Calculation of ci-derivatives in relativistic XMS-CASPT2

Peter John Cherry
Shiozaki group meeting
August 2nd 2017

Properties in XMS-CASPT2

- The XMS-CASPT2 energy is not minimized with respect to the CI and orbital coefficients obtained in the CASSCF calculation.

- This makes differentiating it with respect to perturbations of the Hamiltonian difficult.

- Accordingly, a Lagrangian is defined, which is minimized with respect to these variables:

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

- 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.

Calculation of CI derivatives

- Requires evaluation of terms of this form

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

- Wick’s theorem is used to rewrite this sum over **general** indices as a sum over **active** indices:

$$= \sum_{\mathbf{ijklmnop}} \Gamma_{\mathbf{ij,kl,mn,op}} A_{\mathbf{ij,kl,mn,op}}$$

$$+ \sum_{\mathbf{ijklmn}} \Gamma_{\mathbf{ij,kl,mn}} A_{\mathbf{ij,kl,mn}} + \sum_{\mathbf{ijkl}} \Gamma_{\mathbf{ij,kl}} A_{\mathbf{ij,kl}} + \sum_{\mathbf{ij}} \Gamma_{\mathbf{ij}} A_{\mathbf{ij}} + A$$

RDM derivatives

- RDM derivatives are defined as:

$$\Gamma^{I}_{\mathbf{ijklwxyz}} = \langle I| : a_{\mathbf{i}} a_{\mathbf{j}} a^{\dagger}_{\mathbf{k}} a^{\dagger}_{\mathbf{l}} a^{\dagger}_{\mathbf{w}} a^{\dagger}_{\mathbf{x}} a_{\mathbf{y}} a_{\mathbf{z}} : |J\rangle c_J$$

- As I and J are restricted to the active space, and thanks to the normal ordering, we have:

$$\Gamma^{I}_{\mathbf{ijklwxyz}} = \Gamma^{I}_{\mathbf{ijklwxyz}} = \langle I| : a_{\mathbf{i}} a_{\mathbf{j}} a^{\dagger}_{\mathbf{k}} a^{\dagger}_{\mathbf{l}} a^{\dagger}_{\mathbf{w}} a^{\dagger}_{\mathbf{x}} a_{\mathbf{y}} a_{\mathbf{z}} : |J\rangle c_J$$

“A” tensor

- Formed by summing over all possible contractions of the representations of the operators in the molecular orbital basis:

$$A_{\mathbf{abcdef}} = \sum_{\mathbf{lp}} T^{\dagger}_{\mathbf{ijkl}} g_{\mathbf{mnop}} \delta_{\mathbf{lp}} s_{4,8} + \sum_{\mathbf{lo}} T^{\dagger}_{\mathbf{ijkl}} g_{\mathbf{mnop}} \delta_{\mathbf{lo}} s_{4,7} + \ldots..$$

- The ability to combine all these contractions into one is crucial if the method is to be efficient.

Relativistic case

- The relativistic case is significantly more expensive:
  - Alpha and beta orbitals are treated seperately.
  - Can have spin flipping excitations.
    - Eight index tensors can be 256 times as large.
- May use time reversal symmetry to reduce cost.
- Placing spin constraints on indexes is the first step.

Spin restricted indexes

- Constrain indexes to either alpha or beta

$$\Gamma^{I\alpha\alpha\beta\alpha\beta\beta}_{\mathbf{ijklmn}} = \sum_J \langle I | a^{\alpha\dagger}_{\mathbf{i}} a^{\alpha\dagger}_{\mathbf{j}} a^{\beta\dagger}_{\mathbf{k}} a^{\alpha}_{\mathbf{l}} a^{\beta}_{\mathbf{m}} a^{\beta}_{\mathbf{n}} | J \rangle c_J$$

Non-interacting spin-sectors

Contributions to non-relativistic Γ^{I}_{ijklmn} for $|I\rangle \in [4\alpha 3\beta]$

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

Interacting spin-sectors

Contributions to relativistic Γ^{I}_{ijklmn} for $|I\rangle \in [4\alpha 3\beta]$

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

Interacting spin-sectors

1-electron rdm derivatives which need to be calculated for Γ^{I}_{ijklmn} with $|I\rangle \in [4\alpha 3\beta]$

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

Non-interacting spin-sectors

Contribution $\Gamma^{I\alpha\alpha\alpha\alpha\beta\beta}_{ijklmn}$ for $|I\rangle \in [4\alpha 3\beta]$

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

Non-interacting spin-sectors

Contribution $\Gamma^{I\alpha\alpha\alpha\alpha\beta\beta}_{ijklmn}$ for $|I\rangle \in [4\alpha 3\beta]$

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

Interacting spin-sectors

Time reversal symmetry can *at least* halve the number of terms to be calculated.

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

Interacting spin-sectors

Time reversal symmetry can *at least* halve the number of terms to be calculated.

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

Spin restricted RDM derivatives

- Constrain indexes to either alpha or beta

$$\Gamma^{I\alpha\alpha\beta\alpha\beta\beta}_{\mathbf{ijkmno}} = \sum_{J} \langle I | a^{\alpha\dagger}_{\mathbf{i}} a^{\alpha\dagger}_{\mathbf{j}} a^{\beta\dagger}_{\mathbf{k}} a^{\alpha}_{\mathbf{m}} a^{\beta}_{\mathbf{n}} a^{\beta}_{\mathbf{o}} | J \rangle c_J$$

- For the rdm derivative this is straightforward, but for the “A” tensor :

$$A^{\alpha\alpha\beta\alpha\beta\beta}_{\mathbf{i'j'k'm'n'o'}} = \sum_{\mathbf{lp}} T^{\dagger\alpha\alpha\beta}_{\mathbf{ijkl}} g^{\alpha\beta\beta}_{\mathbf{mnop}} \delta_{\mathbf{lp}} s_{4,8} + \sum_{\mathbf{lo}} T^{\dagger\alpha\alpha\beta}_{\mathbf{ijkl}} g^{\alpha\beta\beta}_{\mathbf{mnop}} \delta_{\mathbf{lo}} s_{4,7} + \ldots..$$

- The factors, s_{cd} , are dependent upon the spin sector.
- Consequently a the contributions to A depend upon the spin sector.

Spin restricted RDM derivatives

- Indicates that we need to perform this contraction for every distinct combination of spin excitations:

$$\sum_{\sigma_4} \sum_{\mathbf{ijklmnop}} \Gamma^{I\sigma_4}_{\mathbf{ij,kl,mn,op}} A^{\sigma_4}_{\mathbf{ij,kl,mn,op}} + \sum_{\sigma_3} \sum_{\mathbf{ijklmn}} \Gamma^{I\sigma_3}_{\mathbf{ij,kl,mn}} A^{\sigma_3}_{\mathbf{ij,kl,mn}}$$

$$+ \sum_{\sigma_2} \sum_{\mathbf{ijkl}} \Gamma^{I\sigma_2}_{\mathbf{ij,kl}} A^{\sigma_2}_{\mathbf{ij,kl}} + \sum_{\sigma_1} \sum_{\mathbf{ij}} \Gamma^{I\sigma_1}_{\mathbf{ij}} A^{\sigma_1}_{\mathbf{ij}} + A$$

- Where, $\sigma_3 = \{s_i s_j, s_k s_l, s_l s_m\}$, e.g., $\{\alpha\beta, \alpha\alpha, \beta\beta\}$.
- Different terms in the summation over σ_i correspond to different indexes, hence we cannot swap the order of the summation.

Switch to alternating order

- Switching from normal order (+++---) to alternating order (+-+-+-), i.e.,

$$\gamma^{I\alpha\alpha\alpha\beta\beta\beta}_{\mathbf{iljmkn}} = \sum_J \langle I | a^{\alpha\dagger}_{\mathbf{i}} a^{\alpha}_{\mathbf{l}} a^{\alpha\dagger}_{\mathbf{j}} a^{\beta}_{\mathbf{m}} a^{\beta\dagger}_{\mathbf{k}} a^{\beta}_{\mathbf{n}} | J \rangle c_J$$

- Commutation relations are used to rewrite rdm derivatives

$$\Gamma^{I\alpha\alpha\beta\alpha\beta\beta}_{\mathbf{ijklmn}} = \sum_J \langle I | a^{\alpha\dagger}_{\mathbf{i}} a^{\alpha\dagger}_{\mathbf{j}} a^{\beta\dagger}_{\mathbf{k}} a^{\alpha}_{\mathbf{l}} a^{\beta}_{\mathbf{m}} a^{\beta}_{\mathbf{n}} | J \rangle c_J$$

$$= \sum_J \left[\gamma^{I\alpha\alpha\beta\alpha\beta\beta}_{ijklmn} + \sum_{qrst} \kappa_{qrst} \delta_{uv} \gamma^{I\sigma_q\sigma_r\sigma_s\sigma_t}_{qrst} + \sum_{uv} \kappa_{qr} \delta_{uv} \delta_{st} \gamma^{I\sigma_q\sigma_r}_{uv} \right] c_J$$

Spin restricted RDM derivatives

- Still need to perform this contraction for every distinct combination of spin excitations:

$$\sum_{\sigma_4}\sum_{\mathbf{ijklmnop}} \gamma^{I\sigma_4}_{\mathbf{ij,kl,mn,op}} A'^{\sigma_4}_{\mathbf{ij,kl,mn,op}} + \sum_{\sigma_3}\sum_{\mathbf{ijklmn}} \gamma^{I\sigma_3}_{\mathbf{ij,kl,mn}} A'^{\sigma_3}_{\mathbf{ij,kl,mn}}$$

$$+ \sum_{\sigma_2}\sum_{\mathbf{ijkl}} \gamma^{I\sigma_2}_{\mathbf{ij,kl}} A'^{\sigma_2}_{\mathbf{ij,kl}} + \sum_{\sigma_1}\sum_{\mathbf{ij}} \gamma^{I\sigma_1}_{\mathbf{ij}} A'^{\sigma_1}_{\mathbf{ij}} + A'$$

- Here, $\sigma_3 = \{s_i s_j, s_k s_l, s_l s_m\}$, e.g., $\{\alpha\beta, \alpha\alpha, \beta\beta\}$
- Different terms in the summation over σ_i correspond to different indexes, hence we cannot swap the order of the summation.

Advantages of alternating order

- No new terms are being calculated; calculation of all rdm derivatives currently requires calculation of all γ_{ij}^{I} .

- Many (>2) index terms can re-expressed as products of two index terms

$$\gamma_{\mathbf{iljmkn}}^{I\sigma_3} = \sum_{JKL} \gamma_{\mathbf{il}}^{IK\sigma_1} \gamma_{\mathbf{jm}}^{KL\sigma_1'} \gamma_{\mathbf{kn}}^{LJ\sigma_1''} c_J$$

$$\gamma_{\mathbf{ij}}^{IK\sigma_1} = \langle I | a_{\mathbf{i}}^{s_i \dagger} a_{\mathbf{j}}^{s_j} | K \rangle$$

- Similarly, all spin excitation sequences are expressed in terms of two spin sequences:

$$\sigma_3 = \{ s_i s_j s_k s_l s_m s_n \} = \sigma_1 \cup \sigma_1' \cup \sigma_1''$$

Faster calculation of contractions

- Can now rewrite the summation as

$$\sum_{\sigma_3} \sum_{\mathbf{ijklmn}} \gamma^{I\sigma_3}_{\mathbf{ij,kl,mn}} A'^{\sigma_3}_{\mathbf{ij,kl,mn}} = \sum_{\sigma_1} \sum_{\mathbf{ij}} \sum_{K} \gamma^{IK\sigma_1}_{\mathbf{ij}} \tilde{\gamma}^{K\sigma_1}_{\mathbf{ij}}$$

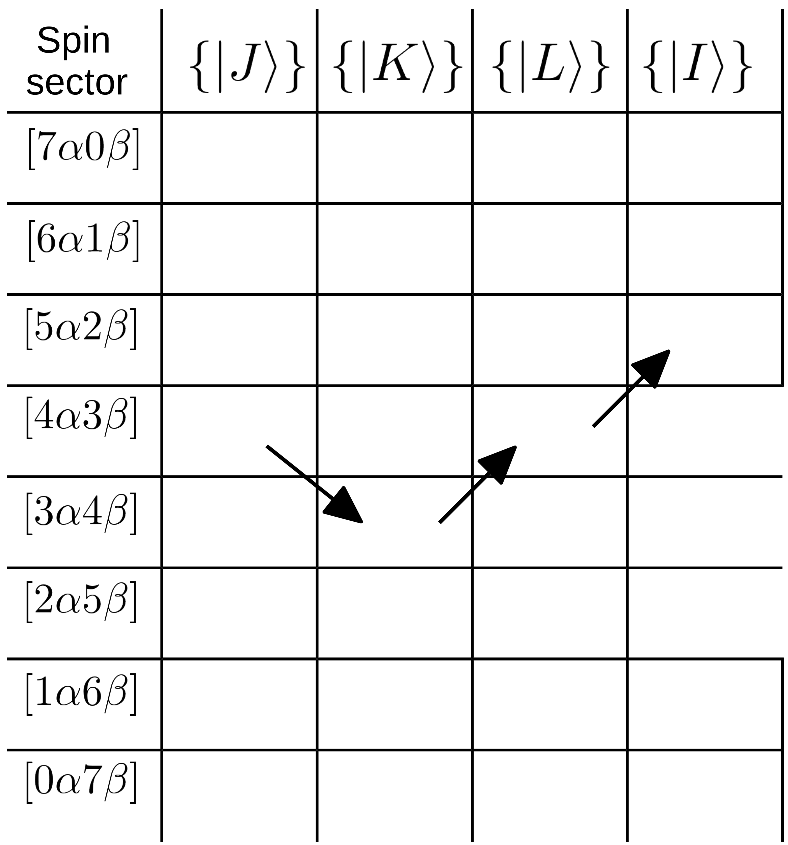
- Where

$$\tilde{\gamma}^{K\sigma_1}_{ij} = \sum_{\sigma_2} \sum_{LJ} \sum_{\mathbf{klmn}} \gamma^{KJ\sigma_2}_{\mathbf{kl,mn}} A'^{\sigma_1\sigma_2}_{\mathbf{ij,kl,mn}}$$

- Avoids the need for storage of a six index RDM derivative.
- Enables summation over all terms where the first two spin indexes are the same.

Spin transition pathways

- Representation in terms of individual transitions can help with application of symmetry :



$$|J\rangle \in [4\alpha 3\beta]$$

$$\gamma^{I}_{\alpha\beta\alpha\beta\beta\alpha} \rightarrow \gamma^{IK}_{\alpha\beta}\gamma^{KL}_{\alpha\beta}\gamma^{LJ}_{\beta\alpha}$$

$$\gamma^{KL}_{\alpha\beta} = \langle K|a^{\dagger}_{\alpha}a_{\beta}|L\rangle$$

Spin transition pathways

- “Forwards” and “backwards” transitions are connected by time reversal

Spin sector	$\{\|J\rangle\}$	$\{\|K\rangle\}$	$\{\|L\rangle\}$	$\{\|I\rangle\}$
$[7\alpha 0\beta]$				
$[6\alpha 1\beta]$				
$[5\alpha 2\beta]$				
$[4\alpha 3\beta]$				
$[3\alpha 4\beta]$				
$[2\alpha 5\beta]$				
$[1\alpha 6\beta]$				
$[0\alpha 7\beta]$				

$$|J\rangle \in [4\alpha 3\beta]$$

$$\gamma^{I}_{\alpha\beta\alpha\beta\beta\alpha} \rightarrow \gamma^{IK}_{\alpha\beta}\gamma^{KL}_{\alpha\beta}\gamma^{LJ}_{\beta\alpha}$$

$$\gamma^{KL}_{\alpha\beta} = \langle K|a^{\dagger}_{\alpha}a_{\beta}|L\rangle$$

$$\gamma^{KL}_{\beta\alpha} = (\gamma^{LK}_{\alpha\beta})^{*}$$

Time reversal symmetry

- Need only calculate the rdm derivatives for half the spin sectors.
- Can apply time reversal applied to only a subset of the indexes:

$$\gamma^{IK}_{s_i s_j}\gamma^{KL}_{\alpha\beta}\gamma^{LJ}_{\beta\alpha} = \gamma^{IK}_{s_i s_j}(\gamma^{KL}_{\beta\alpha}\gamma^{LJ}_{\alpha\beta})^*$$

- Contributions to the “A” tensor also possess such symmetries, e.g.,

$$\sum_{im} T^{\dagger}_{m_\alpha n_\alpha o_\alpha p_\beta} g_{i_\alpha j_\beta k_\alpha l_\beta}\delta_{mn} = -\sum_{im} T^{\dagger}_{i_\alpha n_\alpha o_\alpha p_\beta} g_{i_\alpha j_\alpha l_\beta k_\alpha}\delta_{mn}$$

- All are combined to reduce the range of the sum over σ_2 :

$$\tilde{\gamma}^{K\sigma_1}_{ij} = \sum_{\sigma_2}\sum_{LJ}\sum_{\mathbf{klmn}} \gamma^{KJ\sigma_2}_{\mathbf{kl,mn}} A'^{\sigma_1\sigma_2}_{\mathbf{ij,kl,mn}}$$

Spin transition pathways

- Application of spin constraints is more straightforward

Spin sector	$\{\vert J\rangle\}$	$\{\vert K\rangle\}$	$\{\vert L\rangle\}$	$\{\vert I\rangle\}$
$[7\alpha 0\beta]$				
$[6\alpha 1\beta]$				
$[5\alpha 2\beta]$				
$[4\alpha 3\beta]$				
$[3\alpha 4\beta]$				
$[2\alpha 5\beta]$				
$[1\alpha 6\beta]$				
$[0\alpha 7\beta]$				

$$|J\rangle \in [0\alpha 7\beta]$$

$$\rightarrow \gamma^{KJ}_{\beta\alpha} = 0$$

$$\rightarrow \gamma^{IK}_{\alpha\beta}\gamma^{KL}_{\alpha\beta}\gamma^{LJ}_{\beta\alpha} = 0$$

- This is much less clear with RDM derivatives, as they do not correspond a single transition pathway.

Spin transition pathways

- Application of spin constraints is more straightforward

Spin sector	$\{\|J\rangle\}$	$\{\|K\rangle\}$	$\{\|L\rangle\}$	$\{\|I\rangle\}$
$[7\alpha 0\beta]$				
$[6\alpha 1\beta]$				
$[5\alpha 2\beta]$				
$[4\alpha 3\beta]$				
$[3\alpha 4\beta]$				
$[2\alpha 5\beta]$				
$[1\alpha 6\beta]$				
$[0\alpha 7\beta]$				

$$|J\rangle \in [0\alpha 7\beta]$$

$$\rightarrow \gamma^{KJ}_{\beta\alpha} = 0$$

$$\rightarrow \gamma^{IK}_{\alpha\beta}\gamma^{KL}_{\alpha\beta}\gamma^{LJ}_{\beta\alpha} = 0$$

- This is much less clear with RDM derivatives, as they do not correspond a single transition pathway.

Decomposition of A

- Ideally would decompose "A" tensor into two index components:

$$A_{ijklmn} = a_{ij} \otimes a_{kl} \otimes a_{mn}$$

- Computational cost would then be $3N_{det}N_{act}^2$:

$$\sum_{ijklmn} \gamma^{I}_{jiklmn} A_{ijklmn}$$

$$= \sum_{K} \sum_{ij} \gamma^{I}_{ij} a_{ij} \sum_{L} \sum_{kl} \gamma^{KL}_{kl} a_{kl} \sum_{J} \sum_{mn} \gamma^{LJ}_{mn} a_{mn} c_J$$

$$= \sum_{K} \sum_{ij} \gamma^{I}_{ij} a_{ij} \sum_{L} \sum_{kl} \gamma^{KL}_{kl} a_{kl} \tilde{c}_L$$

$$= \sum_{K} \sum_{ij} \gamma^{I}_{ij} a_{ij} \tilde{\tilde{c}}_K$$

Decomposition of “A” tensor

- Majority of the time we must deal with combinations of two electron operators:

$$A_{ijklqrwxyz} = T^{\dagger}_{ijkl} \otimes f_{qr} \otimes \lambda_{wxyz}$$

- Indexes may be reordered so as to isolate terms belonging to different operators:

$$\rightarrow \sum_{ijklqrwxyz} \gamma^{IJ}_{ijklqrwxyz} A_{ijklqrwxyz}$$

$$= \sum_{ijkl} \sum_{K} \gamma^{IK}_{ijkl} T^{\dagger}_{ijkl} \sum_{L} \sum_{qr} \gamma^{KL}_{qr} f_{qr} \sum_{M} \sum_{wxyz} \gamma^{LJ}_{wxyz} \lambda_{wxyz} c_J$$

Decomposition of “A” tensor

- Replaces a ten index operation, with two four index operation, and one two index operation (performed in sequence).
- If *A* has a decomposition

$$T_{ijkl} \otimes Y_{qrwxyz} \quad \text{or} \quad \lambda_{ijkl} \otimes Y_{qrwxyz}$$

- The contribution will vanish, as neither T nor lambda can have all active indexes.
- The largest tensor we should have to deal with is six indexes, formed from a single contraction between two 2-electron operators, e.g.,

$$A_{ijknop} = \sum_{l} T^{\dagger}_{ijkl} \lambda_{nopl}$$

- Reorder to keep indexes belonging to the same operator together, enabling seperation of the contraction operations with the gamma matrices.

Method Summary

Step 1 : Determine all possible “A”-tensors.

- Determine all unique contractions (symmetry applied here).
- Represent “A”-tensors tensor products of smallest possible tensors.

Step 2 : Use normal ordering to get expression in terms of RDM derivatives with only active indexes.

- Get expressions for all possible transitions.
- Use contraction constraints to purge terms here.

Step 3 : Reorder indexes in each to get expression in terms of γ‘s.

- Merge all gamma terms
- For four and six index tensors, group indexes for like operators.
- Apply further spin constraints.

Step 4 : Loop through spin sectors, performing contractions.

- Calculate contributions to ci-derivative for paired spin sectors simultaneously.

Current status : Debugging application of index range constraints in switch to alternating ordering. Recompiling Smith routines for check against density matrices.

Decomposition of “A” tensor

- In many cases it is possible to decompose the A-tensor into components

$$\sum_{\mathbf{ijklwxyz}} \sum_{J} T^{\dagger}_{\mathbf{ijkl}} \lambda_{\mathbf{wxyz}} f_{\mathbf{qr}} \langle I | a_{\mathbf{i}} a_{\mathbf{j}} a^{\dagger}_{\mathbf{k}} a^{\dagger}_{\mathbf{l}} a^{\dagger}_{\mathbf{q}} a_{\mathbf{r}} a^{\dagger}_{\mathbf{w}} a^{\dagger}_{\mathbf{x}} a_{\mathbf{y}} a_{\mathbf{z}} | J \rangle c_J$$

$$\rightarrow A_{ijklqrwxyz} = T^{\dagger}_{ijkl} \otimes f_{qr} \otimes \lambda_{wxyz}$$

- Reorder to keep indexes belonging to the same operator together, this the integral terms and the gamma matrices to be contracted prior to the end

$$\sum_{L} \sum_{ijkl} \gamma^{IL}_{jikl} T_{ijkl} \sum_{M} \sum_{wxyz} \gamma^{LM}_{wxyz} \lambda_{wxyz} \sum_{J} \sum_{qr} \gamma^{MJ}_{qr} f_{qr}$$

- May be evaluated in sequence; instead of a single ten index term, there are two four index terms, and one two index term.

Decomposition of T

- Most expensive terms are contractions involving , λ_{ijkl} and H_{ijkl}
- The blocks relevant to six index tensors are $T_{aa',ca''}$ and $T_{aa',a''v}$

$$c \rightarrow closed \qquad a \rightarrow active \qquad v \rightarrow virtual$$

- Flatten tensor from four to two indexes:

$$aa \rightarrow \zeta \qquad ca \rightarrow \nu \qquad av \rightarrow \mu$$

$$T_{\zeta,\nu} = \sum_{\rho}^{N_{act}^2} t_{\zeta}^{\rho} \otimes t_{\nu}^{\rho} \epsilon_{\zeta}$$

Decomposition of “A” tensor

- In many cases it is possible to decompose the A-tensor into components

$$\sum_{\mathbf{ijklwxyz}} \sum_{J} T^{\dagger}_{\mathbf{ijkl}} \lambda_{\mathbf{wxyz}} f_{\mathbf{qr}} \langle I | a_{\mathbf{i}} a_{\mathbf{j}} a^{\dagger}_{\mathbf{k}} a^{\dagger}_{\mathbf{l}} a^{\dagger}_{\mathbf{q}} a_{\mathbf{r}} a^{\dagger}_{\mathbf{w}} a^{\dagger}_{\mathbf{x}} a_{\mathbf{y}} a_{\mathbf{z}} | J \rangle c_J$$

$$\rightarrow A_{ijklqrwxyz} = T^{\dagger}_{ijkl} \otimes f_{qr} \otimes \lambda_{wxyz}$$

- Reorder to keep indexes belonging to the same operator together:

$$\sum_{L} \sum_{ijkl} \gamma^{IL}_{jikl} T_{ijkl} \sum_{M} \sum_{wxyz} \gamma^{LM}_{wxyz} \lambda_{wxyz} \sum_{J} \sum_{qr} \gamma^{MJ}_{qr} f_{qr}$$

Decomposition of “A” tensor

- In many cases it is possible to decompose the A-tensor into components

$$A_{ijklqrwxyz} = T^{\dagger}_{ijkl} \otimes f_{qr} \otimes \lambda_{wxyz}$$

$$\sum_{ijkl} \gamma^{IL}_{jikl} T_{ijkl} \sum_{M} \sum_{wxyz} \gamma^{LM}_{wxyz} \lambda_{wxyz} \sum_{J} \sum_{qr} \gamma^{MJ}_{qr} f_{qr}$$

Switch from RDM derivatives

- Commutation relations and resolution of identity can be used to rewrite rdm derivatives

$$\Gamma^{I\alpha\alpha\beta\alpha\beta\beta}_{\mathbf{ijklmn}} = \sum_J \langle I|a^{\alpha\dagger}_{\mathbf{i}} a^{\alpha\dagger}_{\mathbf{j}} a^{\beta\dagger}_{\mathbf{k}} a^{\alpha}_{\mathbf{l}} a^{\beta}_{\mathbf{m}} a^{\beta}_{\mathbf{n}}|J\rangle c_J$$

$$\sum_{JKL} \langle I|a^{\alpha\dagger}_{\mathbf{i}} a^{\alpha}_{\mathbf{l}}|K\rangle\langle K|a^{\alpha\dagger}_{\mathbf{j}} a^{\beta}_{\mathbf{m}}|L\rangle\langle L|a^{\beta\dagger}_{\mathbf{k}} a^{\beta}_{\mathbf{n}}|J\rangle c_J$$

$$+ \sum_{\{q,r,s,t\}} \kappa_{qrst} \sum_{JK} \langle I|a^{\alpha\dagger}_{\mathbf{q}} a^{\alpha}_{\mathbf{r}}|K\rangle\langle K|a^{\alpha\dagger}_{\mathbf{s}} a^{\beta}_{\mathbf{t}}|J\rangle c_J + \sum_{\{u,v\}} \kappa_{uv} s_{\sum_J \langle K|a^{\alpha\dagger}_{\mathbf{u}} a^{\beta}_{\mathbf{v}}|J\rangle c_J}$$

- The factor s_{lp} are dependent upon the spin sector.

- Consequently a the contributions to A depend upon the spin sector.

Switch from RDM derivatives

- Commutation relations and resolution of identity can be used to rewrite rdm derivatives

$$\Gamma^{I\alpha\alpha\beta\alpha\beta\beta}_{\mathbf{ijklmn}} = \sum_J \langle I | a^{\alpha\dagger}_{\mathbf{i}} a^{\alpha\dagger}_{\mathbf{j}} a^{\beta\dagger}_{\mathbf{k}} a^{\alpha}_{\mathbf{l}} a^{\beta}_{\mathbf{m}} a^{\beta}_{\mathbf{n}} | J \rangle c_J$$

$$= \sum_{JKL} \gamma^{IL}_{ij} \gamma^{LK}_{kl} \gamma^{KJ}_{mn} c_J + \sum_{JKL} \sum_{qrst} \kappa_{qrst} \gamma^{IL}_{qr} \gamma^{KJ}_{st} c_J + \sum_{JKL} \sum_{uv} \kappa_{uv} \gamma^{IJ}_{uv} c_J$$

- The factor s_{lp} are dependent upon the spin sector.

- Consequently a the contributions to A depend upon the spin sector.