Relativistic XMS-CASPT2

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Shiozaki group meeting
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Properties in XMS-CASPT2

- A Lagrangian is defined such that:

$$L(\mathbf{t}, \mathbf{c}, \mathbf{z}, \boldsymbol{\lambda}) = E(\mathbf{t}, \mathbf{c}) + \mathbf{z}^{\dagger}\mathbf{g}(\mathbf{c}) + \boldsymbol{\lambda}^{\dagger}\mathbf{g}'(\mathbf{t})$$

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Coefficients from
CASSCF calculation

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Amplitudes from CASPT2

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Conditions from CASSCF

Lagrange multipliers associated
with conditions from CASSCF

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- Define the stationary conditions:

$$\frac{\partial L}{\partial z_\mu} = 0$$

$$\frac{\partial L}{\partial \lambda_\mu} = 0$$

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- Define the stationary conditions:

$$\frac{\partial L}{\partial z_\mu} = 0 \qquad \frac{\partial L}{\partial c_\mu} = \frac{\partial E}{\partial c_\mu} + \sum_\nu z_\nu \left(\frac{\partial g_\nu}{\partial c_\mu} \right) = 0$$

$$\frac{\partial L}{\partial \lambda_\mu} = 0 \qquad \frac{\partial L}{\partial t_\mu} = \frac{\partial E}{\partial t_\mu} + \sum_\nu \lambda_\nu \left(\frac{\partial g'_\nu}{\partial t_\mu} \right) = 0$$

XMS-CASPT2

- Solve two further equations to obtain Lagrange multipliers:
  - The Lambda equation to obtain λ_{MN}.
  - The Z-vector equation to obtain $\mathbf{Z}$, $\mathbf{X}$, $\mathbf{z}_N$, z_{ij}^c, and x_N.

Z-vector and Lambda equations

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  - The Lambda equation to obtain λ_{MN} .
  - The Z-vector equation to obtain $\mathbf{Z}$, $\mathbf{X}$, $\mathbf{z}_N$, z_{ij}^c, and x_N .

- To solve the Z-vector equation we must calculate:

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

Derivative of the Lagrangian with respect to CASSCF reference coefficients

CI derivatives

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

CI derivatives

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CASSCF reference state

Determinant in CAS

CI derivatives

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

CASSCF reference state

Determinant in CAS

pth eigenvector of effective XMS-CASPT2 Hamiltonian

CI derivatives

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

CI derivatives

$$
\begin{aligned}
\frac{\partial L}{\partial \tilde{c}_{Q,K}} &= \sum_M \langle \tilde{M}|\hat{H}|K\rangle R^*_{MP} R_{QP} + \sum_N \langle K|\hat{H}|\tilde{N}\rangle R^*_{QP} R_{KP} \\
&+ \sum_L R^*_{LP} \left(\sum_M \langle \tilde{M}|\hat{T}^\dagger_{LM}\hat{H}|K\rangle R_{QP} + \sum_N \langle K|\hat{T}^\dagger_{LQ}\hat{H}|\tilde{N}\rangle R_{NP} \right) \\
&- E_s \sum_L \left(\sum_M \langle \tilde{M}|\hat{T}^\dagger_{LM}\hat{T}_{LQ}|K\rangle + \sum_N |\hat{T}^\dagger_{LQ}\hat{T}_{LN}|\tilde{N}\rangle \right) \\
&+ \sum_L \left(\sum_M \langle \tilde{M}|\hat{\lambda}^\dagger_{LM}(\hat{f} - \epsilon^{(0)}_L + \epsilon_s)\hat{T}_{LQ}|K\rangle + \sum_N |\hat{\lambda}^\dagger_{LQ}(\hat{f} - \epsilon^{(0)}_L + \epsilon_s)\hat{T}_{LN}|\tilde{N}\rangle \right) \\
&+ \sum_{rs} \Big(\langle K|\hat{E}_{rs}|\tilde{M}\rangle + \langle \tilde{M}|\hat{E}_{rs}|K\rangle \Big) [W_M \mathbf{g}(\mathbf{d}^{(2)}) - N_M \mathbf{f}]_{rs}
\end{aligned}
$$

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\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} \\
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&- 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} \left(\langle K | \hat{E}_{rs} | \tilde{M} \rangle + \langle \tilde{M} | \hat{E}_{rs} | K \rangle \right) [W_M \mathbf{g}(\mathbf{d}^{(2)}) - N_M \mathbf{f}]_{rs}
\end{aligned}
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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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$$\langle \tilde{M} | \hat{\lambda}_{MN} \hat{H} | K \rangle$$

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

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

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

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

Calculation of CI derivatives

- Requires evaluation of terms of this form

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

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

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

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

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

Calculation of CI derivatives

- Requires evaluation of terms of this form

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

- Can be rewritten as a contraction of two tensors:

Calculation of CI derivatives

- Requires evaluation of terms of this form

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

- Can be rewritten as a contraction of two tensors:

$$=\sum_{M}\sum_{ijklmnop}\langle\tilde{M}|\hat{E}_{ij,kl,mn,op}|J\rangle A_{ij,kl,mn,op}$$

Calculation of CI derivatives

- Requires evaluation of terms of this form

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

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- All the indices only range over the **active** orbitals.

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- Can be rewritten as a contraction of two tensors:

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- All the indices only range over the **active** orbitals.
- 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

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

Calculation of CI derivatives

- Requires evaluation of terms of this form

$$\sum_M \sum_I c^{\dagger}_{I,\tilde{M}} \langle I | \hat{E}_{ij,kl,mn,op}) | K \rangle A_{ij,kl,mn,op}$$

$$= \Gamma^K_{ij,kl,mn,op} A_{ij,kl,mn,op}$$

Calculation of CI derivatives

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Reduced density matrix derivative

Weighted MO integrals

Calculation of CI derivatives

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Reduced density matrix derivative

Weighted MO 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.

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.

Non-relativistic CI-vector

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

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

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

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

Interaction between determinants from different spin sectors: $\langle L | v_{xy,zw} \hat{E}_{ey,zw} | K \rangle$

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

Non-relativistic case:

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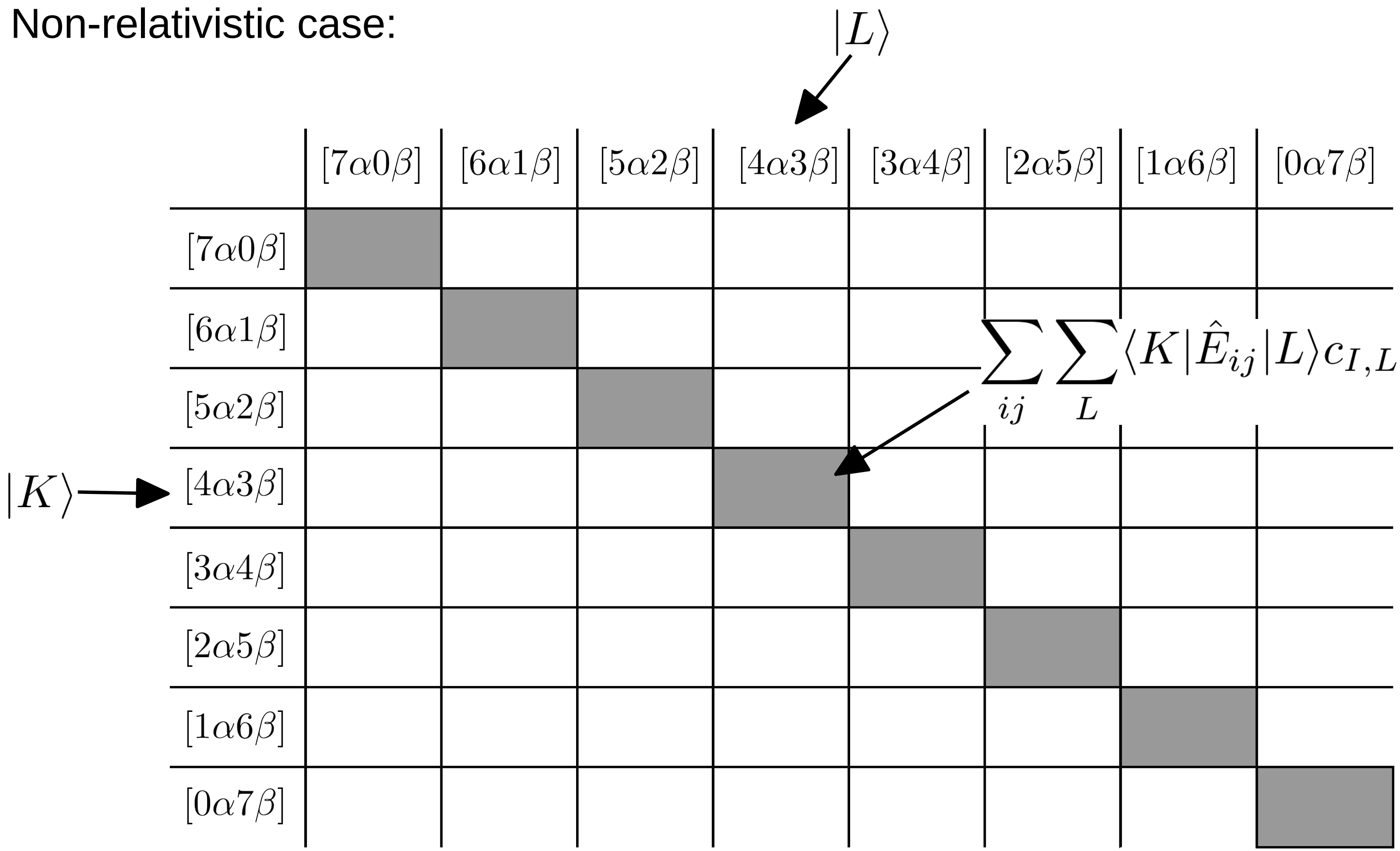
Interaction between spin-sectors

Non-relativistic case:



Interaction between spin-sectors

Maximum number of spin flips is two: $\langle I | v_{xy,zw} \hat{E}_{ey,zw} | K \rangle$

	$[7\alpha 0\beta]$	$[6\alpha 1\beta]$	$[5\alpha 2\beta]$	$[4\alpha 3\beta]$	$[3\alpha 4\beta]$	$[2\alpha 5\beta]$	$[1\alpha 6\beta]$	$[0\alpha 7\beta]$
$[7\alpha 0\beta]$								
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$[1\alpha 6\beta]$								
$[0\alpha 7\beta]$								

Interaction between spin-sectors

Can be rewritten : $$\left[\sum_J \langle I|\hat{E}_{xy}|J\rangle\langle J|\hat{E}_{zw}|K\rangle - \langle I|\hat{E}_{xy}|K\rangle\delta_{yz}\right]v_{xy,zw}$$

	$[7\alpha0\beta]$	$[6\alpha1\beta]$	$[5\alpha2\beta]$	$[4\alpha3\beta]$	$[3\alpha4\beta]$	$[2\alpha5\beta]$	$[1\alpha6\beta]$	$[0\alpha7\beta]$
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$[0\alpha7\beta]$								

Interaction between spin-sectors

Different number of configurations in each spin sector!

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...	$c^{7,0}_{N_{det,7,0}}$	...	...	...	...	...	...	$c^{[0,7]}_{N_{det,[0,7]}}$
...		...	...	...	...	...	...	
			...	...	...	...		
		$c^{[6,1]}_{N_{det,[6,1]}}$	...	...	...	...	$c^{[1,6]}_{N_{det,[1,6]}}$	
			...	...	...	...		
			...	...	...	...		
				...	...			
			$c^{[5,2]}_{N_{det,[5,2]}}$	...	...	$c^{[2,5]}_{N_{det,[2,5]}}$		
				...	...			
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Spin sector looping for RDM derivatives

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

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

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- Generate all possible sequences of excitation types for a given spin-sector.

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- Generate all possible sequences of excitation types for a given spin-sector.
- Classify different rdm derivatives by these types, e.g., $\Gamma^{MK}_{\alpha\beta\,\alpha\beta\,\beta\beta\,\alpha\alpha}$
- Each is the approximately the same size as a non-relativistic rdm derivative.
- At worst, each spin sector will have 4^4=256 such terms, though many contributions can be ruled out.

Time reversal symmetry

- Different kinds of excitations are connected via time reversal:

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

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

- Can substantially reduce the number of rdm derivatives which need to be calculated, e.g.,

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

- Do not need both of $E_{\alpha\alpha}$ and $E_{\beta\beta}$ or both $E_{\alpha\beta}$ and $E_{\beta\alpha}$.
- Maximum number of distinct terms per spinsector is 2^4=16.
- Similar transitions will occur repeatedly, enabling reuse of terms.

Calculation of CI derivatives

- Need to obtain A tensor containing molecular orbital integrals

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

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

- As many as eight excitation operators e.g.,

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

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$$= \sum_{\mathbf{ijkl}} \sum_{I} T^{\dagger}_{\mathbf{ijkl}} \sum_{\mathbf{wxyz}} \langle 0 | \left(\Pi_q a_{I_q} \right) a_{\mathbf{i}} a_{\mathbf{j}} a^{\dagger}_{\mathbf{k}} a^{\dagger}_{\mathbf{l}} a^{\dagger}_{\mathbf{w}} a^{\dagger}_{\mathbf{x}} a_{\mathbf{y}} a_{\mathbf{z}} g_{wxyz} \left(\Pi_s a^{\dagger}_{K_s} \right) | 0 \rangle$$

Wick’s Theorem

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

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<u>Normal ordering</u>

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

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

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

<u>Contraction (!!)</u>

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

- Difference between normal ordered form and original ordering.

Advantages of normal ordering

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

$$\sum_{\mathbf{ijkl}} \sum_{I} T^{\dagger}_{\mathbf{ijkl}} \sum_{\mathbf{wxyz}} \langle 0| \left(\Pi_q a_{I_q} \right) a_{\mathbf{i}} a_{\mathbf{j}} a^{\dagger}_{\mathbf{k}} a^{\dagger}_{\mathbf{l}} a^{\dagger}_{\mathbf{w}} a^{\dagger}_{\mathbf{x}} a_{\mathbf{y}} a_{\mathbf{z}} g_{\mathbf{wxyz}} \left(\Pi_s a^{\dagger}_{K_s} \right) |0\rangle$$

Advantages of normal ordering

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

$$\sum_{\mathbf{ijkl}} \sum_{I} T^{\dagger}_{\mathbf{ijkl}} \sum_{\mathbf{wxyz}} \langle 0| \left(\Pi_q a_{I_q} \right) a_{\mathbf{i}} a_{\mathbf{j}} a^{\dagger}_{\mathbf{k}} a^{\dagger}_{\mathbf{l}} a^{\dagger}_{\mathbf{w}} a^{\dagger}_{\mathbf{x}} a_{\mathbf{y}} a_{\mathbf{z}} g_{\mathbf{wxyz}} \left(\Pi_s a^{\dagger}_{K_s} \right) |0\rangle$$

$$\rightarrow \langle 0| \left(\Pi_q a_{I_q} \right) a^{\dagger}_{\mathbf{k}} a^{\dagger}_{\mathbf{l}} a^{\dagger}_{\mathbf{w}} a^{\dagger}_{\mathbf{x}} a_{\mathbf{i}} a_{\mathbf{j}} a_{\mathbf{y}} a_{\mathbf{z}} g_{\mathbf{wxyz}} \left(\Pi_s a^{\dagger}_{K_s} \right) |0\rangle$$

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$$= \begin{cases} 0 & \text{if} \quad w, x, k, l \notin \{I_q\}_{q=1,..,N} \\ 0 & \text{if} \quad i, j, y, z \in \{K_s\}_{s=1,..,N} \\ \pm g_{wxyz} & \text{otherwise} \end{cases}$$

END

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

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

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

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

[4,3] [3,4]

XMS-CASPT2

Solve for initial XMS-CASPT2 energy

↓

Solve for Lamda coefficients

↓

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

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

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

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:

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

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

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

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