Interface for property calculations using multireference wavefunctions

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Shiozaki group meeting
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Overall goal

Constructing a general tool for evaluation of expressions of the form:

$$\langle \Psi_M | \hat{B}_{b_1 b_2 \ldots} \hat{C}_{c_1 c_2 \ldots} \hat{D}_{d_1 d_2 \ldots} | \Psi_N \rangle$$

$$= \langle \Psi_M | \hat{a}^\dagger_{b_1} \hat{a}_{b_2} \ldots \hat{a}^\dagger_{c_1} \hat{a}_{c_2} \ldots \hat{a}^\dagger_{d_1} \hat{a}_{d_2} \ldots | \Psi_N \rangle B_{b_1 b_2 \ldots} C_{c_1 c_2 \ldots} D_{d_1 d_2 \ldots}$$

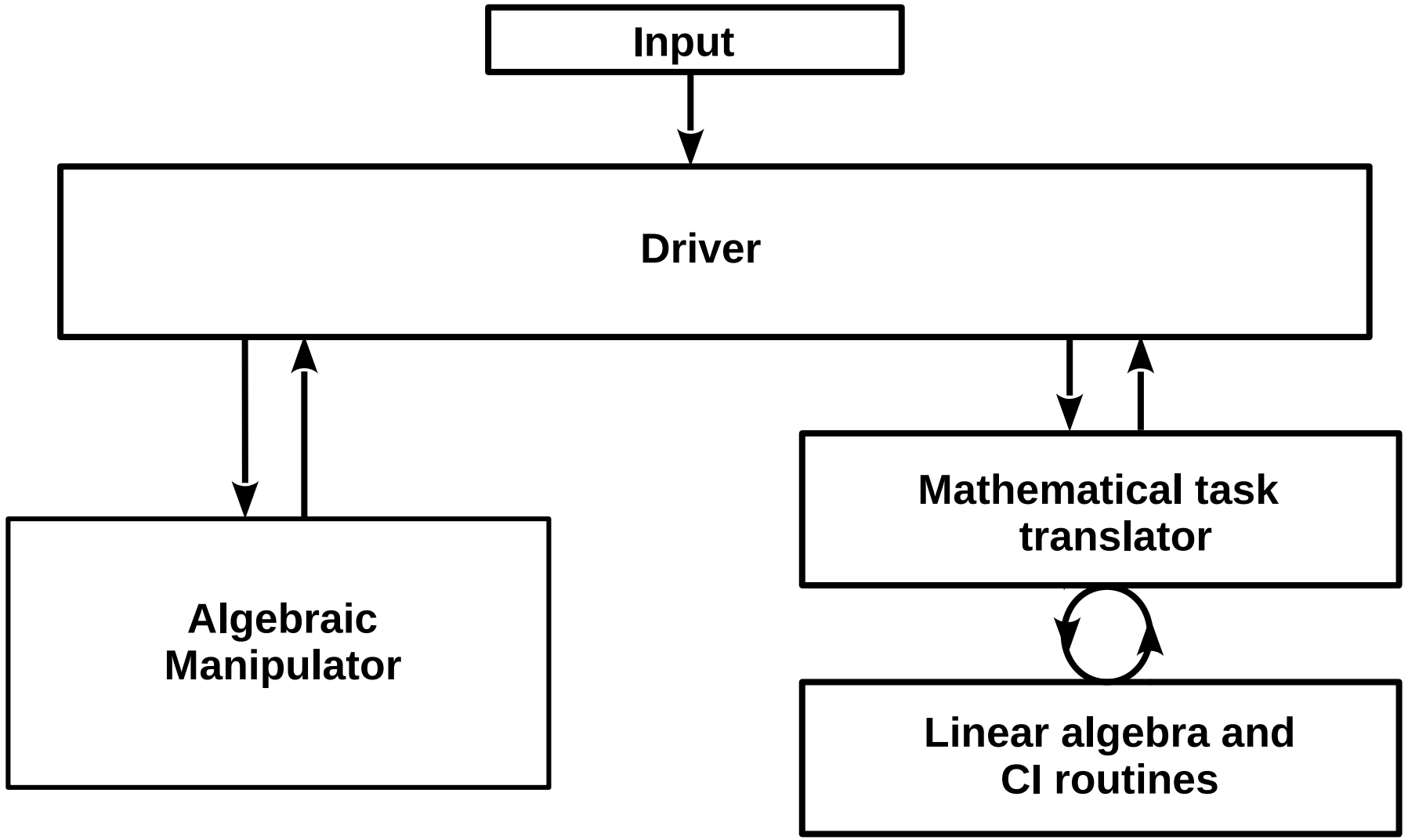
Working for terms of this form*

$$\langle \Psi_M | \hat{H}_{wxyz} \hat{T}_{ijkl} | \Psi_N \rangle$$

Terms with greater numbers of tensors are implemented, but need further testing

Can specify the ranges of each of the indexes; the program will utilize this information to develop an efficient procedure for evaluating the expression.

Program Structure



Algebraic task list

Algebraic task list might look like:

$$A_{ijklmn} = \text{ contract } [H_{abcd}, T_{wxyz}](a, z)$$
$$A_{ijkl} = \text{ contract } [A_{ijklmn}](m, n)$$
$$\text{build } \gamma_{ijkl}$$
$$X = \text{ contract } [\gamma_{ijkl}, A_{ijkl}](i, j, k, l)$$

Primary term types

Expectation value (“full”) type terms :

$$\sum_{IJ} \sum_{\substack{b_1 b_2 \ldots \\ c_1 c_2 \ldots \\ d_1 d_2 \ldots}} c_I^{M\dagger} \langle I | \hat{a}_{b_1}^\dagger \hat{a}_{b_2} \ldots \hat{a}_{c_1}^\dagger \hat{a}_{c_2} \ldots \hat{a}_{d_1}^\dagger \hat{a}_{d_2} \ldots | J \rangle c_J^N B_{b_1 b_2 \ldots} C_{c_1 c_2 \ldots} D_{d_1 d_2 \ldots}$$

CI-derivative type terms :

$$\sum_{J} \sum_{\substack{b_1 b_2 \ldots \\ c_1 c_2 \ldots \\ d_1 d_2 \ldots}} \langle I | \hat{a}_{b_1}^\dagger \hat{a}_{b_2} \ldots \hat{a}_{c_1}^\dagger \hat{a}_{c_2} \ldots \hat{a}_{d_1}^\dagger \hat{a}_{d_2} \ldots | J \rangle c_J^N B_{b_1 b_2 \ldots} C_{c_1 c_2 \ldots} D_{d_1 d_2 \ldots}$$

Excitation derivative type terms:

$$\sum_{IJ} \sum_{\substack{c_1 c_2 \ldots \\ d_1 d_2 \ldots}} c_I^{M\dagger} \langle I | \hat{a}_{b_1}^\dagger \hat{a}_{b_2} \ldots \hat{a}_{c_1}^\dagger \hat{a}_{c_2} \ldots \hat{a}_{d_1}^\dagger \hat{a}_{d_2} \ldots | J \rangle c_J^N C_{c_1 c_2 \ldots} D_{d_1 d_2 \ldots}$$

Input parsing

- Input must be parsed so that it can be broken down into a sequence of calculations of involving the three basic expression types.
- The simplest approach; to store every possible term generated using the input ranges, is not practical.
- The correspondence between the quantities the user inputs, and the quantities which should be calculated/stored, is not one-to-one.
- Deducing the computational proceedure from an equation alone is difficult.

Input parsing

- Often we wish to find some coefficients, T_{Ω}^{LN}, used to define some perturbation to the wavefunction, e.g.,

$$|\Psi_L\rangle \approx |L\rangle + |\Psi_L^{(1)}\rangle$$

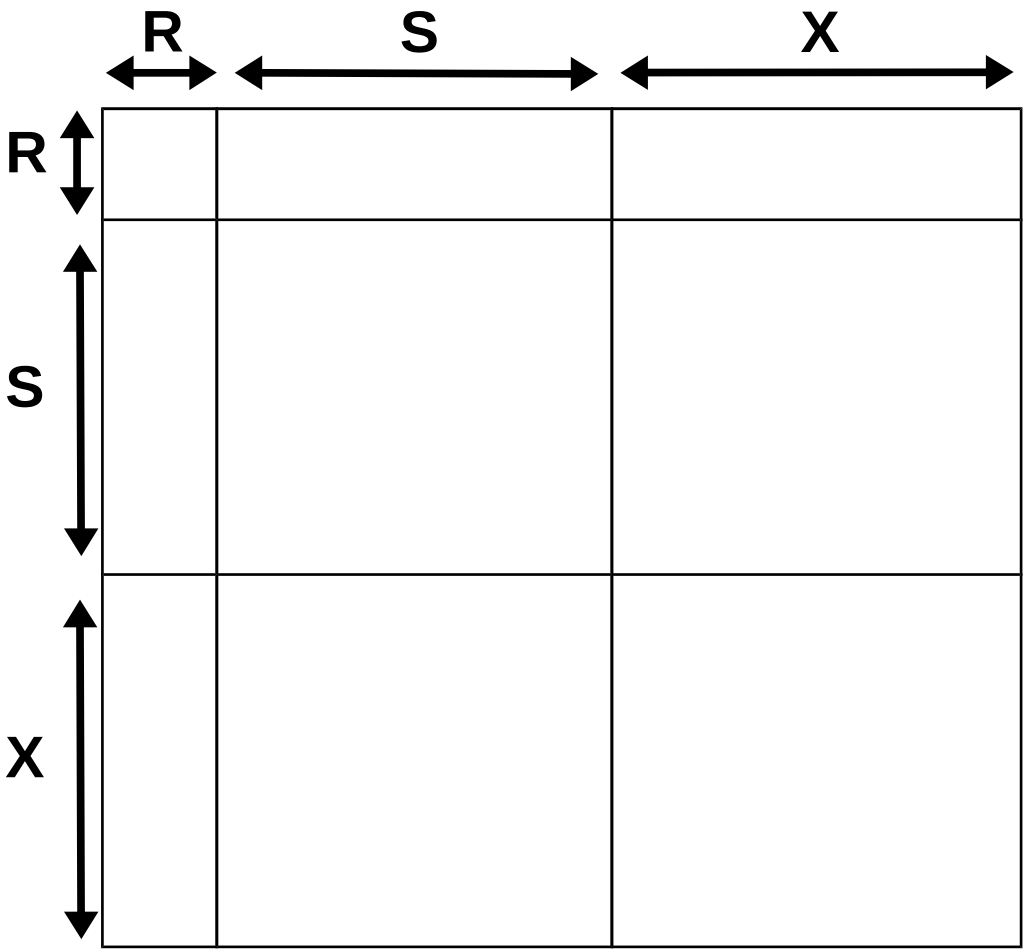
$$|\Psi_L^{(1)}\rangle = \sum_N \sum_{\Omega} T_{\Omega}^{LN} \hat{E}_{\Omega} |N\rangle$$

N, L : States in the reference space.

Ω : Orbital excitation indexes.

Note: Rotations associated with XMS-CASPT2 are not mentioned explicitly in this notation.

Multi-state perturbtion theory



R : Reference space

R+S : CASCI space

X : External space

$$|\Psi_L\rangle \approx |\Psi_L^{(0)}\rangle + |\Psi_L^{(1)}\rangle$$

in R **in X**

Input parsing

- These may be found through use of an update equation of form

$$\Delta T_{\Omega}^{LN} = \frac{R_{\Omega}^{LN}}{D_{\Omega'}^{L'N'}}$$

- The user is asked to input expressions for R_{Ω}^{LN} and $D_{\Omega'}^{L'N'}$
- Note that not all indexes need to be specified (e.g., if one term does not depend upon one of the indexes).
- To specify an equation, the used specifies the equation type, defines the terms needed for this equation, and the method of solution.

Input parsing

- Each equation is broken down into a number of “expressions”, e.g.,

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

- This is then broken into two “terms”:

$$\sum_N \langle M|\hat{E}_\Omega^\dagger(\hat{H}-\epsilon_L)\hat{T}^{LN}|N\rangle \qquad \text{Term 1}$$

$$\langle M|\hat{E}_\Omega^\dagger\hat{H}|L\rangle \qquad \text{Term 2}$$

- Summation over an index ranges applies to an entire term.

Input parsing

- Every term will result in a algebraic task list of form

$$\begin{aligned}\text{Term } 1 = &\sum_{MN}\sum_{ijklmnop} \Gamma^{MN}_{ijklmnop} A^{MN}_{ijklmnop} \\ &+ \sum_{MN}\sum_{ijklmn} \Gamma^{MN}_{ijklmn} A^{MN}_{ijklmn} \\ &+ \sum_{MN}\sum_{ijkl} \Gamma^{MN}_{ijkl} A^{MN}_{ijkl} \\ &+ \sum_{MN}\sum_{ij} \Gamma^{MN}_{ij} A^{MN}_{ij} \quad + \sum_{MN} A^{MN}\end{aligned}$$

- Merging task lists from multiple terms is very useful, and doing so is made far simpler if index summations range over the entire term.

Input parsing

- Terms are further broken down into individual “BraKet”s:

$$\sum_N \langle M|\hat{E}_\Omega^\dagger(\hat{H}-\epsilon_L)\hat{T}^{LN}|N\rangle \qquad \text{Term 1}$$

$$\langle M|\hat{E}_\Omega^\dagger \hat{H}\hat{T}^{LN}|N\rangle \qquad \text{BraKet 1}$$

→

$$\langle M|\hat{E}_\Omega^\dagger \epsilon_L \hat{T}^{LN}|N\rangle \qquad \text{BraKet 2}$$

- These are (typically) never evaluated independently, but are the basic unit of operation for the algebraic manipulator.

Input parsing

- Each “BraKet” has involves a number of tensor operators (“TensOp”).
- The “BraKet” and “TensOp” classes have an index free and index specific variants.
- The index specific variants are generated by functions in the index free variants.
- These functions take a map of index range definitions constructed by the equation object.
- Whilst rather convoluted, having the basic objects in the algebraic manipulator defined independently of the indexes they contain is extremely useful when it comes to merging terms and applying symmetry.

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Update equation

- These may be found through use of an update equation of form

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- Note that not all indexes need to be specified (e.g., if one term does not depend upon one of the indexes).
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CI-dervative type terms :

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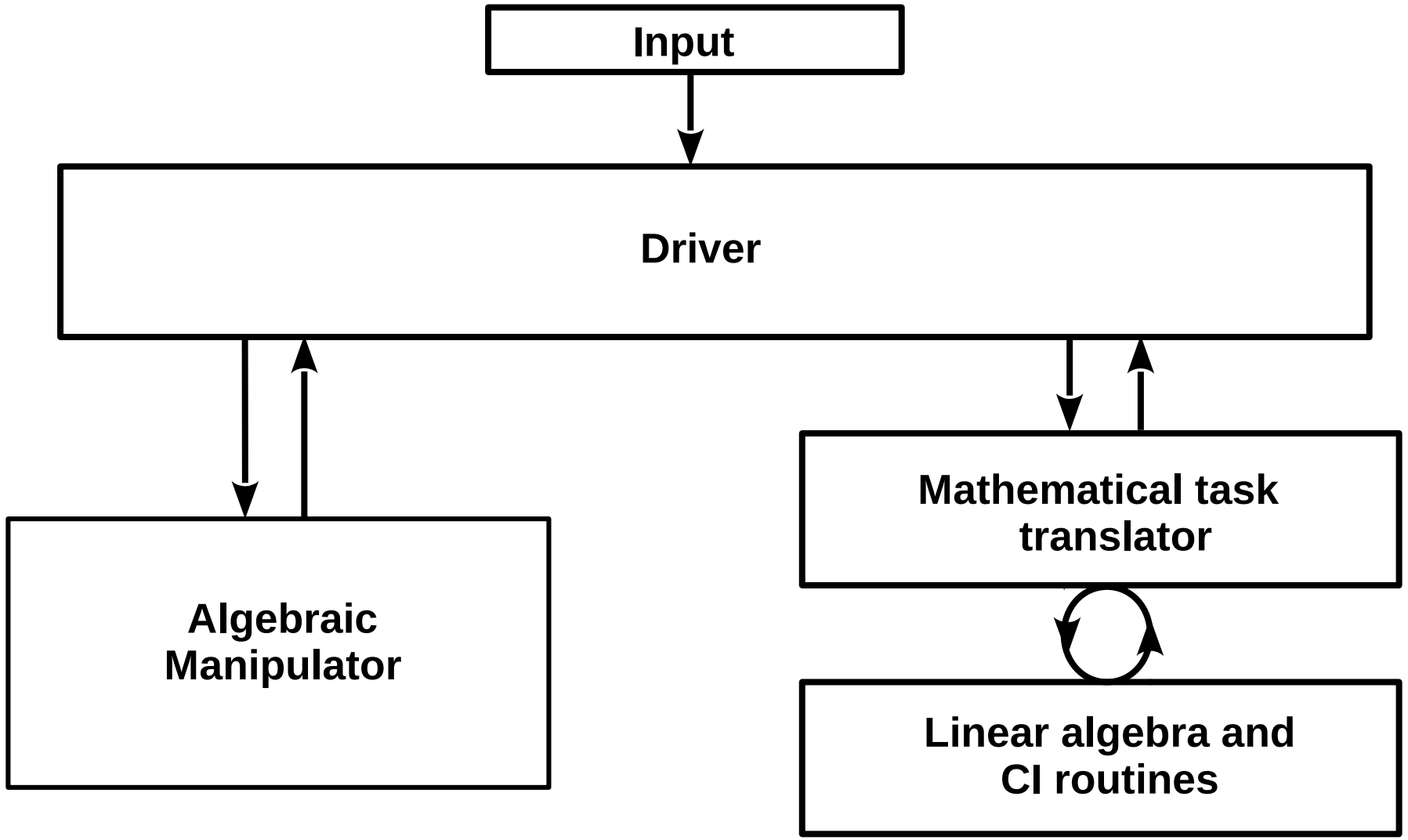
Excitation derivative type terms:

$$\sum_{IJ} \sum_{\substack{c_1 c_2 \ldots \\ d_1 d_2 \ldots}} c_I^{M\dagger} \langle \Psi_M | \hat{a}_{c_1}^\dagger \hat{a}_{c_2} \ldots \hat{a}_{d_1}^\dagger \hat{a}_{d_2} \ldots | \Psi_J \rangle c_J^N C_{c_1 c_2 \ldots} D_{d_1 d_2 \ldots}$$

R_Ω^{LN} is of this type

Program Structure



Excitation derivative terms

- Consider :

$$X_\Omega = \langle M|\hat{E}^\dagger_\Omega \hat{H}|L\rangle =$$

$$X_{\omega_1\omega_2\omega_3\omega_4} = \sum_{h_1h_2h_3h_4} \sum_{IJ} \langle I|\hat{\omega}_4\hat{\omega}_3\hat{\omega}_2^\dagger\hat{\omega}_1^\dagger\hat{h}_1^\dagger\hat{h}_2^\dagger\hat{h}_3\hat{h}_4|J\rangle c_I^{M\dagger} c_J^N H_{h_1h_2h_3h_4}$$

- Where $\hat{h}_i = \hat{a}_{h_i}$ and $\hat{h}_i^\dagger = \hat{a}_{h_i}^\dagger$.
- Cannot normal order and use normal rearrangement tricks; may result in contraction of the ω indexes!

Excitation derivative terms

- Split the term in two using the resolution of the identity :

$$X_{\omega_1\omega_2\omega_3\omega_4} = \sum_{h_1h_2h_3h_4} \sum_{IKJ} \langle I|\hat{\omega}_4\hat{\omega}_3\hat{\omega}_2^\dagger\hat{\omega}_1^\dagger|K\rangle\langle K|\hat{h}_1^\dagger\hat{h}_2^\dagger\hat{h}_3\hat{h}_4|J\rangle c_I^{M\dagger} c_J^N H_{h_1h_2h_3h_4}$$

- Reorder the second BraKet so it is a sum of anti-normal ordered terms, e.g.,

$$\sum_{h_1h_2h_3h_4} \sum_{IKJ} \langle I|\hat{\omega}_4\hat{\omega}_3\hat{\omega}_2^\dagger\hat{\omega}_1^\dagger|K\rangle\langle K|\hat{h}_3\hat{h}_4\hat{h}_1^\dagger\hat{h}_2^\dagger|J\rangle c_I^{M\dagger} c_J^N H_{h_1h_2h_3h_4}$$

Excitation derivative terms

- Decompose $\mathbf{X}$ into different types of blocks
  - Type 1 : No pair of creation and annihilation indexes have the same range.
  - Type 2 : One pair of creation and annihilation indexes have the same range.
  - Type 3 : All creation and annihilation indexes have the same range (not relevant to CASPT2).

$$\sum_{h_1 h_2 h_3 h_4} \sum_{IKJ} \langle I|\hat{\omega}_4 \hat{\omega}_3 \hat{\omega}_2^\dagger \hat{\omega}_1^\dagger|K\rangle \langle K|\hat{h}_3 \hat{h}_4 \hat{h}_1^\dagger \hat{h}_2^\dagger|J\rangle c_I^{M\dagger} c_J^N H_{h_1 h_2 h_3 h_4}$$

- Assuming that $|I\rangle$ and $|J\rangle$ are in the same ci-sector it is apparent that

$$|K\rangle = \hat{a}_{h_3} \hat{a}_{h_4} \hat{a}_{h_1}^\dagger \hat{a}_{h_2}^\dagger |J\rangle$$

$$|K\rangle = \hat{\omega}_1^\dagger \hat{\omega}_2^\dagger \hat{\omega}_3^\dagger \hat{\omega}_4 |I\rangle$$

Excitation derivative terms

- Consider the block of $\mathbf{X}$ where

$$\omega_1, \omega_2 \in \quad closed \qquad\qquad \omega_3, \omega_4 \in \quad virtual$$

- Every creation index on the right can be paired with an annihilation index on the left:

$$\sum_{h_1 h_2 h_3 h_4} \sum_{IKJ} \langle I|\hat{\omega}_4 \hat{\omega}_3 \hat{\omega}_2^\dagger \hat{\omega}_1^\dagger|K\rangle \langle K|\hat{h}_3 \hat{h}_4 \hat{h}_1^\dagger \hat{h}_2^\dagger|J\rangle c_I^{M\dagger} c_J^N H_{h_1 h_2 h_3 h_4} \times (\delta_{h_3 \omega_1} \delta_{h_4 \omega_2} + \delta_{h_3 \omega_2} \delta_{h_4 \omega_1})$$

$$= \sum_{h_1 h_2 h_3 h_4} \sum_{IKJ} \langle I|\hat{\omega}_4 \hat{\omega}_3 \hat{h}_1^\dagger \hat{h}_2^\dagger|J\rangle c_I^{M\dagger} c_J^N H_{h_1 h_2 h_3 h_4} (\delta_{h_3 \omega_1} \delta_{h_4 \omega_2} + \delta_{h_3 \omega_2} \delta_{h_4 \omega_1})$$

Excitation derivative terms

- Now normal order the indexes in the braket on the right*, and repeat the operation, with annihilation ω and creation h :

$$\sum_{h_1 h_2 h_3 h_4} \sum_{IKJ} \langle I|\hat{\omega}_4\hat{\omega}_3\hat{\omega}_2^\dagger\hat{\omega}_1^\dagger|K\rangle\langle K|\hat{h}_1^\dagger\hat{h}_2^\dagger\hat{h}_3\hat{h}_4|J\rangle c_I^{M\dagger} c_J^N H_{h_1h_2h_3h_4}$$
$$\times(\delta_{h_3\omega_1}\delta_{h_4\omega_2} + \delta_{h_3\omega_2}\delta_{h_4\omega_1})$$
$$\times(\delta_{h_1\omega_3}\delta_{h_2\omega_4} + \delta_{h_1\omega_4}\delta_{h_2\omega_3})$$

$$= \sum_{h_1 h_2 h_3 h_4} \sum_{IJ} \langle I|J\rangle c_I^{M\dagger} c_J^N H_{h_1h_2h_3h_4}$$

$$\times(\delta_{h_3\omega_1}\delta_{h_4\omega_2} + \delta_{h_3\omega_2}\delta_{h_4\omega_1})(\delta_{h_1\omega_3}\delta_{h_2\omega_4} + \delta_{h_1\omega_4}\delta_{h_2\omega_3})$$

  - Note that the braket containing delta functions is essentially specifies a reordering of the indexes of $\mathbf{H}$.

Excitation derivative terms

- The disappearance of terms is thanks to the constraints that the indexes of $\mathbf{X}$ are unique.

- If there are more than physical operator indexes than excitation indexes less things disapper. Consider

$$\langle M|E_{\Omega_1}\hat{f}\hat{T}|N\rangle$$

- If there are six physical operator indexes, and a block of type 2, we have terms of the form:

$$\sum_{\substack{T_1T_2T_3T_4\\f_1f_2}}\sum_{IJ}\langle I|\hat{a}_z^\dagger\hat{a}_w^\dagger\hat{a}_y\hat{a}_z|J\rangle c_I^{M\dagger}c_J^N T_{t_1t_2t_3t_4}f_{f_1f_2}$$

$$\times(\delta_{h_3\omega_1}\delta_{h_4\omega_2}+\delta_{h_3\omega_2}\delta_{h_4\omega_1})(\delta_{h_1\omega_3}\delta_{h_2\omega_4}+\delta_{h_1\omega_4}\delta_{h_2\omega_3})$$

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$$\times(\delta_{t_3\omega_1}\delta_{t_4\omega_2} + \delta_{t_3\omega_2}\delta_{f_2\omega_1} + ...)(\delta_{t_1\omega_3}\delta_{t_2\omega_4} + \delta_{f_1\omega_1}\delta_{t_2\omega_3} + ...)$$

Excitation derivative terms

- A key advantage is that this approach is easily adaptable to cases where the determinants are not in the same spin sector.
- The need to account for this possibility prevents many other simplifications from being made.

Tensor contractions task list

- Often have terms which involve more than two tensors:

$$\langle M|\hat{B}^{\dagger}\hat{C}\hat{D}|N\rangle$$

- Often have contractions of the form:

$$\sum_{\substack{b_4 \\ c_1 c_2 \\ d_1 d_2 d_3}} B_{b_1 b_2 b_3 b_4} C_{c_1 c_2 c_3 c_4} D_{d_1 d_2 d_3 d_4} \delta_{d_1 d_2} \delta_{d_3 c_1} \delta_{c_2 b_4}$$

- Memory constraints mean we would prefer to avoid building the tensor

$$\mathbf{B} \otimes \mathbf{C} \otimes \mathbf{D}$$

Tensor contractions task list

$$\sum_{\substack{b_4 \\ c_1 c_2 \\ d_1 d_2 d_3}} B_{b_1 b_2 b_3 b_4} C_{c_1 c_2 c_3 c_4} D_{d_1 d_2 d_3 d_4} \delta_{d_1 d_2} \delta_{d_3 c_1} \delta_{c_2 b_4}$$

- Different ways orders of performing contractions do not have the same computational cost/memory usage.

- More efficient way of evaluating the above

$$\sum_{b_4 c_1} B_{b_1 b_2 b_3 b_4} \sum_{c_2 d_3} C_{c_1 c_2 c_3 c_4} \sum_{d_1 d_2} D_{d_1 d_2 d_3 d_4} \delta_{d_1 d_2} \delta_{d_3 c_1} \delta_{c_2 b_4}$$

Tensor contractions task list

- Alternatively written:

$$T_1 = [(D, .)(1, 2)]$$

$$T_2 = [(C, T_1), (1, 2)]$$

$$T_3 = [(B, T_2), (4, 2)]$$

- All the tensor contraction task list should perform all intra-tensor contractions before performing any inter-tensor contractions.

- This prevents large tensor blocks from being stored.

- Whilst happening already for pairs of tensors, this was not happening properly for three or more tensors.

Summary

- New routines for algebraic manipulation of excitation derivative terms.
- Reworking tensor contraction list generation.
- New structure for input parsing.
- Fixing issues which I had overlooked previously.
- Still implementing CASPT2 equations.

Resolvent formalism for XMS-CASPT2

XMS-CASPT2 is notably different to MS-CASPT2 in the form of the amplitude equation:

XMS-CASPT2 describes the interaction of different states within the reference space, and this is essential for an accurate description of degenerate and quasi-degenerate cases.

Currently uses state averaged Fock operator, and this approximation yields good results at the non-relativistic level.

State Averaging in reativistic XMS-CASPT2

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Resolvant formalism for many-body perturbation theory

State averaging in the quasi-degenerate case is problematic when the wavefunctions corresponding to the states differ substantially.

Banerjee, Murkherjee and Simons (BMS) propose a method of dealing with this in the second of the above papers, albeit in a different context.

Base around Greens functions and the Gellman-Low theorem, but their approach can be used to obtain CASPT2 amplitude equation.

Aim to reformulate the derivation of XMS-CASPT2 using BMS strategy, so can take advantage of their approach.

Rough outline of BMS approach to quasi-degenerate case

State averaging would not be an issue if all states in the reference space were degenerate.

Define the unperturbed Hamiltonian as:

All states in the reference space are degenerate eigenvectors of H1,
States are non-degenerate under H2.

Now redefine the perturbation V as :

V' = V + H2

This

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Progress

Step 1 : Get operator information.

- Split input tensors up into blocks and identify symmetries between blocks.

Step 2 : Simplify expression

- Use expression manipulator to reduce the number of terms to be calculated.

Step 3 : Generate computational proceedure.

- Generate a task list to obtain contracted A-tensors and corresponding RDM/RDM derivatives.

Step 4 : Execute computational proceedure.

- Obtain A-tensors/RDM matrices and contract.

Step 5 : Loop over spin sectors and states. ← Needs retesting

- Repeat for all necessary spin sectors.

Step 6 : Implement CASPT2 equations. ← Doing now

Example equation of interest

- Typically deal with equations of the form:

$$\sum_{abcd}\sum_{uvwx}\sum_{N}\langle\Psi_M|\hat{E}^{\dagger}_{abuv}(\hat{f}-\epsilon^0_L-\epsilon_s)\hat{T}^{LN}_{cdwx}|\Psi_N\rangle$$

$$+\sum_{ijkl}\sum_{ef}\sum_{yz}\langle\Psi_M|\hat{E}^{\dagger}_{efyz}\hat{H}_{ijkl}|\Psi_L\rangle=0$$

- Processing requires the following capabilities:
  - Specification of the ranges of Bra-Ket index summation.
  - Specification of the ranges of orbital index summation .
  - Identification and use of :
    - *Permutation symmetry of indexes.*
    - *Symmetry of molecular orbital integrals.*
    - *Symmetry of between states (e.g., Kramers symmetry).*
  - Ability to combine terms appropriately.

Program Structure