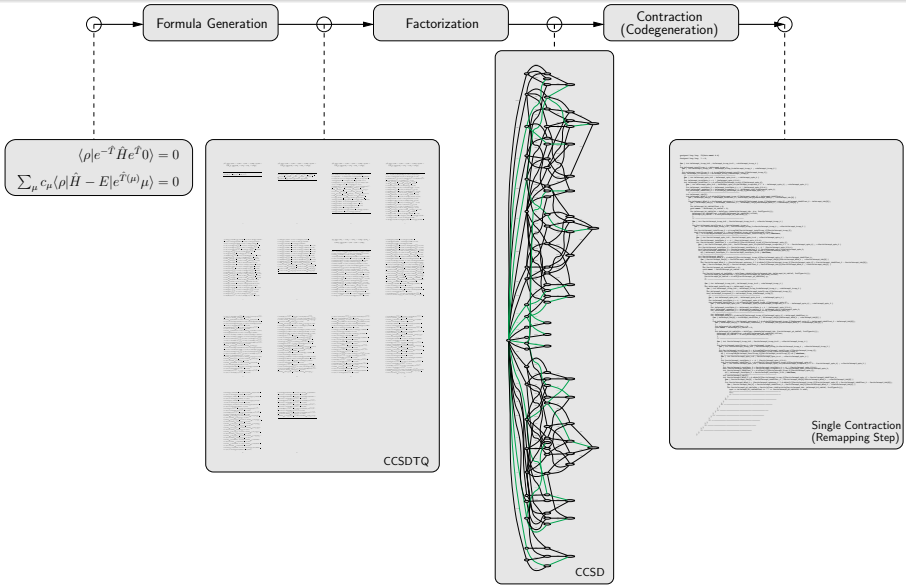
    $\rightarrow$ e.g. CCSD, $S = S_z = 4$, BCH truncation after 4-fold commutator: 16,037,596 LOC

  - compilation time

- nevertheless: general and correct scaling

Contents

Implementation Pipeline



Algebraic / Diagrammatic Engine Capabilities

- CI

$$\langle\rho|(\hat{H}_N - E_{\text{corr}})(1+\hat{C})\Phi_0\rangle$$

- Coupled cluster expressions (unlinked form, linked form)

$$\langle\rho|(\hat{H}_N - E_{\text{corr}})e^{\hat{T}}\Phi_0\rangle, \quad \langle\rho|e^{-\hat{T}}\hat{H}_N e^{\hat{T}}\Phi_0\rangle$$

- $\hat{\Lambda}$ equations

$$\langle\rho|\hat{\Lambda}e^{-\hat{T}}\hat{H}_N e^{\hat{T}}\Phi_0\rangle$$

- Expectation values e.g.

$$\langle\rho|e^{\hat{T}^\dagger}\hat{H}_N e^{\hat{T}}\Phi_0\rangle$$

- Powers of Hamiltonian

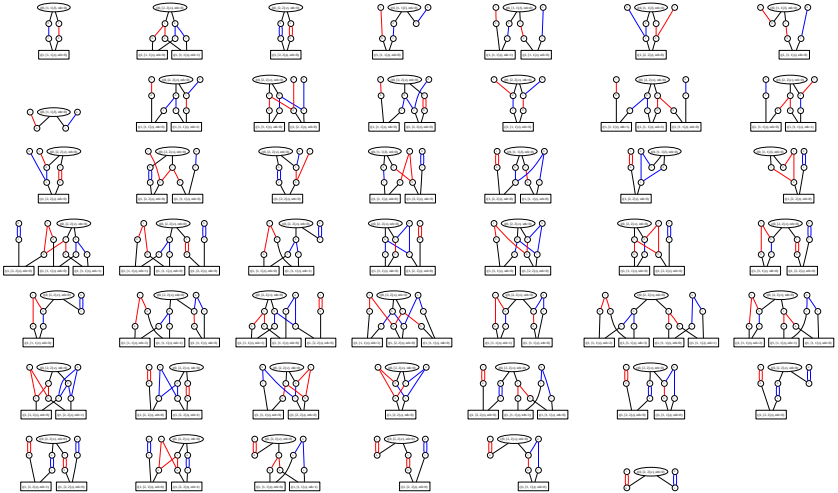
$$\langle\rho|e^{\hat{T}^\dagger}(\hat{H}_N)^n e^{\hat{T}}\Phi_0\rangle$$

- 3-body interaction Hamiltonians

$$\langle\rho|e^{-\hat{T}}(\hat{F}_N + \hat{V}_N + \hat{W}_N)e^{\hat{T}}\Phi_0\rangle$$

$\langle 0, S, D|e^{-T}\hat{H}e^{T}|0\rangle$, (48 Diagrams)

$\hat{T} = \hat{T}_1 + \hat{T}_2$, $e^{\hat{T}} = \sum_{i=0}^{\infty} \frac{1}{i!}\hat{T}^i$



$\langle 0|e^{T^\dagger}\hat{H}e^{T}|0\rangle$, (319 Diagrams)

$\hat{T} = \hat{T}_1 + \hat{T}_2$, $e^{\hat{T}} \sim 1 + \hat{T} + \frac{1}{2!}\hat{T}^2$ (no termination)

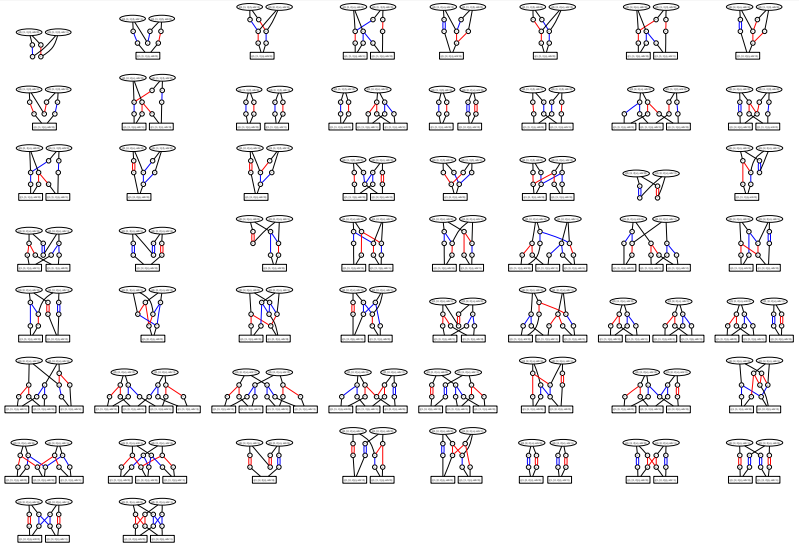
$\langle 0|e^{T^\dagger}\hat{H}^2 e^T|0\rangle$, (9410 Diagrams)

$\hat{T} = \hat{T}_1 + \hat{T}_2$, $e^{\hat{T}} \sim 1 + \hat{T} + \frac{1}{2!}\hat{T}^2$ (no termination)

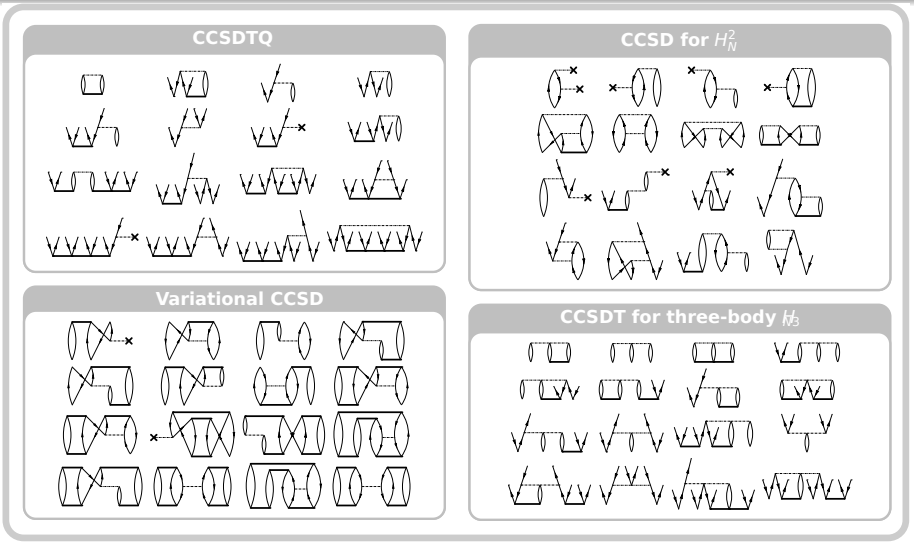
. . .

$\langle 0|e^{-T}\hat{H}^2e^{T}|0\rangle$, (58 Diagrams)

$\hat{T} = \hat{T}_1 + \hat{T}_2$, $e^{\hat{T}} = \sum_{i=0}^{\infty} \frac{1}{i!}\hat{T}^i$



Automatically Layouted Diagrams[a]



[a] N. Herrmann, M. Hanrath, Theor. Chem. Acc. 138 (2019) 117

Factorization

Coupled cluster equations

$$\text{Residual } = \ldots + \frac{1}{2}\sum_{iab}\langle Ai||ab\rangle t_{Ii}^{ab} + \ldots + \frac{1}{4}\sum_{ijab}\langle ij||ab\rangle t_{i}^{a} t_{Ij}^{Ab} + \ldots$$

Factorization means:

- General $\rightarrow$ binary tensor contractions

$$\sum_{\dots} \dots x^{\dots}_{\dots} y^{\dots}_{\dots} z^{\dots}_{\dots} \quad \rightarrow \quad \dots \left(\sum_{\dots} x^{\dots}_{\dots} \left(\sum_{\dots} y^{\dots}_{\dots} z^{\dots}_{\dots} \right) \right)$$

- Definition (choice) of suitable intermediates

Goal: Minimization of costs (operation count/memory)

Possible optimizations

- Contraction **order** of multiple products

$$a \cdot (b \cdot c) \quad \leftrightarrow \quad (a \cdot b) \cdot c$$

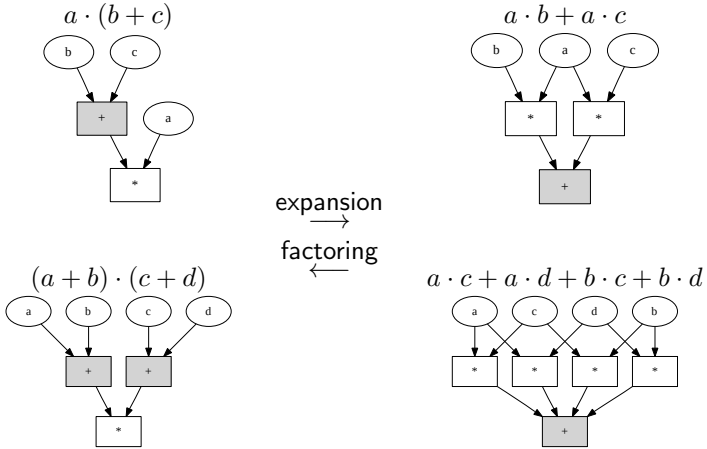
- **Factoring out**

$$a \cdot b + a \cdot c = a \cdot (b + c)$$

- **Reusage** of intermediates

$$\boldsymbol{a} \cdot b, \ \boldsymbol{a} \cdot c$$

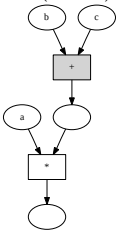
- Examples:



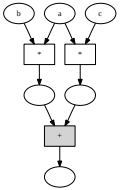
- Expansion: canonical form ($\sum \prod \ldots$)
- Factoring out: ambiguous ($\sum \ldots \prod \ldots \sum \ldots \prod \ldots \ldots$)

- Examples:

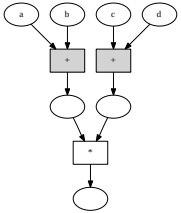
$a \cdot (b + c)$



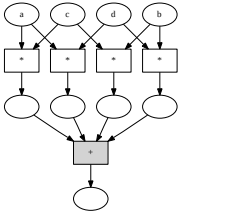
$a \cdot b + a \cdot c$



$(a + b) \cdot (c + d)$



$a \cdot c + a \cdot d + b \cdot c + b \cdot d$



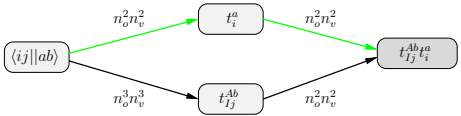
Optimization of Factorization

- Order matters

$$Z_I^A = \sum_{ijab} \langle ij||ab\rangle t_i^a t_{Ij}^{Ab}$$

		Ops	Mem			Ops	Mem
Z_I^A	$= \sum_{jb} t_{Ij}^{Ab} \underbrace{\sum_{ia} \langle ij\|\|ab\rangle t_i^a}_{X_j^b}$	$n_o^2 n_v^2$	$n_o n_v$	Z_I^A	$= \sum_{ia} t_i^a \underbrace{\sum_{jb} \langle ij\|\|ab\rangle t_{Ij}^{Ab}}_{X_{I,i}^{A,a}}$	$n_o^3 n_v^3$	$n_o^2 n_v^2$
	$= \sum_{jb} t_{Ij}^{Ab} X_j^b$	$n_o^2 n_v^2$	—		$= \sum_{ia} t_i^a X_{I,i}^{A,a}$	$n_o^2 n_v^2$	—

- Graphical representation



Factorization (Example from CCSDTQ)

Scaling

$$Z_{IJKL}^{ABCD} = \sum_{ijab} \langle ij||ab\rangle t_i^a t_{Ij}^{CD} t_{JKL}^{ABb} \qquad \binom{n_o}{4}\binom{n_v}{4}\binom{n_o}{2}\binom{n_v}{2} \sim n_o^6 n_v^6$$

$$= \sum_b t_{JKL}^{ABb} \sum_j t_{Ij}^{CD} \underbrace{\sum_{ia} \langle ij||ab\rangle t_i^a}_{X_j^b} \qquad n_o n_v n_o n_v \sim n_o^2 n_v^2$$

$$= \sum_b t_{JKL}^{ABb} \underbrace{\sum_j t_{Ij}^{CD} X_j^b}_{Y_I{}^{CD,b}} \qquad n_o \binom{n_v}{2} n_o n_o \sim n_o^3 n_v^2$$

$$Z_{IJKL}^{ABCD} = \sum_b t_{JKL}^{ABb} Y_I^{CD,b} \qquad \binom{n_o}{4}\binom{n_v}{4} n_v \sim n_o^4 n_v^5$$

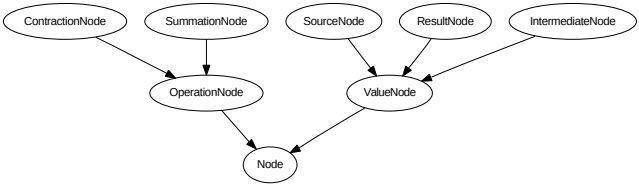
Σ: $\sim n_o^4 n_v^5$

Color Legend:

- external holes
- external particles
- summed holes
- summed particles
- not yet summed holes
- not yet summed particles

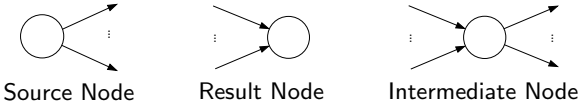
Nodes in Graph

- Node hierarchy



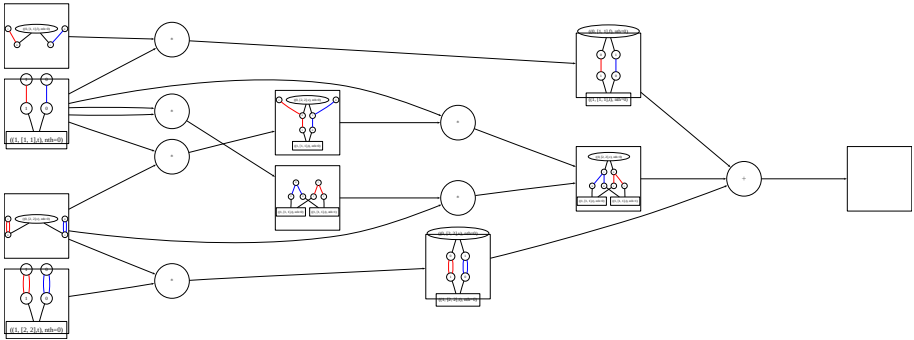
- Node notation
  - Operation nodes

  - Value nodes



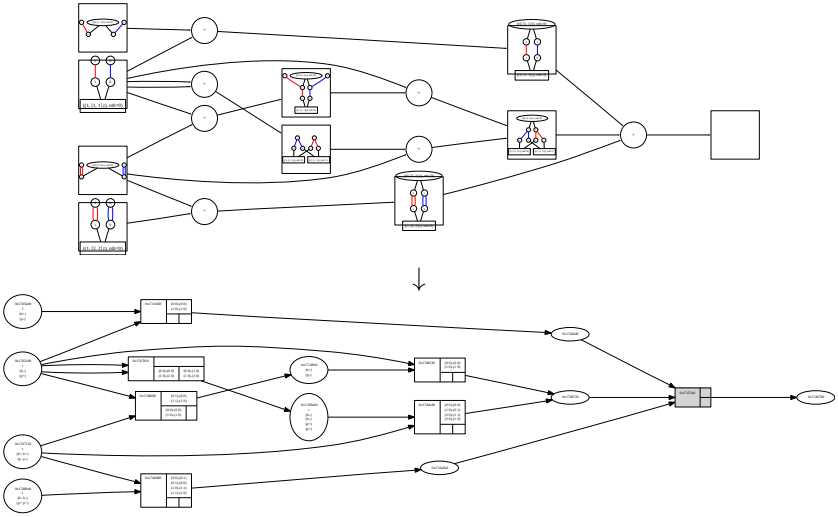
Ellimination of Equivalent Nodes

Value Aware Factorization Graph: "Graph of Graphs"

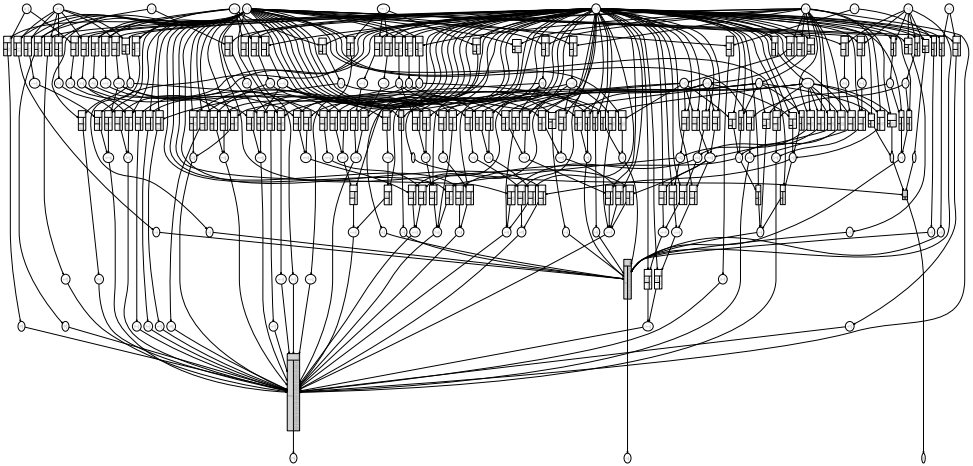


Graph Transformation

"Graph of Graphs" with implicit contraction → graph with explicit contraction



Graph before Factorization



Complexity? Complexity $= 1.27779 \cdot 10^{36}$
Human being: complexity $= 4^{3 \cdot 10^9} \sim 10^{1.8 \cdot 10^9}$

Efficient Parametrization of Factorization

- Problem:
  Find a compact and efficient parametric representation of the factorization problem (including factoring out) that separates the combinatorical problem from actual algebraic manipulations.

Factor Ordering

- Consider

$$t_i^A t_I^a f_i^a + t_i^A t_I^a t_j^b v_{ij}^{ab}$$

- Factor ordering

$$[t_i^A [t_I^a [f_i^a]]] + [t_i^A [t_I^a [t_j^b [v_{ij}^{ab}]]]]$$

- It is $[t_j^b [v_{ij}^{ab}]] = X_i^a$
- $[f_i^a]$ and $[X_i^a]$ are compatible
- Remaining factors $t_i^A t_I^a$ same $\Rightarrow$ we may write

$$[t_i^A [t_I^a [f_i^a + X_i^a]]]$$

- Not possible for

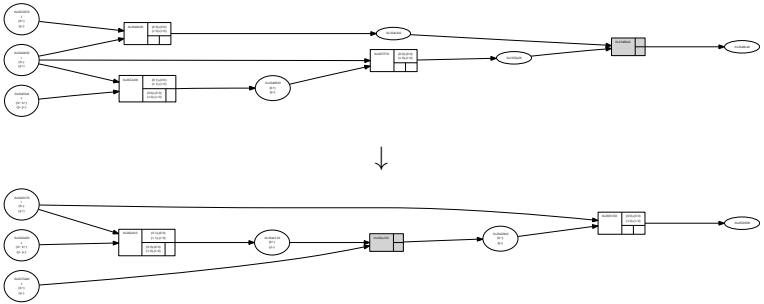
$$[t_i^A [t_I^a [f_i^a]]] + [t_i^A [t_{IJ}^{aB} [t_j^b [v_{ij}^{ab}]]]]$$

- On the other hand

$$[t_i^A [t_I^a [f_i^a]]] + [t_j^A [t_I^b [t_i^a [v_{ij}^{ab}]]]]$$

Value node identification after "+" movement

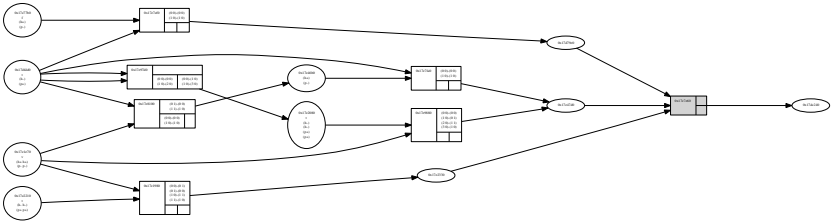
- Consider factorization process (movement of "+")
  1. $x = 0$
  2. $x \leftarrow x + f_i^a$
  3. $x \leftarrow x + t_j^b v_{ij}^{ab}$
- x contains $f_i^a + t_j^b v_{ij}^{ab}$
- Explicit storage in value node redundant
- Graphical illustration of factoring out:



Translation: Population Individuum $\rightarrow$ Factored Out Graph

Term: $\langle 0|e^{-\hat{T}}\hat{H}_N e^{\hat{T}}0\rangle$, $\hat{T} = \hat{T}_1 + \hat{T}_2$

- Before factoring out



- After factoring out