1 Gamma generator

Consider a term

$$\sum_{ijkl}\sum_{mnop}\sum_{IJ}\langle I|i^\dagger j^\dagger klm^\dagger n^\dagger op|J\rangle c_I^M c_J^N Y_{ijkl}^{ML} Z_{mnop}^{NP}, \tag{1}$$

where I and J each denote a Slater determinant, and L, M, N, P are state indexes. $\mathbf{Y}^{ML}$ and $\mathbf{Z}^{NP}$ are representations of operators and $\hat{Y}$ and $\hat{Z}$ in the molecular orbital basis. For the time being the state dependence of the operator representations will be ignored, but has important consequences for exploitation of symmetry, and will be discussed at length later.

The proceedure most commonly employed by code generators is to use Wick's theorem to rearrange expressions, such as (1), into a series of normal ordered terms, e.g.,

$$\begin{aligned}
&= \sum_{stuvwxyz}\sum_{IJ}\langle I|s^\dagger t^\dagger u^\dagger v^\dagger wzyx|J\rangle c_I c_J^* A_{stuvwxyz},\\
&+ \sum_{stuwxy}\sum_{IJ}\langle I|s^\dagger t^\dagger u^\dagger wzy|J\rangle c_I c_J^* A_{stuwxy},\\
&+ \sum_{stwx}\sum_{mnop}\sum_{IJ}\langle I|s^\dagger t^\dagger wz|J\rangle c_I c_J^* A_{stwx},\\
&+ \sum_{sw}\sum_{mnop}\sum_{IJ}\langle I|s^\dagger w|J\rangle c_I c_J^* A_{sw}\\
&+ \sum_{sw}\sum_{mnop} A.
\end{aligned}$$

Where the tensors $A_{ijkl\ldots}$ are formed by performing the contractions between and reorderings of the indexes of tensors on Y and Z as determined from the commutation relations of the creation and annihilation operations, e.g.,

$$A_{stwx} = \sum_r^R \hat{\wp}_r \sum_{\{u,y\}}^{c1} \delta uy \sum_{\{v,z\}}^{c2} \delta vz Y_{ijkl} Z_{mnop},$$

where the $c1$ and $c2$ are sets of pairs of indexes to be contracted, e.g.,

$$c2 = \{\{i,k\}\},\{j,k\}\},\{l,m\}\}.....\} \tag{2}$$

and $\hat{\wp}_r$ which transforms the ordered set of indexes $\{u,v,s,t,w,x,y,z\}$ into some permutation, $r \in R$, of the ordered set of indexes $\{i,j,k,l,m,n,o,p\}$, whilst also acting to multiply the result of the summation by an appropriate factor.

A major advantage of this is that it enables constraints to be on the values over which the

molecular orbital indexes; all indexes on annihilation operators must correspond to orbitals occupied in $|J\rangle$, and creation operators must correspond to orbitals occupied in $|I\rangle$. This is a consequence of how determinants are constructed in active space based methods. A generic determinant can be written

$$\Psi_K = \sum_{p}^{p\in S_X} \epsilon_x \bigotimes_{i=0}^{n} \psi_{x_i}, \tag{3}$$

where X is a set of molecular orbital indexes $\{x_0, ..., x_n\}$, ϵ is the nth rank Levi-Cevita tensor, p is a member of the symmetric group S_X, consisting of all possible permutations on the set of indexes, $X = \{x_0, ..., x_n\}$, of molecular orbitals ψ_{x_i} from which the determinant is constructed.

In CI based methods it is common to use the fact that each distinct ordered set, X, of indexes corresponds to a different determinant (given all sets being compared have their indexes ordered according to some standard set of rules). In active space based methods number of determinants used to define the wavefunction is constrained to only those determinants which corresponding to sets $X \in F^{CAS}$, where

$$F^{CAS} = \{X | (X = X^c \cup X^a) \wedge (X^a \subset P) \wedge (\text{card}(X) = n_{act})\}$$

where P is the list of all "active" molecular orbital indexes, X^a is a subset of set of n_{act} orbitals occupied in the determinant defined by X, and where X^c is the list of closed orbital indexes, all of which are occupied in all determinants.

Unfortunately, F^{CAS} can get very large, leading to computational difficulties. One way of trying to manage this is to decompose the set of active orbital indexes, P, up into subsets;

$$P = \bigcup_{j=0} P_j, \tag{4}$$

and performing a similar decomposition on the sets of molecular orbital indexes X;

$$X = X_c \cup \bigcup_{j=0} X_j \qquad \text{where} \qquad X_j \subset P_j. \tag{5}$$

This leads to a related decomposition of F^{CAS} into smaller subspaces;

$$F^{CAS} = \cup_{n_1,..,n_N} F^{CAS}_{p_1,...,p_N},$$

where the indexes $p_1, ..., p_N$, define the number of elements any given $X \in F^{CAS}_{p_1,...,p_N}$ may have in common with each of the different subsets of P.

For example, suppose P is split into μ and ν indexes;

$$P = P_\mu \cup P_\nu. \tag{6}$$

For the case where

$$\text{card}(P_\mu) = 2, \quad \text{card}(P_\nu) = 4, \quad \text{and} \quad n_{act} = 3$$

The space, F^{CAS}, can then be split up according to how many γ and ν electrons are occupied in a given element;

$$F^{CAS} = F^{CAS}_{3,0} \cup F^{CAS}_{2,1} \cup F^{CAS}_{1,2}$$

$$F^{CAS}_{3,0} = \{X| \wedge (X^a_\mu \subset P_{mu}) \wedge (\text{card}(X)_\mu = n_{act}\}$$

$$F^{CAS}_{2,1} = \{X| \wedge (X^a_\mu \subset P_{mu}) \wedge (\text{card}(X)_\mu = n_{act} - 1\} \wedge (X^a_\nu \subset P_{nu}) \wedge (\text{card}(X)_\nu = 1\}$$

$$F^{CAS}_{1,2} = \{X| \wedge (X^a_\mu \subset P_{\mu}) \wedge (\text{card}(X)_\mu = n_{act} - 2\} \wedge (X^a_\nu \subset P_{nu}) \wedge (\text{card}(X)_\nu = 2\}$$

$$X = X^c \cup X^a_\mu \cup X^a_\nu.$$

I shall hereafter refer to these subspaces of F^{CAS} as ci-sectors (and in specific cases, spin-sectors). Decomposing the active space in this manner has a number of benefits, as the different ci-sectors may not interact, the most prominent example of this is the non-interaction of ci-sectors with different numbers of occupied α and β orbitals in the non-relativistic framework. However, even if they do, the decomposition of the active space makes it is possible to handle this interaction a piece wise manner, i.e., deal with interactions between two ci-sectors at a time. *Note : Please correct me if I am wrong, but I interpret relativistic CI as a kind of A.S.D., albeit with very different rules governing the interactions between the different sectors. I realize the implementations and approaches to optimization are very different.*

One major advantage is that decomposition of the active-space into different components facilitates the block wise decomposition of the reduced density matrices (RDMs), as a block of an RDM can being defined by the CI-sectors to which the Bra and Ket belong. Using the above decomposition of the active space as an example;

$$\sum_{J}^{\in\mathcal{F}_{all}} \sum_{I}^{\in\mathcal{F}_{all}} \langle I|i^\dagger j^\dagger m^\dagger n^\dagger klop|J\rangle c_I^M c_J^N$$

$$\sum_{\mathcal{F}_{sub}}^{\in\mathcal{F}_{all}} \sum_{\mathcal{F}_{sub}}^{\in\mathcal{F}_{all}} \sum_{I}^{\in\mathcal{F}_{sub}} \sum_{J}^{\in\mathcal{F}_{sub}} \langle I|i^\dagger j^\dagger m^\dagger n^\dagger klop|J\rangle c_I^M c_J^N,$$

where $\mathcal{F}_{sub}$ is one of the sub-spaces into which the total Fock space $\mathcal{F}_{all}$ has been decomposed. Unfortunately, this decomposition brings with it a number of complexities which are not present

for undecomposed active spaces. However, as we shall hopefully see, the reduction in the size, number, and complexity is substanstial, and is particularly valuable when treating multi-reference, relativistic wavefunctions.

Allowance for the fact that Bra and Ket may belong to different CI-sectors, the blockwise decomposition of the molecular orbital tensors, and the exploitation of symmetry which exists within and between different blocks *and* different CI-sectors, are the distinguishing features of the program.

1.1 Blockwise handling of terms

That different the Bra and Ket may have different CI-sectors has important ramifications for the program structure, however, before discussing these in depth it is necessary to discuss the basics of the task list construction.

As discussed in section(), we typically wish to evaluate terms of the following form;

$$\sum_{ijkl}\sum_{mnop}\sum_{IJ}\langle I|i^\dagger j^\dagger k l m^\dagger n^\dagger o p|J\rangle c_I^M c_J^N Y_{ijkl}^{ML} Z_{mnop}^{NP}. \tag{7}$$

In (7) the sum over the orbital indexes $\{i,j,k,l\}$ and $\{m,n,o,p\}$ runs over all indexes specified by tensors $\mathbf{Y}$ and $\mathbf{Z}$ respectively. However, we can rewrite the above in terms of summations over the ci-sectors and blocks into which these tensors may be decomposed;

$$\sum_{B^Y}\sum_{B^Z}\sum_{ijkl}^{B^Y}\sum_{mnop}^{B^Z}\sum_{IJ}\langle I|i^\dagger j^\dagger k l m^\dagger n^\dagger o p|J\rangle c_I^M c_J^N Y_{ijkl}^{ML} Z_{mnop}^{NP}. \tag{8}$$

Here B^Y and B^Z are blocks of $\mathbf{Y}$ and $\mathbf{Z}$ which define the ranges over which the summations of the molecular orbital indexes are to occur.

Many of the contributions from these various tensor blocks will vanish, but exactly which will vanish is dependent on the CI-sector to which $|I\rangle$ and $|J\rangle$ belong. For example, if

$$|I\rangle \in \mathcal{F}_{\mu=2,\nu=1} \qquad \text{and} \qquad |J\rangle \in \mathcal{F}_{\mu=3,\nu=0},$$

then the cumulative action of the creation and annihilation operators within the BraKet must be to destroy one electron in range r^μ, and create one in r^ν. All terms corresponding to blocks which do not meet this criterion can immediately be discarded. This idea can be taken further:

If the expression is rearranged into normal order,

$$\sum_{B^Y}\sum_{B^Z}\sum_{ijkl}^{B^Y}\sum_{mnop}^{B^Z}\sum_{IJ}\langle I|i^\dagger j^\dagger m^\dagger n^\dagger klop|J\rangle c_I^M c_J^N Y_{ijkl}^{ML} Z_{mnop}^{NP}. \tag{9}$$

then not only do we retain the above constraint, it is also known that terms corresponding to a combination of blocks, B^Y and B^Z, where *any* of the indexes k, l, o, p are in range ν, will vanish. An analagous constraint involing constraints on the ranges of the creation opeators is obtained by putting the expression into anti-normal ordering;

$$\sum_{B^Y}\sum_{B^Z}\sum_{ijkl}^{B^Y}\sum_{mnop}^{B^Z}\sum_{IJ}\langle I|klopi^\dagger j^\dagger m^\dagger n^\dagger|J\rangle c_I^M c_J^N Y_{ijkl}^{ML} Z_{mnop}^{NP}. \tag{10}$$

By applying this proceedure we ensure that only indexes within the active space are left within the BraKet, which is computationally significant as the dimension of the active orbitals range, r^a, is typically much smaller than the other blocks or the molecular orbital tensors (such as the core, r^c, or virtual r_c blocks).

Whilst this rearrangement will generate new terms in accordance with the commutation relations of the creation and annihilation operators, all of these new terms will be of lower rank than the original. This fact, combined with the range constraints and elimination of terms means that the increase number of computational tasks to be performed is generally well worth it.

Perhaps most importantly of all is that it means that all calculations can be done piece-wise, treating only one combination of CI-sectors at a time. This is particularly useful when calculating expressions requiring reduced density matrix derivatives;

$$\Gamma_{ijklmn}^I \sum_J \langle I|i^\dagger j^\dagger m^\dagger n^\dagger opkl|J\rangle c_J, \tag{11}$$

which due to the lack of a summation over one of the CI-indexes, I, can prove extremely large. This would prove highly problematic for implementations of energy derivative expressions in the relativistic framework. However, the block decomposition of molecular orbital tensors, the decomposition of the active space, and the seperation of blocks into a real and imaginary components, ensures that the peak memory requirements of the calculations need not exceed those for similar expressions in a non-relativstic framework.

A disadvantage is that the algebraic operations of rearranging the tensors must be performed for every possible block, of which there can in principal be millions[1]. Fortunately, there are a

[1]If each range is divided in to six, and we have ten indexes, then $6^{10} = 60466176$.

number of ways to mitigate this, but it is not so trivial an issue that it can be completely ignored.

The reordering sequence specified above; normal ordering followed by anti-normal ordering, encapsulates the most important principals used by the algebraic manipulator. However, more efficient task lists can be generated by following these with other reorderings, whose structure is determined by the properties of the block, and ultimately, the term being calculated. In order to understand why this approach is taken, and how these reorderings are chosen and generated, it is necessary to discuss the implementation of symmetry.

2 Handling of Block Symmetry

Initially, the state dependence of the operators seems perculiar; the molecular orbitals themselves do not differ between states, hence the state dependence of the representations suggests that it is not possible to interpret these operators as describing interactions between 1, 2, or n-electrons. In fact, such state dependent operators do not correspond to physical interactions per se, but are instead a tool used to aid in the description of representation of a perturbed state interms via interaction of a number of unperturbed states. An important consequence of this is that the symmetry of the operator representations is determined by the form of the equations from which they are obtained, rather than from consideration of the form of operators themselves.