Properties with Relativistic XMS-CASPT2

Peter John Cherry
Shiozaki group meeting
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$$L(\mathbf{t}, \mathbf{c}, \mathbf{z}, \boldsymbol{\lambda}) = E(\mathbf{t}, \mathbf{c}) + \mathbf{z}^{\dagger}\mathbf{g}(\mathbf{c}) + \boldsymbol{\lambda}^{\dagger}\mathbf{g}'(\mathbf{t})$$

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Amplitudes from CASPT2

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Coefficients from CASSCF calculation

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Conditions from CASSCF

Lagrange multipliers associated with conditions from CASSCF

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- Typically, differentiating this Lagrangian with respect to some perturbative parameter is much easier than differentiating the XMS-CASPT2 energy.

Z-vector and Lambda equations

- The Z constraint can be obtained by solution of the “Z-vector equation”.
- This requires, amongst other things, calculation of the CI-deratives:

$$y_{I,N} = \frac{\partial L_{PT2}}{\partial c_{I,N}} \longrightarrow$$

Derivative of the CASPT2 Lagrangian with respect to CASSCF reference coefficients.

CI derivatives

$$\frac{\partial L}{\partial \tilde{c}_{Q,K}} = \sum_{M} \langle \tilde{M} | \hat{H} | K \rangle R^{*}_{MP} R_{QP} + \sum_{N} \langle K | \hat{H} | \tilde{N} \rangle R^{*}_{QP} R_{KP} + \ldots$$

CI derivatives

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CASSCF reference state

Determinant in CAS

CI derivatives

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CASSCF reference state

Determinant in CAS

pth eigenvector of effective XMS-CASPT2 Hamiltonian

CI derivatives

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$$+ \sum_L R^*_{LP} \left(\sum_M \langle \tilde{M}|\hat{T}^\dagger_{LM}\hat{H}|K\rangle R_{QP} + \sum_N \langle K|\hat{T}^\dagger_{LQ}\hat{H}|\tilde{N}\rangle R_{NP} \right)$$

$$- E_s \sum_L \left(\sum_M \langle \tilde{M}|\hat{T}^\dagger_{LM}\hat{T}_{LQ}|K\rangle + \sum_N |\hat{T}^\dagger_{LQ}\hat{T}_{LN}|\tilde{N}\rangle \right)$$

$$+ \sum_L \left(\sum_M \langle \tilde{M}|\hat{\lambda}^\dagger_{LM}(\hat{f} - \epsilon^{(0)}_L + \epsilon_s)\hat{T}_{LQ}|K\rangle + \sum_N |\hat{\lambda}^\dagger_{LQ}(\hat{f} - \epsilon^{(0)}_L + \epsilon_s)\hat{T}_{LN}|\tilde{N}\rangle \right)$$

$$+ \sum_{rs} \Big(\langle K|\hat{E}_{rs}|\tilde{M}\rangle + \langle \tilde{M}|\hat{E}_{rs}|K\rangle \Big) [W_M \mathbf{g}(\mathbf{d}^{(2)}) - N_M \mathbf{f}]_{rs}$$

Calculation of CI derivatives

- Requires evaluation of terms of this form

$$\langle \tilde{M} | \hat{\lambda}_{MN} \hat{H} | K \rangle$$

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$$\hat{H} = \sum_{xy} h(1) \hat{E}_{xy} + \frac{1}{2} \sum_{xy} v(1,2) \hat{E}_{xy,zw}$$

$$|\tilde{M}\rangle = \sum_{I} c_{\tilde{M},I} |I\rangle$$

$$\hat{\lambda}_{LN} = \sum_{\Omega} \lambda_{\Omega,LN} \hat{E}_{\Omega}$$

$$|\tilde{M}\rangle = \sum_{N} |M\rangle U_{NM}$$

Calculation of CI derivatives

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$$\sum_{M}\sum_{\Omega}\sum_{I}\sum_{xy}\langle I|c^{\dagger}_{\tilde{M},I}U^{\dagger}_{MN}\lambda^{\dagger}_{LM,\Omega}\hat{E}^{\dagger}_{\Omega}(h(1)\hat{E}_{xy}+\frac{1}{2}v(1,2)\hat{E}_{xy,zw})|K\rangle$$

$$\hat{H}=\sum_{xy}h(1)\hat{E}_{xy}+\frac{1}{2}\sum_{xy}v(1,2)\hat{E}_{xy,zw}$$

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$$\sum_{M}\sum_{\boldsymbol{\Omega}}\sum_{I}\sum_{\mathbf{xy}}\langle I|c^{\dagger}_{\tilde{M},I}U^{\dagger}_{MN}\lambda^{\dagger}_{LM,\boldsymbol{\Omega}}\hat{E}^{\dagger}_{\boldsymbol{\Omega}}(h(1)\hat{E}_{\mathbf{xy}}+\frac{1}{2}v(1,2)\hat{E}_{\mathbf{xy,zw}})|K\rangle$$

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- Excitations from Hamiltonian.
- Excitations associated with XMS-CASPT2.

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→ **General Indices**
(virtual, active, closed)

Calculation of CI derivatives

- Requires evaluation of terms of this form

$$\sum_{M}\sum_{\mathbf{\Omega}}\sum_{I}\sum_{\mathbf{xy}}\langle I|c^{\dagger}_{\tilde{M},I}U^{\dagger}_{MN}\lambda^{\dagger}_{LM,\mathbf{\Omega}}\hat{E}^{\dagger}_{\mathbf{\Omega}}(h(1)\hat{E}_{\mathbf{xy}}+\frac{1}{2}v(1,2)\hat{E}_{\mathbf{xy,zw}})|K\rangle$$

- This sum over **general** indices can be rewritten as a sum over **active** indices:

Calculation of CI derivatives

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- This sum over **general** indices can be rewritten as a sum over **active** indices:

$$=\sum_{M}\sum_{\mathbf{ijklmnop}}\Gamma^{M,K}_{\mathbf{ij,kl,mn,op}}A_{\mathbf{ij,kl,mn,op}}$$

Reduced density matrix derivative

Weighted MO integrals

Calculation of CI derivatives

- Requires evaluation of terms of this form

$$\sum_{M}\sum_{\mathbf{\Omega}}\sum_{I}\sum_{\mathbf{xy}}\langle I|c^{\dagger}_{\tilde{M},I}U^{\dagger}_{MN}\lambda^{\dagger}_{LM,\mathbf{\Omega}}\hat{E}^{\dagger}_{\mathbf{\Omega}}(h(1)\hat{E}_{\mathbf{xy}}+\frac{1}{2}v(1,2)\hat{E}_{\mathbf{xy,zw}})|K\rangle$$

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$$=\sum_{M}\sum_{\mathbf{ijklmnop}}\Gamma^{M,K}_{\mathbf{ij,kl,mn,op}}A_{\mathbf{ij,kl,mn,op}}$$

- Computationally efficient; can be evaluated without the need to store any eight index tensors.

- This is Jae's recent work:

Calculation of CI derivatives

- Requires evaluation of terms of this form

$$\sum_{\mathbf{ijkl}} \sum_{I} T^{\dagger}_{\mathbf{ijkl}} \sum_{\mathbf{wxyz}} g_{\mathbf{wxyz}} \langle I | a_{\mathbf{i}} a_{\mathbf{j}} a^{\dagger}_{\mathbf{k}} a^{\dagger}_{\mathbf{l}} a^{\dagger}_{\mathbf{w}} a^{\dagger}_{\mathbf{x}} a_{\mathbf{y}} a_{\mathbf{z}} | K \rangle$$

$$= \Gamma^{K}_{\mathbf{ij,kl,mn,op}} A_{\mathbf{ij,kl,mn,op}}$$

Dependent upon CI-coefficients and active space

Dependent upon operator ordering and molecular orbital integrals.

- The $\Gamma_{ij,kl,mn,op}$ terms have been manually coded.
- The $A_{ij,kl,mn,op}$ terms can be obtained from code generated using SMITH3.

Advantages of normal ordering

- Situation is simplified once creation and annihilation operators are normal ordered:

$$\sum_{\mathbf{ijkl}} \sum_{I} T^{\dagger}_{\mathbf{ijkl}} \sum_{\mathbf{wxyz}} g_{\mathbf{wxyz}} \langle I | a_{\mathbf{i}} a_{\mathbf{j}} a^{\dagger}_{\mathbf{k}} a^{\dagger}_{\mathbf{l}} a^{\dagger}_{\mathbf{w}} a^{\dagger}_{\mathbf{x}} a_{\mathbf{y}} a_{\mathbf{z}} | K \rangle$$

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$$\rightarrow \langle 0| \left(\Pi_q^{\in S_I} a_q \right) a^{\dagger}_{\mathbf{k}} a^{\dagger}_{\mathbf{l}} a^{\dagger}_{\mathbf{w}} a^{\dagger}_{\mathbf{x}} a_{\mathbf{i}} a_{\mathbf{j}} a_{\mathbf{y}} a_{\mathbf{z}} \left(\Pi_r^{\in S_K} a^{\dagger}_r \right) |0\rangle$$

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$$= \begin{cases} 0 & \text{if} \quad \mathbf{w}, \mathbf{x}, \mathbf{k}, \mathbf{l} \notin S_I \\ 0 & \text{if} \quad \mathbf{i}, \mathbf{j}, \mathbf{y}, \mathbf{z} \notin S_K \\ \pm 1 & \text{otherwise} \end{cases}$$

Wick’s Theorem

- Any operator can be written as a sum of normal ordered terms.

  Normal ordering

$$: \hat{a}_i \hat{a}_j^\dagger \hat{a}\dagger_k := \hat{a}_j^\dagger \hat{a}_k^\dagger \hat{a}_i$$

- All creation operators on the left, all annihilation operators on the right.

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  Contraction (!!)

$$\overbrace{\hat{a}_i \hat{a}_j^\dagger} = \hat{a}_i \hat{a}_j^\dagger - : \hat{a}_i \hat{a}_j^\dagger := \hat{a}_i \hat{a}_j^\dagger - \hat{a}_j^\dagger \hat{a}_i$$

- Difference between normal ordered form and original ordering.

Wick's Theorem

- For operators with more than two excitations, sum over all possible contractions:

$$a_i a_j a_k^\dagger a_l^\dagger =: a_i a_j a_k^\dagger a_l^\dagger : + \sum_{\substack{one \\ cont.}} : a_i a_j a_k^\dagger a_l^\dagger : + \sum_{\substack{two \\ cont.}} : a_i a_j a_k^\dagger a_l^\dagger :$$

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$$=: a_i a_j a_k^\dagger a_l^\dagger :$$

$$-\delta_{ik} : a_j a_l^\dagger : +\delta_{il} : a_j a_k^\dagger : +\delta_{jk} : a_i a_l^\dagger : -\delta_{jl} : a_i a_k^\dagger :$$

$$-\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}$$

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- A series of normal ordered operators, with factors determined from the properties of the creation and annihilation operators.

Wick's Theorem

- Rewrite sum over matrix elements for a two electron operator using Wick's theorem.

$$\sum_I \langle I | a_i a_j a_k^\dagger a_l^\dagger | K \rangle$$

$$S_I, S_K \subset S_{act}$$

$$|I\rangle = \left(\Pi_q^{q \in S_I} a_q^\dagger\right)|0\rangle$$

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Normal ordered terms will vanish if any of the indices are not in the S_I or S_K.

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Normal ordered terms will vanish if any of the indices are not in the **active** space.

$$S_I, S_K \subset S_{act}$$

$$|I\rangle = \left(\Pi_{\mathbf{q}}^{\mathbf{q} \in S_I} a_\mathbf{q}^\dagger \right) |0\rangle$$

$$|K\rangle = \left(\Pi_{\mathbf{r}}^{\mathbf{r} \in S_K} a_\mathbf{r}^\dagger \right) |0\rangle$$

I and K are determinants in the **active** space

Wick's Theorem

- Introduce rdm derivatives for terms with active indices:

$$\sum_I c_I^\dagger \langle I | a_{\mathbf{i}} a_{\mathbf{j}} a_{\mathbf{k}}^\dagger a_{\mathbf{l}}^\dagger | K \rangle$$

$$= \langle I | c_I^\dagger \sum_I \Big(: a_{\mathbf{i}} a_{\mathbf{j}} a_{\mathbf{k}}^\dagger a_{\mathbf{l}}^\dagger : - \delta_{\mathbf{ik}} : a_{\mathbf{j}} a_{\mathbf{l}}^\dagger : + \delta_{\mathbf{il}} : a_{\mathbf{j}} a_{\mathbf{k}}^\dagger : + \delta_{\mathbf{jk}} : a_{\mathbf{i}} a_{\mathbf{l}}^\dagger : - \delta_{\mathbf{jl}} : a_{\mathbf{i}} a_{\mathbf{k}}^\dagger : - \delta_{\mathbf{ik}} \delta_{\mathbf{jl}} + \delta_{\mathbf{il}} \delta_{\mathbf{jk}} \Big) | K \rangle$$

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RDM derivatives

$$\Gamma^K_{\mathbf{klij}} = \sum_I c_I^\dagger \langle I | : a_j a_i a_k^\dagger a_l^\dagger : | K \rangle$$

$$\Gamma^K_{\mathbf{ij}} = \sum_I c_I^\dagger \langle I | : a_j a_i^\dagger : | K \rangle$$

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$$\sum_I c_I^\dagger \langle I | a_{\mathbf{i}} a_{\mathbf{j}} a_{\mathbf{k}}^\dagger a_{\mathbf{l}}^\dagger | K \rangle$$

$$= \Gamma^K_{\mathbf{klij}} - \delta_{\mathbf{ik}}\Gamma^K_{\mathbf{lj}} + \delta_{\mathbf{il}}\Gamma^K_{\mathbf{kj}} + \delta_{\mathbf{jk}}\Gamma^K_{\mathbf{li}} - \delta_{\mathbf{jl}}\Gamma^K_{\mathbf{ki}} - \delta_{\mathbf{ik}}\delta_{\mathbf{lj}} + \delta_{\mathbf{il}}\delta_{\mathbf{kj}}$$

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$$\sum_{\mathbf{ijkl}} \sum_{I} c_I^\dagger T_{\mathbf{ij}} h_{\mathbf{kl}} \langle I | a_{\mathbf{j}}^\dagger a_{\mathbf{i}} a_{\mathbf{k}} a_{\mathbf{l}}^\dagger | K \rangle$$

$$= \sum_{\mathbf{ijkl}} T_{\mathbf{ij}} h_{\mathbf{kl}} \left(\Gamma^K_{\mathbf{klij}} - \delta_{\mathbf{ik}} \Gamma^K_{\mathbf{lj}} + \delta_{\mathbf{il}} \Gamma^K_{\mathbf{kj}} + \delta_{\mathbf{jk}} \Gamma^K_{\mathbf{li}} - \delta_{\mathbf{jl}} \Gamma^K_{\mathbf{ki}} - \delta_{\mathbf{ik}} \delta_{\mathbf{lj}} + \delta_{\mathbf{il}} \delta_{\mathbf{kj}} \right)$$

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- Rearrange to seperate active and general indices

$$= \sum_{\mathbf{ijkl}} \Gamma^K_{\mathbf{jikl}} T_{\mathbf{ij}} h_{\mathbf{kl}} - \sum_{\mathbf{jl}} \Gamma^K_{\mathbf{lj}} \sum_{\mathbf{k}} T_{\mathbf{kj}} h_{\mathbf{kl}} + \sum_{\mathbf{jk}} \Gamma^K_{\mathbf{kj}} \sum_{\mathbf{l}} T_{\mathbf{lj}} h_{\mathbf{kl}}$$

$$+ \sum_{\mathbf{li}} \Gamma^K_{\mathbf{il}} \sum_{\mathbf{k}} T_{\mathbf{ik}} h_{\mathbf{kl}} - \sum_{\mathbf{ki}} \Gamma^K_{\mathbf{ki}} \sum_{\mathbf{l}} T_{\mathbf{il}} h_{\mathbf{kl}} + \sum_{\mathbf{kl}} (T_{\mathbf{lk}} - T_{\mathbf{kl}}) h_{\mathbf{kl}}$$

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$$= \sum_{\mathbf{ijkl}} \Gamma^K_{\mathbf{jikl}} A_{\mathbf{jikl}} - \sum_{\mathbf{jl}} \Gamma^K_{\mathbf{jl}} A'_{\mathbf{jl}} + \sum_{\mathbf{ij}} \Gamma^K_{\mathbf{jk}} A''_{\mathbf{jk}}$$

$$+ \sum_{\mathbf{il}} \Gamma^K_{\mathbf{il}} A'''_{\mathbf{il}} - \sum_{\mathbf{ik}} \Gamma^K_{\mathbf{ik}} A''''_{\mathbf{ik}} + A''''' N_{det}$$

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Calculation of CI derivatives

- Requires evaluation of terms of this form

$$\sum_{M}\sum_{\mathbf{\Omega}}\sum_{I}\sum_{\mathbf{xy}}\langle I|c^{\dagger}_{\tilde{M},I}U^{\dagger}_{MN}\lambda^{\dagger}_{LM,\mathbf{\Omega}}\hat{E}^{\dagger}_{\mathbf{\Omega}}(h(1)\hat{E}_{\mathbf{xy}}+\frac{1}{2}v(1,2)\hat{E}_{\mathbf{xy,zw}})|K\rangle$$

- This sum over **general** indices can be rewritten as a sum over **active** indices:

$$=\sum_{M}\sum_{\mathbf{ijklmnop}}\Gamma^{M,K}_{\mathbf{ij,kl,mn,op}}A_{\mathbf{ij,kl,mn,op}}$$

- Computationally efficient; can be evaluated without the need to store any eight index tensors.

- This is Jae's recent work:

Difference between relativistic and non-relativistic framework

- Alpha and beta orbitals are treated independently ➡ twice as many active orbitals.
- Alpha and beta orbitals can interact ➡ twice as many possible excitation operators.

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- Four electron density matrix is (potentially) $4^4 = 256$ times larger.

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- Determinants with difference numbers of alpha and beta electrons may interact.
- RDM derivatives could be > 256 times larger.
- This issue can be managed by use of time reversal symmetry.

CI strings

- A determinant, *I*, can be defined by a set of indices of the occupied active orbitals, e.g.,

$$S_I = \{i_1, i_2, ..., i_{N_{act,el}}\}$$

- The set of all active determinants can then be written

$$S = \{S_I | S_I \subset \{1, 2, ..., N_{act}\} \quad \text{and} \quad card(S_I) = N_{act,el}\}$$

CI strings

- Split up the CI-string space into alpha and beta subspaces:

$$S^{n_\alpha} = \{S_I^{n_\alpha} | S_I^{n_\alpha} \subset \{1, 2, ..., N_{orb}/2\} \quad \text{and} \quad card(S_I^{n_\alpha}) = n_\alpha\}$$

$$S^{n_\beta} = \{S_I^{n_\beta} | S_I^{n_\beta} \subset \{1, 2, ..., N_{orb}/2\} \quad \text{and} \quad card(S_I^{n_\beta}) = n_\beta\}$$

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- A spin-sector is the Cartesian product of an alpha and a beta subspace:

$$S^{[n_\alpha, n_\beta]} = S^{n_\alpha} \times S^{n_\beta} = \{S_I | S_I \subset \{1, 2, ..., N_{orb}\} \quad \text{and} \quad card(S_I) = n_\alpha + n_\beta\}$$

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- Combine the alpha and beta string spaces to get the full CI-string space, e.g.,

$$S = \bigcup_{i=1}^{N_{el}} S^{[(N_{el}-i),i]}$$

Non-relativistic CI-vector

Non-relativistic CI-vector only has determinants from a single spin sector:

$$|M\rangle = \sum_I c_{M,I}|I\rangle$$

$$|I\rangle \in \{\ \ |K\rangle\ \ |\ \ \langle K|\hat{s}_z|K\rangle = (X-Y)\}$$

Conf.	$[X\alpha Y\beta]$
$\|1\rangle$	c_1
$\|2\rangle$	c_2
...	...
...	...
...	...
...	...
$\|N_{det}\rangle$	$c_{N_{det}}$

Interaction between spin-sectors

Non-relativistic case:

	$[7\alpha 0\beta]$	$[6\alpha 1\beta]$	$[5\alpha 2\beta]$	$[4\alpha 3\beta]$	$[3\alpha 4\beta]$	$[2\alpha 5\beta]$	$[1\alpha 6\beta]$	$[0\alpha 7\beta]$
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Interaction between spin-sectors

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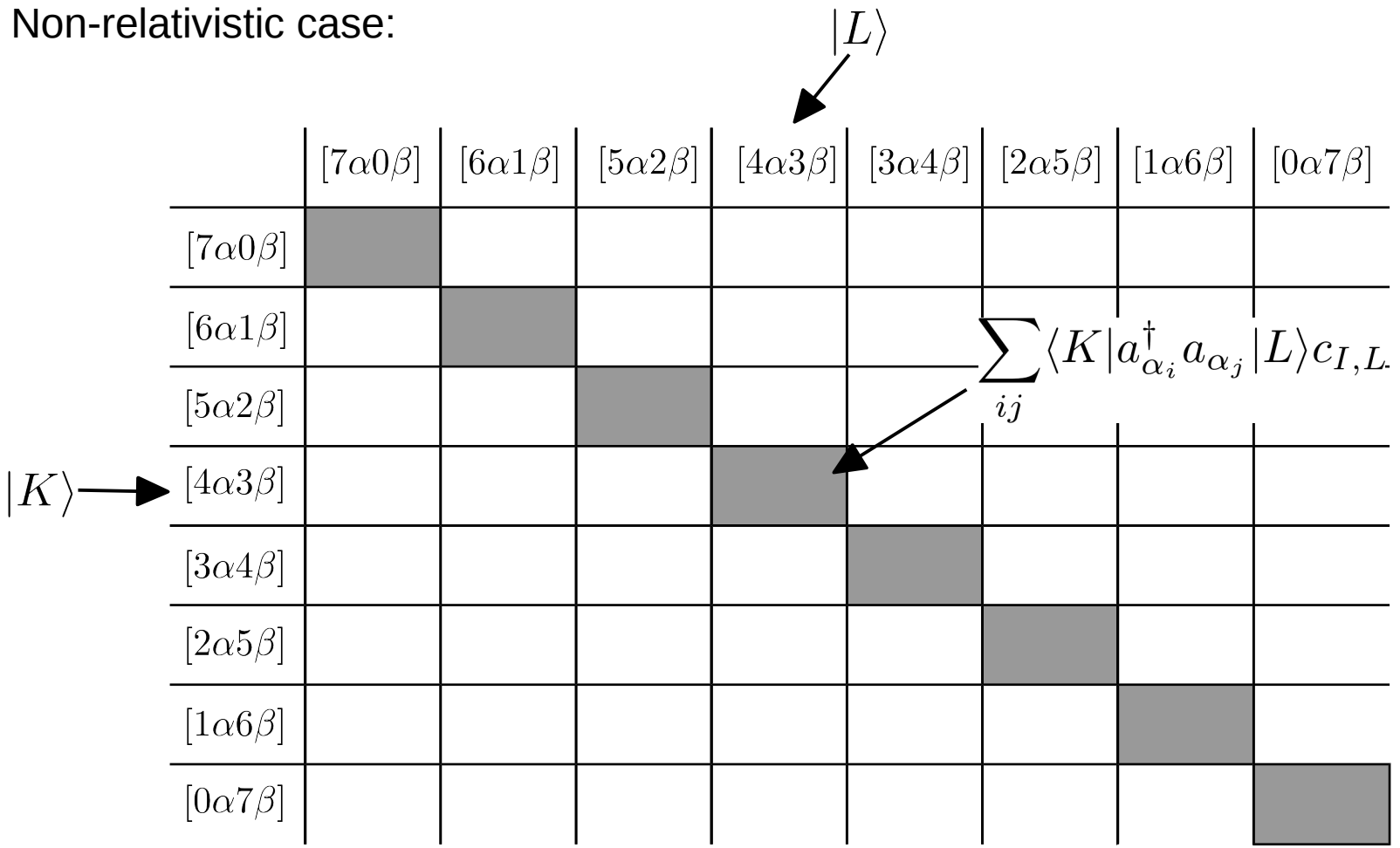


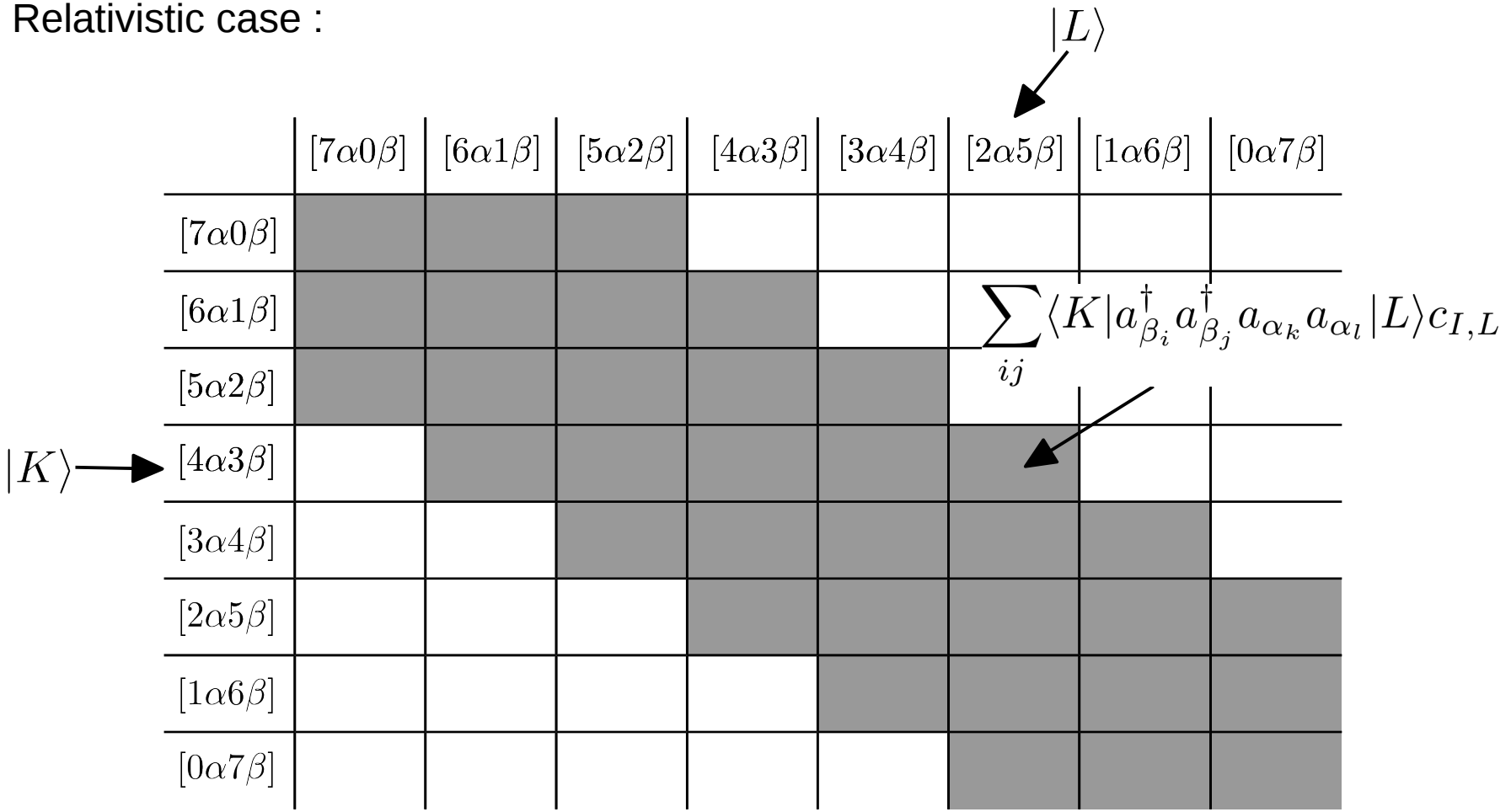
Relativistic CI-vector

Spin-orbit coupling terms results in contributions from determinants in different spin sectors:

Conf. #	Spin sectors							
	$[7\alpha 0\beta]$	$[6\alpha 1\beta]$	$[5\alpha 2\beta]$	$[4\alpha 3\beta]$	$[3\alpha 4\beta]$	$[2\alpha 5\beta]$	$[1\alpha 6\beta]$	$[0\alpha 7\beta]$
1	...	...	...	...	...	...	...	...
...	$c^{7,0}_{N_{det,7,0}}$	...	...	...	...	...	...	$c^{[0,7]}_{N_{det,[0,7]}}$
...		...	...	...	...	...	...	
			...	...	...	...		
		$c^{[6,1]}_{N_{det,[6,1]}}$	...	...	...	...	$c^{[1,6]}_{N_{det,[1,6]}}$	
			...	...	...	...		
			...	...	...	...		
				...	...			
			$c^{[5,2]}_{N_{det,[5,2]}}$	...	...	$c^{[2,5]}_{N_{det,[2,5]}}$		
				...	...			
				...	...			
				$c^{[4,3]}_{N_{det,[4,3]}}$	$c^{[3,4]}_{N_{det,[3,4]}}$			

Interaction between spin-sectors

Relativistic case :



Applying Time Reversal Symmetry

- Different kinds of excitations are connected via time reversal:

$$\hat{T}|\alpha\rangle = |\beta\rangle \qquad \hat{T}\hat{T}|\alpha\rangle = -|\alpha\rangle$$

$$\hat{T}a_x^\dagger|0\rangle = a_{\overline{x}}^\dagger|0\rangle \qquad \hat{T}\hat{T}a_x^\dagger|0\rangle = -a_x^\dagger|0\rangle$$

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- Can relate terms in different spin sectors:

$$\Gamma^K_{x_\beta y_\alpha} = \Gamma^I_{x_\alpha y_\beta}{}^*$$ where $S_I \in S^{[i_\alpha, j_\beta]}$ and $S_K \in S^{[j_\alpha, i_\beta]}$

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- Do not need both of $E_{\alpha\alpha}$ and $E_{\beta\beta}$ or both $E_{\alpha\beta}$ and $E_{\beta\alpha}$.
- Number of distinct quantities to be calculated is reduced by a factor of ~2^4.

Spin sector looping for RDM derivatives

- Define a seperate RDM for each spin sector.
- Classify excitations into four types:

$$E_{i_\alpha j_\alpha}\colon \alpha \to \alpha \qquad E_{i_\beta j_\alpha}\colon \alpha \to \beta \qquad E_{i_\alpha j_\beta}\colon \beta \to \alpha \qquad E_{i_\beta j_\beta}\colon \beta \to \beta$$

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- Classify different rdm derivatives by different combinations of theses types, e.g.,

$$\Gamma^{K,\alpha\alpha,\beta\alpha,\beta\alpha}_{ijklmn} = \sum_I c_I^\dagger \langle I | a^\dagger_{i_\alpha} a^\dagger_{j_\alpha} a^\dagger_{k_\beta} a_{l_\alpha} a_{m_\beta} a_{n_\alpha} | K \rangle$$

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- Each is the approximately the same size as a non-relativistic rdm derivative.

Applying Wick's Theorem

$$\sum_I \langle I | a_i a_j a_k^\dagger a_l^\dagger | K \rangle$$

$$= \sum_I c_I^\dagger \langle I | \Big(: a_\mathbf{i} a_\mathbf{j} a_\mathbf{k}^\dagger a_\mathbf{l}^\dagger : - \delta_\mathbf{ik} : a_\mathbf{j} a_\mathbf{l}^\dagger : + \delta_\mathbf{il} : a_\mathbf{j} a_\mathbf{k}^\dagger : + \delta_\mathbf{jk} : a_\mathbf{i} a_\mathbf{l}^\dagger : - \delta_\mathbf{jl} : a_\mathbf{i} a_\mathbf{k}^\dagger : - \delta_\mathbf{ik}\delta_\mathbf{jl} + \delta_\mathbf{il}\delta_\mathbf{jk} \Big) | K \rangle$$

Normal ordered terms will vanish if any of the indices are not in the **active** space.

Application of spin constraints

$$\sum_I c_I^\dagger \langle I | a_{\mathbf{i}_\alpha} a_{\mathbf{j}_\alpha}^\dagger a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} | K \rangle \quad \longleftarrow \alpha\alpha\beta\alpha$$

$$= \sum_I c_I^\dagger \langle I | \Big(: a_{\mathbf{i}_\alpha} a_{\mathbf{j}_\alpha}^\dagger a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} : + \delta_{\mathbf{i}_\alpha \mathbf{j}_\alpha} : a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} : - \delta_{\mathbf{i}_\alpha \mathbf{k}_\beta} : a_{\mathbf{j}_\alpha}^\dagger a_{\mathbf{l}_\alpha} :$$
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$$S_I, S_K \subset S$$

$$|I\rangle = \left(\Pi_q^{q \in S_I} a_q^\dagger \right) |0\rangle$$

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Application of spin constraints

$$\sum_I c_I^\dagger \langle I | a_{\mathbf{i}_\alpha} a_{\mathbf{j}_\alpha}^\dagger a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} | K \rangle$$

$$= \sum_I c_I^\dagger \langle I | \Big(: a_{\mathbf{i}_\alpha} a_{\mathbf{j}_\alpha}^\dagger a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} : + \delta_{\mathbf{i}_\alpha \mathbf{j}_\alpha} : a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} : - \delta_{\mathbf{j}_\alpha \mathbf{l}_\alpha} : a_{\mathbf{i}_\alpha} a_{\mathbf{k}_\beta}^\dagger : \Big) | K \rangle$$

$$S_I \subset S_{\mathbf{n}_\alpha, \mathbf{n}_\beta}$$

$$S_K \subset S_{(\mathbf{n}_\alpha + \mathbf{x}), (\mathbf{n}_\beta - \mathbf{x})}$$

$$|I\rangle = \left(\Pi_q^{q \in S_I} a_q^\dagger \right) |0\rangle$$

$$|K\rangle = \left(\Pi_r^{r \in S_K} a_r^\dagger \right) |0\rangle$$

Application of spin constraints

$$\sum_I c_I^\dagger \langle I | a_{\mathbf{i}_\alpha} a_{\mathbf{j}_\alpha}^\dagger a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} | K \rangle$$

$$= \sum_I c_I^\dagger \langle I | \Big(: a_{\mathbf{i}_\alpha} a_{\mathbf{j}_\alpha}^\dagger a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} : + \delta_{\mathbf{i}_\alpha \mathbf{j}_\alpha} : a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} : - \delta_{\mathbf{j}_\alpha \mathbf{l}_\alpha} : a_{\mathbf{i}_\alpha} a_{\mathbf{k}_\beta}^\dagger : \Big) | K \rangle$$

$S_I \subset S_{\mathbf{n}_\alpha, \mathbf{n}_\beta}$ ⟶ I and K belong to different spin sectors

$S_K \subset S_{(\mathbf{n}_\alpha + \mathbf{x}), (\mathbf{n}_\beta - \mathbf{x})}$

$$|I\rangle = \left(\Pi_q^{q \in S_I} a_q^\dagger \right) |0\rangle$$

$$|K\rangle = \left(\Pi_r^{r \in S_K} a_r^\dagger \right) |0\rangle$$

Application of spin constraints

$$\sum_I c_I^\dagger \langle I | a_{\mathbf{i}_\alpha} a_{\mathbf{j}_\alpha}^\dagger a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} | K \rangle$$

$$= \sum_I c_I^\dagger \langle I | \Big(: a_{\mathbf{i}_\alpha} a_{\mathbf{j}_\alpha}^\dagger a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} : + \delta_{\mathbf{i}_\alpha \mathbf{j}_\alpha} : a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} : - \delta_{\mathbf{j}_\alpha \mathbf{l}_\alpha} : a_{\mathbf{i}_\alpha} a_{\mathbf{k}_\beta}^\dagger : \Big) | K \rangle$$

$S_I \subset S_{\mathbf{n}_\alpha, \mathbf{n}_\beta}$

$S_K \subset S_{(\mathbf{n}_\alpha + \mathbf{x}), (\mathbf{n}_\beta - \mathbf{x})}$

$|I\rangle = \left(\Pi_q^{q \in S_I} a_q^\dagger \right) |0\rangle$

$|K\rangle = \left(\Pi_r^{r \in S_K} a_r^\dagger \right) |0\rangle$

$\longrightarrow$ I and K belong to different spin sectors

If $x > 2$ then :

$\langle I | : a_{\mathbf{i}_\alpha} a_{\mathbf{j}_\beta}^\dagger a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} : | K \rangle = 0$

Application of spin constraints

$$\sum_I c_I^\dagger \langle I | a_{\mathbf{i}_\alpha} a_{\mathbf{j}_\alpha}^\dagger a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} | K \rangle$$

$$= \sum_I c_I^\dagger \langle I | \Big(: a_{\mathbf{i}_\alpha} a_{\mathbf{j}_\alpha}^\dagger a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} : + \delta_{\mathbf{i}_\alpha \mathbf{j}_\alpha} : a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} : - \delta_{\mathbf{j}_\alpha \mathbf{l}_\alpha} : a_{\mathbf{i}_\alpha} a_{\mathbf{k}_\beta}^\dagger : \Big) | K \rangle$$

$S_I \subset S_{\mathbf{n}_\alpha, \mathbf{n}_\beta}$

$S_K \subset S_{(\mathbf{n}_\alpha + \mathbf{x}), (\mathbf{n}_\beta - \mathbf{x})}$

$|I\rangle = \left(\Pi_q^{q \in S_I} a_q^\dagger \right) |0\rangle$

$|K\rangle = \left(\Pi_r^{r \in S_K} a_r^\dagger \right) |0\rangle$

⟶ I and K belong to different spin sectors

If $x > 2$ then :

$\langle I | : a_{\mathbf{i}_\alpha} a_{\mathbf{j}_\beta}^\dagger a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} : | K \rangle = 0$

If $x > 1$ then :

$\langle I | : a_{\mathbf{i}_\alpha} a_{\mathbf{j}_\beta}^\dagger : | K \rangle = 0$

Application of spin constraints

- Rewrite as a contraction of tensors with only active indices:

$$\sum_{\mathbf{ijkl}} \sum_{I} T_{\mathbf{i}_\alpha \mathbf{j}_\beta} h_{\mathbf{k}_\beta \mathbf{l}_\alpha} c_I^\dagger \langle I | a_{\mathbf{i}_\alpha} a_{\mathbf{j}_\beta}^\dagger a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} | K \rangle$$

$$= \sum_{\mathbf{ijkl}} T_{\mathbf{i}_\alpha \mathbf{j}_\beta} h_{\mathbf{k}_\beta \mathbf{l}_\alpha} \left(\Gamma^{K,\alpha\beta\alpha\alpha}_{\mathbf{j}_\alpha \mathbf{k}_\beta \mathbf{i}_\alpha \mathbf{l}_\alpha} + \delta_{\mathbf{i}_\alpha \mathbf{j}_\alpha} \Gamma^{K,\beta\alpha}_{\mathbf{k}_\beta \mathbf{l}_\alpha} - \delta_{\mathbf{j}_\alpha \mathbf{l}_\alpha} \Gamma^{K,\beta\alpha}_{\mathbf{k}_\beta \mathbf{i}_\alpha} : \right)$$

- Which terms are included in tensors is spin sector dependent:

$$= \sum_{\mathbf{ijkl}} \Gamma^{K,\alpha\beta\alpha\alpha}_{\mathbf{j}_\alpha \mathbf{k}_\beta \mathbf{i}_\alpha \mathbf{l}_\alpha} A_{\mathbf{j}_\alpha \mathbf{k}_\beta \mathbf{i}_\alpha \mathbf{l}_\alpha} + \sum_{\mathbf{kl}} \Gamma^{K,\beta\alpha}_{\mathbf{k}_\beta \mathbf{l}_\alpha} A'_{\mathbf{k}_\beta \mathbf{l}_\alpha} + \sum_{\mathbf{ki}} \Gamma^{K,\beta\alpha}_{\mathbf{k}_\beta \mathbf{i}_\alpha} A''_{\mathbf{k}_\beta \mathbf{i}_\alpha}$$

Application of spin constraints

- Rewrite as a contraction of tensors with only active indices:

$$\sum_{\mathbf{ijkl}} \sum_{I} T_{\mathbf{i}_\alpha \mathbf{j}_\beta} h_{\mathbf{k}_\beta \mathbf{l}_\alpha} c_I^\dagger \langle I | a_{\mathbf{i}_\alpha} a_{\mathbf{j}_\beta}^\dagger a_{\mathbf{k}_\beta}^\dagger a_{\mathbf{l}_\alpha} | K \rangle$$

$$= \sum_{\mathbf{ijkl}} T_{\mathbf{i}_\alpha \mathbf{j}_\beta} h_{\mathbf{k}_\beta \mathbf{l}_\alpha} \left(\Gamma^{K,\alpha\beta\alpha\alpha}_{\mathbf{j}_\alpha \mathbf{k}_\beta \mathbf{i}_\alpha \mathbf{l}_\alpha} + \delta_{\mathbf{i}_\alpha \mathbf{j}_\alpha} \Gamma^{K,\beta\alpha}_{\mathbf{k}_\beta \mathbf{l}_\alpha} - \delta_{\mathbf{j}_\alpha \mathbf{l}_\alpha} \Gamma^{K,\beta\alpha}_{\mathbf{k}_\beta \mathbf{i}_\alpha} : \right)$$

- Which terms are included in tensors is spin sector dependent:

$$= \sum_{\mathbf{ijkl}} \Gamma^{K,\alpha\beta\alpha\alpha}_{\mathbf{j}_\alpha \mathbf{k}_\beta \mathbf{i}_\alpha \mathbf{l}_\alpha} A^{(4),\alpha\beta\alpha\alpha}_{\mathbf{j}_\alpha \mathbf{k}_\beta \mathbf{i}_\alpha \mathbf{l}_\alpha} + \sum_{\mathbf{kl}} \Gamma^{K,\beta\alpha}_{\mathbf{k}_\beta \mathbf{l}_\alpha} A^{(2),\beta\alpha}_{\mathbf{k}_\beta \mathbf{l}_\alpha}$$

Spin-unconstrained version ($\alpha\alpha\alpha\alpha$)

- Rewrite as a contraction of tensors with only active indices:

$$\sum_{\mathbf{ijkl}} \sum_{I} c_I^\dagger T_{\mathbf{ij}} h_{\mathbf{kl}} \langle I | a_{\mathbf{j}}^\dagger a_{\mathbf{i}} a_{\mathbf{k}} a_{\mathbf{l}}^\dagger | K \rangle$$

$$= \sum_{\mathbf{ijkl}} T_{\mathbf{ij}} h_{\mathbf{kl}} \left(\Gamma^K_{\mathbf{klij}} - \delta_{\mathbf{ik}} \Gamma^K_{\mathbf{lj}} + \delta_{\mathbf{il}} \Gamma^K_{\mathbf{kj}} + \delta_{\mathbf{jk}} \Gamma^K_{\mathbf{li}} - \delta_{\mathbf{jl}} \Gamma^K_{\mathbf{ki}} - \delta_{\mathbf{ik}} \delta_{\mathbf{lj}} + \delta_{\mathbf{il}} \delta_{\mathbf{kj}} \right)$$

- Which terms are included in tensors is spin sector dependent:

$$= \sum_{\mathbf{ijkl}} \Gamma^K_{\mathbf{jikl}} A_{\mathbf{jikl}} - \sum_{\mathbf{jl}} \Gamma^K_{\mathbf{jl}} A'_{\mathbf{jl}} + \sum_{\mathbf{ij}} \Gamma^K_{\mathbf{jk}} A''_{\mathbf{jk}} + \sum_{\mathbf{il}} \Gamma^K_{\mathbf{il}} A'''_{\mathbf{il}} - \sum_{\mathbf{ik}} \Gamma^K_{\mathbf{ik}} A''''_{\mathbf{ik}} + A''''' N_{det}$$

Spin-unconstrained version ($\alpha\alpha\alpha\alpha$)

- Rewrite as a contraction of tensors with only active indices:

$$\sum_{\mathbf{ijkl}} \sum_{I} c_I^\dagger T_{\mathbf{ij}} h_{\mathbf{kl}} \langle I | a_{\mathbf{j}}^\dagger a_{\mathbf{i}} a_{\mathbf{k}} a_{\mathbf{l}}^\dagger | K \rangle$$

$$= \sum_{\mathbf{ijkl}} T_{\mathbf{ij}} h_{\mathbf{kl}} \left(\Gamma^K_{\mathbf{klij}} - \delta_{\mathbf{ik}} \Gamma^K_{\mathbf{lj}} + \delta_{\mathbf{il}} \Gamma^K_{\mathbf{kj}} + \delta_{\mathbf{jk}} \Gamma^K_{\mathbf{li}} - \delta_{\mathbf{jl}} \Gamma^K_{\mathbf{ki}} - \delta_{\mathbf{ik}} \delta_{\mathbf{lj}} + \delta_{\mathbf{il}} \delta_{\mathbf{kj}} \right)$$

- Which terms are included in tensors is spin sector dependent:

$$= \sum_{\mathbf{ijkl}} \Gamma^K_{\mathbf{jikl}} A^{(4)}_{\mathbf{jikl}} + \sum_{\mathbf{jl}} \Gamma^K_{\mathbf{jl}} A^{(2)}_{\mathbf{jl}} + A^{(0)}_{\mathbf{jk}}$$

Spin-unconstrained version ($\alpha\alpha\alpha\alpha$)

- Rewrite as a contraction of tensors with only active indices:

$$\sum_{\mathbf{ijkl}} \sum_{I} c_I^\dagger T_{\mathbf{ij}} h_{\mathbf{kl}} \langle I | a_{\mathbf{j}}^\dagger a_{\mathbf{i}} a_{\mathbf{k}} a_{\mathbf{l}}^\dagger | K \rangle$$

$$= \sum_{\mathbf{ijkl}} T_{\mathbf{ij}} h_{\mathbf{kl}} \left(\Gamma^K_{\mathbf{klij}} - \delta_{\mathbf{ik}} \Gamma^K_{\mathbf{lj}} + \delta_{\mathbf{il}} \Gamma^K_{\mathbf{kj}} + \delta_{\mathbf{jk}} \Gamma^K_{\mathbf{li}} - \delta_{\mathbf{jl}} \Gamma^K_{\mathbf{ki}} - \delta_{\mathbf{ik}} \delta_{\mathbf{lj}} + \delta_{\mathbf{il}} \delta_{\mathbf{kj}} \right)$$

- Which terms are included in tensors is spin sector dependent:

$$= \sum_{\mathbf{ijkl}} \Gamma^K_{\mathbf{jikl}} A^{(4)}_{\mathbf{jikl}} + \sum_{\mathbf{jl}} \Gamma^K_{\mathbf{jl}} A^{(2)}_{\mathbf{jl}} + A^{(0)}_{\mathbf{jk}}$$

Spin dependence of integral tensors

- Expressions to calculate molecular orbital tensors are spin-sector and spin excitation dependent

$$A^{(2),\alpha\alpha\alpha\alpha} = -\sum_{\mathbf{ij}} \Gamma^{K}_{\mathbf{j}_\alpha \mathbf{l}_\alpha} A'_{\mathbf{j}_\alpha \mathbf{l}_\alpha} + \sum_{\mathbf{ij}} \Gamma^{K}_{\mathbf{j}_\alpha \mathbf{l}_\alpha} A''_{\mathbf{j}_\alpha \mathbf{l}_\alpha} + \sum_{\mathbf{ij}} \Gamma^{K}_{\mathbf{j}_\alpha \mathbf{l}_\alpha} A'''_{\mathbf{j}_\alpha \mathbf{l}_\alpha} - \sum_{\mathbf{ij}} \Gamma^{K}_{\mathbf{j}_\alpha \mathbf{l}_\alpha} A''''_{\mathbf{j}_\alpha \mathbf{l}_\alpha}$$

$$A^{(2),\alpha\alpha\beta\alpha} = \sum_{\mathbf{kl}} \Gamma^{K,\beta\alpha}_{\mathbf{k}_\beta \mathbf{l}_\alpha} A'''''_{\mathbf{k}_\beta \mathbf{l}_\alpha} + \sum_{\mathbf{ki}} \Gamma^{K,\beta\alpha}_{\mathbf{k}_\beta \mathbf{i}_\alpha} A'''''_{\mathbf{k}_\beta \mathbf{i}_\alpha}$$

- The expressions for the tensors change by more than just the indexes.

Modifications to SMITH3

- This behaviour of $A^{\beta\alpha\alpha\beta\alpha\beta}_{ij,kl,mn}$ is specific to the spin-sector looping case.
- To accomodate it, SMITH needs to be adapted in the following ways:
    - Enable use of multiple combinations of different indices for alpha and beta spin sectors.
    - Remove spin-dependence.
    - Incorporate spin-sector dependence of summation of molecular orbital tensors.
    - Incorporate spin-excitation dependence of summation of molecular orbital tensors.

4-component vs 2-component

- Douglas-Kroll-Hess second order approach is an effective way to include relativistic effects.
- Works by (approximately) block diagonalizing the 4-component Hamiltonian.

$$[\hat{H}^{DKH2}] = [\hat{\epsilon}_2]^{\dagger}_{s,l}[\hat{\epsilon}_1]^{\dagger}_{s,l} \begin{bmatrix} [\hat{H}]_{ll} & [\hat{H}]_{ls} \\ [\hat{H}]_{sl} & [\hat{H}]_{ss} \end{bmatrix} [\hat{\epsilon}_1]_{s,l}[\hat{\epsilon}_2]_{s,l} = \begin{bmatrix} [\hat{H}']_{ll} & 0 \\ 0 & [\hat{H}']_{ss} \end{bmatrix}$$

$$\hat{H}^{DKH2} = \hat{\epsilon}_2^{\dagger}\hat{\epsilon}_1^{\dagger}\hat{H}\hat{\epsilon}_1\hat{\epsilon}_2$$

- Transformations $\hat{\epsilon}_1$ and $\hat{\epsilon}_2$ are dependent upon the Hamiltonian.
- Derivatives with respect to a change in the Hamiltonian require derivatives of these transformations.
- This is often computationally expensive, and in the case of a perturbation by a vector potential, notoriously difficult to program.

Hylleras functional

- First order terms in the perturbation expansion:

$$\hat{H}_0|\Psi^{(1)}\rangle + \hat{V}|\Psi^{(0)}\rangle = E^{(0)}|\Psi^{(1)}\rangle + E^{(1)}|\Psi^{(0)}\rangle$$

$$\langle\Psi^{(1)}|\hat{H}_0 - E_0|\Psi^{(1)}\rangle + \langle\Psi^{(1)}|\hat{V} - E^{(1)}|\Psi^{(0)}\rangle = 0$$

$$E^{(1)} = \langle\Psi^{(0)}|\hat{V}|\Psi^{(0)}\rangle$$

$$E^{(2)} = \langle\Psi^{(0)}|\hat{V}|\Psi^{(1)}\rangle$$

$$E^{(2)} = \langle\Psi^{(0)}|\hat{V}|\Psi^{(1)}\rangle + \langle\Psi^{(1)}|\hat{H}_0 - E_0|\Psi^{(1)}\rangle + \langle\Psi^{(1)}|\hat{V} - E^{(1)}|\Psi^{(0)}\rangle$$

$$\langle\Psi^{(0)}|\Psi^{(1)}\rangle = 0$$

$$E^{(2)} = 2\Re e[\langle\Psi^{(0)}|\hat{V}|\Psi^{(1)}\rangle] + \langle\Psi^{(1)}|\hat{H}_0 - E_0|\Psi^{(1)}\rangle$$

$$|\Psi_L^{(1)}\rangle = \sum_N \hat{T}_{LN}|\tilde{N}\rangle = \sum_N \sum_\Omega \hat{E}_\Omega|\tilde{N}\rangle T_{LN}$$

XMS-CASPT2

- XMS-CASPT2 : Extended multistate complete active space second order perturbation theory.
- Initial wavefunction from a CASSCF calculation:

$$|M\rangle = \sum_I c_{I,M}|I\rangle$$

- Generate new set of states by diagonalizing the Fock operator in the space formed by these states:

$$\sum_M \langle L|\hat{f}|M\rangle U_{MN} = U_{LN}\tilde{E}_N \rightarrow |\tilde{M}\rangle = \sum_N U_{MN}|N\rangle$$

XMS-CASPT2

- First-order perturbation to the wavefunction is expanded in basis of excited determinants:

$$|\Psi_L^{(1)}\rangle = \sum_N \hat{T}_{LN}|\tilde{N}\rangle = \sum_N \sum_\Omega \hat{E}_\Omega |\tilde{N}\rangle T_{LN}$$

Sum over states in CASSCF reference space

XMS-CASPT2

- First-order perturbation to the wavefunction is expanded in basis of excited determinants:

$$|\Psi_L^{(1)}\rangle = \sum_N \hat{T}_{LN}|\tilde{N}\rangle = \sum_N \sum_\Omega \hat{E}_\Omega |\tilde{N}\rangle T_{LN}$$

T amplitudes

Single and double excitations between inactive, active and virtual orbitals.

Excitation operator

XMS-CASPT2

- First-order perturbation to the wavefunction is expanded in basis of excited determinants:

$$|\Psi_L^{(1)}\rangle = \sum_N \hat{T}_{LN}|\tilde{N}\rangle = \sum_N \sum_\Omega \hat{E}_\Omega |\tilde{N}\rangle T_{LN}$$

- The T amplitudes for a given state are those which satisfy

$$\sum_N \langle \tilde{M}|\hat{E}_\Omega^\dagger (\hat{f} - E_L^{(0)})\hat{T}_{LN}|\tilde{N}\rangle + \langle \tilde{M}|\hat{E}_\Omega^\dagger \hat{H}|\tilde{L}\rangle = 0$$

XMS-CASPT2

- First-order perturbation to the wavefunction is expanded in basis of excited determinants:

$$|\Psi_L^{(1)}\rangle = \sum_N \hat{T}_{LN}|\tilde{N}\rangle = \sum_N \sum_\Omega \hat{E}_\Omega|\tilde{N}\rangle T_{LN}$$

- The T amplitudes for a given state are those which satisfy

$$\sum_N \langle\tilde{M}|\hat{E}_\Omega^\dagger(\hat{f} - E_L^{(0)})\hat{T}_{LN}|\tilde{N}\rangle + \langle\tilde{M}|\hat{E}_\Omega^\dagger\hat{H}|\tilde{L}\rangle = 0$$

State averaged
Fock Matrix

Zeroth order
energy of state L

XMS-CASPT2

- XMS-CASPT2 energy
  - T amplitudes.
  - Orbital rotations.
  - CI coefficients.
-

XMS-CASPT2

Spin-orbit coupling terms results in coupling between determinants from different spin sectors:

Conf.	$[7\alpha 0\beta]$	$[6\alpha 1\beta]$	$[5\alpha 2\beta]$	$[4\alpha 3\beta]$	$[3\alpha 4\beta]$	$[2\alpha 5\beta]$	$[1\alpha 6\beta]$	$[0\alpha 7\beta]$
$\|1\rangle$	...	...	...	...	...	...	...	...
	$c^{7,0}_{N_{det},7,0}$	...	...	...	...	...	...	$c^{[0,7]}_{N_{det},[0,7]}$
		...	...	...	...	...	...	
			...	...	...	...		
		$c^{[6,1]}_{N_{det},[6,1]}$	...	...	...	...	$c^{[1,6]}_{N_{det},[1,6]}$	
			...	...	...	...		
			...	...	...	...		
				...	...			
			$c^{[5,2]}_{N_{det},[5,2]}$	...	...	$c^{[2,5]}_{N_{det},[2,5]}$		
				...	...			
				...	...			
				$c^{[4,3]}_{N_{det},[4,3]}$	$c^{[3,4]}_{N_{det},[3,4]}$			

XMS-CASPT2

Solve for initial XMS-CASPT2 energy

↓

Solve for Lamda coefficients

↓

$$Y_{xy} = \frac{\partial L}{\partial \kappa_x y}$$

$$d^{(1)}_{xy}, d^{(2)}_{xy}, D^{(1)}_{xy,zw}$$

$$y_{I,N} = \frac{\partial L_{PT2}}{\partial c_{I,N}}$$

Solve Z-vector equation

Difference between relativistic and non-relativistic framework

- Alpha and beta orbitals are treated seperately.
- Different spin-sectors can interact via spin-orbit coupling and spin-other-orbit interactions.
- Potentially much more expensive.

$$\Theta^{\tilde{M},K}_{ij,kl,mn,op} = \sum_{I} c^{\dagger}_{I,\tilde{M}} \langle I|\hat{E}_{ij,kl,mn,op})|K\rangle$$

Time reversal symmetry

- Can substantially reduce the number of rdm derivatives which need to be calculated:

$$\hat{T}|\alpha\rangle = |\beta\rangle \qquad \hat{T}\hat{T}|\alpha\rangle = -|\alpha\rangle$$

$$\hat{T}a_x^\dagger|0\rangle = a_{\overline{x}}^\dagger|0\rangle \qquad \hat{T}\hat{T}a_x^\dagger|0\rangle = -a_x^\dagger|0\rangle$$

$$\langle I|a_{x_\beta}^\dagger a_{y_\alpha}|K\rangle = \left(\hat{T}\langle I|a_{x_\alpha}^\dagger a_{y_\beta}|K\rangle\right)^*$$

$$\Gamma_{x_\beta y_\alpha} = \langle I|E_{x_\beta y_\alpha}|K\rangle = \left(\hat{T}\langle I|E_{x_\beta y_\alpha}|K\rangle\right)^* = \Gamma^*_{x_\alpha y_\beta}$$

CI seperation

- Rewrite so no explicit orbital indices

$$\sum_{I}^{S_I \in \{S\}} \sum_{ik} T_{ik} \sum_{jl} h_{jl} c_I^\dagger \langle 0| \left(\Pi_q^{S_I} a_q \right) a_i a_j a_k^\dagger a_l^\dagger \left(\Pi_r^{S_K} a_r^\dagger \right) |0\rangle$$

- Define a pair of determinants

$$|I\rangle = a_x^\dagger a_y |I'\rangle \rightarrow S_I = S_{I'} - k + j$$

$$\sum_{ik} T_{ik} \sum_{jl} h_{jl} c_{I'}^\dagger \langle 0| \left(\Pi_q^{S_{I'}} a_q \right) a_i a_j a_k^\dagger a_l^\dagger \left(\Pi_r^{S_K} a_r^\dagger \right) |0\rangle$$

$$= \sum_{ik} T_{ik} \sum_{jl} h_{jl} c_{I'}^\dagger \langle 0| \left(\Pi_q^{S_I} a_q \right) a_x a_y^\dagger a_i a_j a_k^\dagger a_l^\dagger \left(\Pi_r^{S_K} a_r^\dagger \right) |0\rangle$$

CI seperation

- Rewrite using Wick's theorem:

$$\sum_{I}^{S_I \in \{S\}} \sum_{ik} T_{ik} \sum_{jl} h_{jl} c_I^\dagger \langle 0 | \left(\Pi_q^{S_I} a_q \right) a_i a_j a_k^\dagger a_l^\dagger \left(\Pi_r^{S_K} a_r^\dagger \right) | 0 \rangle$$

$$= \sum_{I}^{S_I \in S} \sum_{ik} T_{ik} \sum_{jl} h_{jl} c_I^\dagger (\theta_{I,i}^+ \theta_{I,j}^+ \theta_{K,k}^- \theta_{K,l}^- - \delta_{ik} \theta_{K,j}^- \theta_{I,l}^+ + \delta_{il} \theta_{K,j}^- \theta_{I,k}^+ + \delta_{jk} \theta_{K,i}^- \theta_{I,l}^+ - \delta_{jl} \theta_{K,i}^- \theta_{I,k}^+ - \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$$

$$\theta_{I,x}^+ = \begin{cases} 1 & \text{if} \quad x \notin S_I \\ 0 & \text{if} \quad x \in S_I \end{cases}$$

$$\theta_{K,x}^- = \begin{cases} 1 & \text{if} \quad x \in S_K \\ 0 & \text{if} \quad x \notin S_K \end{cases}$$

CI seperation

- Rewrite so no explicit orbital indices

$$\sum_{I}^{S_I \in \{S\}} \sum_{ik} T_{ik} \sum_{jl} h_{jl} c_I^\dagger \langle 0| \left(\Pi_q^{S_I} a_q\right) \left(\Pi_m^{O_\mu} a_m\right) \left(\Pi_n^{O_\nu} a_n^\dagger\right) \left(\Pi_r^{S_K} a_r^\dagger\right) |0\rangle$$

- Define a pair of determinants

$$|I\rangle = a_x^\dagger a_y |I'\rangle \rightarrow S_I = S_{I'} - k + j$$

CI seperation

- Rewrite so no explicit orbital indices

$$\sum_{I}^{S_I \in \{S\}} \sum_{ik} T_{ik} \sum_{jl} h_{jl} c_I^\dagger \langle 0| \left(\Pi_q^{S_I} a_q\right) \left(\Pi_m^{O_\mu} a_m\right) \left(\Pi_n^{O_\nu} a_n^\dagger\right) \left(\Pi_r^{S_K} a_r^\dagger\right) |0\rangle$$

- Define a pair of determinants

$$|I\rangle = a_x^\dagger a_y |I'\rangle \rightarrow S_I = S_{I'} - k + j$$

CI seperation

- The determinants I and K can be defined by a set of indices of the occupied active orbitals, e.g.,

$$S = \{I_i I_i, ..., I_{N_{act,el}}\}$$

- The set of all active determinants can then be written

$$\{S_I | S_I \subset \{1, 2, ..., N_{act}\} \quad \text{and} \quad card(S_I) = N_{act,el}\}$$

- Replace the sum over determinants with a sum over these sets

$$\sum_I \sum_{ij} T_{ik} \sum_{jl} h_{jl} \langle 0 | \left(\Pi_q a_{I_q} \right) a_i a_j a_k^\dagger a_l^\dagger \left(\Pi_r a_{K_r}^\dagger \right) | 0 \rangle$$

CI seperation

- The determinants I and K can be defined by a set of indices of the occupied active orbitals, e.g.,

$$S = \{I_i I_i, ..., I_{N_{act,el}}\}$$

- The set of all active determinants can then be written

$$\{S_I | S_I \subset \{1, 2, ..., N_{act}\} \quad \text{and} \quad card(S_I) = N_{act,el}\}$$

- Replace the sum over determinants with a sum over these sets

$$\sum_I \sum_{ij} T_{ik} \sum_{jl} h_{jl} c_I^\dagger \langle 0| \left(\Pi_q^{\in S_I} a_q \right) a_i a_j a_k^\dagger a_l^\dagger \left(\Pi_r^{\in S_K} a_r^\dagger \right) |0\rangle$$

Smith procedure

- Define base operators from which all terms will be built:

```
shared_ptr<Operator> t2dagger1 = make_shared<Op>("t2dagger", _X, _C, _X, _X);
```

- These consist of a set of coefficients and a some labels specifying excitation ranges.
- These excitation indices either specify an element of the T or lambda vectors, or specfiy a block of there specified operator.
- The excitation ranges are of type “index” but they are not actual indexes themselves, just strings corresponding to labels (at least initially).
- Then make lists of combinations of these operators, e.g.

```
list<shared_ptr<Operator>> da9 = {proje, t2dagger1, ex_1b, l20};
```

Smith procedure

- This list of operators is then used to construct a diagram:

```
auto dda0 = make_shared<Diagram>(da0, 1, "");
```

- By calling different members of the diagram class we can construct the terms necessary for evaluation of all the terms in the perturbation diagram associated with this set of operators.

- We can then combine several diagrams to construct an Equation :

```
auto eda0 = make_shared<Equation>(dda0, theory);
```

- This has functions to identify like terms in the different diagrams, which prevents similar terms from being evaluated.

- Note that in most cases each diagram only ranges over a subset of all the orbitals in which we are interested, whereas the equation ranges over all orbitals of interest.

Smith procedure

- Finally we construct the rdm_ for each of the diagrams included in our equations.

```
edb0->active();
```

- This uses the indices from the diagrams, as well as whether we are dealing normal rdms or rdm derivatives.
- The objects defined thus far completely outline the problem to be solved, but at present they are little more than a collection of names of opearators and index ranges.
- To generate the code structure we use our Equation to construct a Residual object.
- The Residual class is derived from Tree .
- Tree loops over each of the diagrams in the equation and for each diagram constructs a ListTensor; a list containing all the information about (indices, operator type and ordering etc.,) the tensor in that diagram.

CI strings

- Split up the CI-string space into alpha and beta subspaces:

$$S^{n_\alpha} = \{S_I^{n_\alpha} | S_I^{n_\alpha} \subset \{1, 2, ..., N_{orb}\} \quad \text{and} \quad card(S_I^{n_\alpha}) = n_\alpha\}$$

$$S^{n_\beta} = \{S_I^{n_\beta} | S_I^{n_\beta} \subset \{1, 2, ..., N_{orb}\} \quad \text{and} \quad card(S_I^{n_\beta}) = n_\beta\}$$

$$S_I = S_I^{n_\alpha} \cup S_I^{n_\beta}$$

- Define spin-sector as the Cartesian product of an alpha and a beta subspace:

$$S^{[n_\alpha, n_\beta]} = S^{n_\alpha} \cup S^{n_\beta} \qquad \text{where} \qquad n_\alpha + n_\beta = N_{el}$$

- Combine the alpha and beta string spaces to get the full CI-string space, e.g.,

$$S = \bigcup_{i=1}^{N_{el}} \{S^{(N_{el}-i)_\alpha} \times S^{i_\beta}\} = \bigcup_{i=1}^{N_{el}} S^{[(N_{el}-i), i]}$$

Wick's Theorem

- For operators with more than two excitations, sum over all possible contractions:

$$a_i a_j a_k^\dagger a_l^\dagger =: a_i a_j a_k^\dagger a_l^\dagger : + \sum_{\substack{one \\ cont.}} : a_i a_j a_k^\dagger a_l^\dagger : + \sum_{\substack{two \\ cont.}} : a_i a_j a_k^\dagger a_l^\dagger :$$

$$=: a_i a_j a_k^\dagger a_l^\dagger :$$

$$+ : a_i a_j a_k^\dagger a_l^\dagger : - \delta_{ik} : a_j a_l^\dagger : + \delta_{il} : a_j a_k^\dagger : + \delta_{jk} : a_i a_l^\dagger : - \delta_{jl} : a_i a_k^\dagger : + : a_i a_j a_k^\dagger a_l^\dagger :$$

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$$=: a_i a_j a_k^\dagger a_l^\dagger :$$

$$-\delta_{ik} : a_j a_l^\dagger : +\delta_{il} : a_j a_k^\dagger : +\delta_{jk} : a_i a_l^\dagger : -\delta_{jl} : a_i a_k^\dagger :$$

CI strings

- A determinant, I, can be defined by a set of indices of the occupied active orbitals, e.g.,

$$S_I = \{i_1, i_2, ..., I_{N_{act,el}}\}$$

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- The set of all active determinants can then be written

$$S = \{S_I | S_I \subset \{1, 2, ..., N_{act}\} \text{ and } card(S_I) = N_{act,el}\}$$