1 Excitation derivative terms

In the following, and "excitation derivative term" is one with the following form:

$$\sum_{\substack{x_1x_2\ldots\\ y_1y_2\ldots\\ \ldots}} X_{x_1x_2\ldots}Y_{y_1y_2\ldots}\ldots \sum_I\sum_J \langle I|\hat{E}^\dagger_\Omega a^\dagger_{x_1}a_{x_2}\ldots a^\dagger_{y_1}a_{y_2}\ldots.|J\rangle c_I^{M\dagger}c_J^N$$

$$= \sum_{\substack{x_1x_2\ldots\\ y_1y_2\ldots\\ \ldots}} X_{x_1x_2\ldots}Y_{y_1y_2\ldots}\ldots \sum_I\sum_J \langle I|a_{\omega_1}a_{\omega_2}\ldots a^\dagger_{x_1}a_{x_2}\ldots a^\dagger_{y_1}a_{y_2}\ldots.|J\rangle c_I^{M\dagger}c_J^N, \tag{1}$$

where the $\hat{E}^\dagger_\Omega$ is an operator which excites electrons from orbitals in the space used to represent the reference wavefunctions, $\{|N\rangle\}$, and into some virtual space. The $X_{x_1x_2}$ and $Y_{y_1y_2}$ are the representations of the two-electron operators, $\hat{X}$ and $\hat{Y}$, in the molecular orbital basis.

Evaluation of such terms is used when to solving XMS-CASPT2 amplitude equation:

$$\sum_{\Omega'}\langle\tilde{M}|\hat{E}^\dagger_\Omega(\hat{H}-\epsilon_L)\hat{T}^{LM}_{\Omega'}|\tilde{N}\rangle + \langle\tilde{M}|\hat{E}^\dagger_\Omega\hat{H}|\tilde{L}\rangle$$

For now we can just consider the second term, which written out with all summations over orbitals and ci-indexes made explicit is

$$X_{\omega_1\omega_2\omega_3\omega_4} = \sum_{H_1H_2H_3H_4}\sum_I\sum_J \langle I|\hat{a}_{\omega_4}\hat{a}_{\omega_3}\hat{a}^\dagger_{\omega_2}\hat{a}^\dagger_{\omega_1}\hat{a}^\dagger_{h_1}\hat{a}^\dagger_{h_2}\hat{a}_{h_3}\hat{a}_{h_4}|J\rangle c_I^{M\dagger}c_J^N H_{h_1h_2h_3h_4} \tag{2}$$

This cannot be dealt with using the same techniques as terms all the orbital indexes are summed over; rearranging all the terms into normal order would cause contractions with the ω indexes of X. Still, we want a method of evaluation which only involves contraction of the operator tensors with a reduced density matrix (or similar) with only active indexes.
To accomplish this, split the term up into two subsections using the resolution of identity[1].

$$X_{\omega_1\omega_2\omega_3\omega_4} = \sum_{h_1h_2h_3h_4}\sum_{IJK} \langle I|\hat{a}_{\omega_4}\hat{a}_{\omega_3}\hat{a}^\dagger_{\omega_2}\hat{a}^\dagger_{\omega_1}|K\rangle\langle K|\hat{a}^\dagger_{h_1}\hat{a}^\dagger_{h_2}\hat{a}_{h_3}\hat{a}_{h_4}|J\rangle c_I^{M\dagger}c_J^N h_{h_1h_2h_3h_4} \tag{3}$$

We can now rearrange this so that the second BraKet $\langle K|...|J\rangle$ is a sum of *anti*-normal ordered terms, e.g.,

$$\sum_{h_1h_2h_3h_4}\sum_{IKJ} \langle I|\hat{a}_{\omega_4}\hat{a}_{\omega_3}\hat{a}^\dagger_{\omega_2}\hat{a}^\dagger_{\omega_1}|K\rangle\langle K|\hat{a}_{h_3}\hat{a}_{h_4}\hat{a}^\dagger_{h_1}\hat{a}^\dagger_{h_2}|J\rangle c_I^{M\dagger}c_J^N h_{h_1h_2h_3h_4} \tag{4}$$

It is apparent that

$$|K\rangle = \hat{a}^\dagger_{\omega_1}\hat{a}^\dagger_{\omega_2}\hat{a}_{\omega_3}\hat{a}_{\omega_4}|I\rangle \tag{5}$$

[1]This is to illustrate the rationale behind the algorithm; such a resolution of identity is not required in the final procedure.

$$|K\rangle = \hat{a}_{h_3}\hat{a}_{h_4}\hat{a}^\dagger_{h_1}\hat{a}^\dagger_{h_2}|J\rangle \tag{6}$$

Now we split the $\mathbf{X}$ into three kinds of blocks. Blocks of the first kind are such that no creation index is in the same range as any annihilation index. In blocks of the second kind, one pair of creation and annihiliation indexes may exist in the same space. In blocks of the final kind, all indexes are in active indexes[2].

If we consider blocks where all indexes are different, and in the special case where $I\rangle$ and $|K\rangle$ are defined within the same space, then it is apparent from (5) and (6) that every non-active creation ω index must cancel with a non-active annihilation h index. Suppose we are dealing with the block of $\mathbf{X}$ such that

$\omega_1 =$ core,

$\omega_2 =$ core,

$\omega_3 =$ virtual,

$\omega_4 =$ virtual.

This leads to contributions to the block $X_{\omega_1\omega_2\omega_3\omega_4}$

$$\sum_{h_1h_2h_3h_4}\sum_{IJK}\langle I|\hat{a}_{\omega_4}\hat{a}_{\omega_3}\hat{a}^\dagger_{\omega_2}\hat{a}^\dagger_{\omega_1}\hat{a}_{h_3}\hat{a}_{h_4}\hat{a}^\dagger_{h_1}\hat{a}^\dagger_{h_2}|J\rangle c_I^{M\dagger}c_J^N h_{h_1h_2h_3h_4}(\delta_{h_3,\omega_1}\delta_{h_4,\omega_2}+\delta_{h_3,\omega_2}\delta_{h_4,\omega_1}).$$

$$= \sum_{h_1h_2h_3h_4}\sum_{IJK}\langle I|\hat{a}_{\omega_4}\hat{a}_{\omega_3}\hat{a}^\dagger_{h_1}\hat{a}^\dagger_{h_2}|J\rangle c_I^{M\dagger}c_J^N h_{h_1h_2h_3h_4}(\delta_{h_3,\omega_1}\delta_{h_4,\omega_2}+\delta_{h_3,\omega_2}\delta_{h_4,\omega_1}). \tag{7}$$

We can now reorder the h indexes into normal-ordering, and repeat the process, only this time pairing every non-active annihilation ω index with a non-active creation h index of the same range:

$$\sum_{h_1h_2h_3h_4}\sum_{IJK}\langle I|\hat{a}_{\omega_4}\hat{a}_{\omega_3}\hat{a}^\dagger_{h_1}\hat{a}^\dagger_{h_2}|J\rangle c_I^{M\dagger}c_J^N h_{h_1h_2h_3h_4}(\delta_{h_3,\omega_1}\delta_{h_4,\omega_2}+\delta_{h_3,\omega_2}\delta_{h_4,\omega_1})(\delta_{h_1,\omega_3}\delta_{h_2,\omega_4}+\delta_{h_1,\omega_3}\delta_{h_2,\omega_3}).$$

$$\sum_{h_1h_2h_3h_4}\sum_{IJK}\langle I|J\rangle c_I^{M\dagger}c_J^N h_{h_1h_2h_3h_4}(\delta_{h_3,\omega_1}\delta_{h_4,\omega_2}+\delta_{h_3,\omega_2}\delta_{h_4,\omega_1})(\delta_{h_1,\omega_3}\delta_{h_2,\omega_4}+\delta_{h_1,\omega_3}\delta_{h_2,\omega_3}). \tag{8}$$

This process is then repeated for all the different blocks of $\mathbf{X}$. As is apparent from the above the dimension of the density matrix can be reduced substantially, but this is at the cost of extensive reordering of the tensor $\mathbf{h}$. However, provided symmetry of $\mathbf{h}$ is properly taken into account many of these reorderings are equivalent or closely related, enabling many of the terms in the reordering to be merged. It should be noted that $\langle I|J\rangle$ may never equal 1 in the relativistic case, as the $|I\rangle$ and $|J\rangle$ may be from different spin sectors.

[2]Typically, the CASPT2 amplitudes have no such block.

This method can be applied to more complicated terms, e.g.,

$$\sum_{\substack{t_1t_2t_3t_4\\f_1f_2}}\sum_{IKJ}\langle I|\hat{a}_{\omega_4}\hat{a}_{\omega_3}\hat{a}^\dagger_{\omega_2}\hat{a}^\dagger_{\omega_1}|K\rangle\langle K|\hat{a}_{f_2}\hat{a}_{t_3}\hat{a}_{t_4}\hat{a}^\dagger_{f_1}\hat{a}^\dagger_{t_1}\hat{a}^\dagger_{t_2}|J\rangle c_I^{M\dagger}c_J^N T_{t_1t_2t_3t_4}f_{f_1f_2} \tag{9}$$

Which for the block $X_{\omega_1\omega_2\omega_3\omega_4}$ with ω_1 and ω_2 virtual, and ω_3 and ω_4 active would yield

$$\sum_{\substack{t_1t_2t_3t_4\\f_1f_2}}\sum_{IKJ}\langle I|\hat{a}_w\hat{a}_x|J\rangle c_I^{M\dagger}c_J^N T_{t_1t_2t_3t_4}f_{f_1f_2}(\delta_{t_1,\omega_1}\delta_{t_2,\omega_2}+\delta_{t_1,\omega_2}\delta_{t_2,\omega_1}+...), \tag{10}$$

where the w are x are the non-contracted active indexes. Note that as all the ω destructors are active, none of the f or t indexes are contracted with them, resulting in only one bracket. More importantly, there is a reduced density matrix, however as all the indexes on X are now paired up. This results in a contraction between a two index reduced density matrix, and a six index tensor, formed from $\mathbf{T}\otimes\mathbf{f}$, with a sum over all the appropriate reordering relations specified by the δ functions.

As a rule of thumb, if the projector has n non-active indexes, and m is the total number of indexes on the molecular orbital intergral tensors, e.g., $m=6$ for $T_{t_1t_2t_3t_4}f_{f_1f_2}$, then we will need to contract several different index reorderings of an m rank tensor with and $m-n$ rank reduced density matrix.