A Tool for Multireference Perturbation Theory Calculations

Why not DFT or TDDFT?

- Interested in spin dynamics in actinide systems, particularly single molecular magnets (SMMs):
  - Do not want to use broken symmetry DFT to probe the behavior of electron spins [1][2].
  - Non-collinear 4c-TDDFT is still under development [3].

[1] P. J. Cherry, S. Komorovsky, V. G. Malkin, and O. L. Malkina, Mol. Phys., 115, 75–89 (2017)

[2] P. J. Cherry, V. G. Malkin, O. L. Malkina, and J. R. Asher, J. Chem. Phys. 145, 174108 (2016)

[3] S. Komorovksy, P. J. Cherry, and M. Repisky, "Four-component relativistic time-dependent density-functional theory using stable noncollinear DFT ansatz applicable to both closed- and open-shell systems" (In preparation).

Single Molecular Magnets

- Single molecular magnets (SMMs) are a being investigated for use in quantum computers.
- A key feature is the how long the magnetization is maintained.
- Heavily dependent on spin-orbit coupling.
- Performance at high temperatures is important for practical viability.

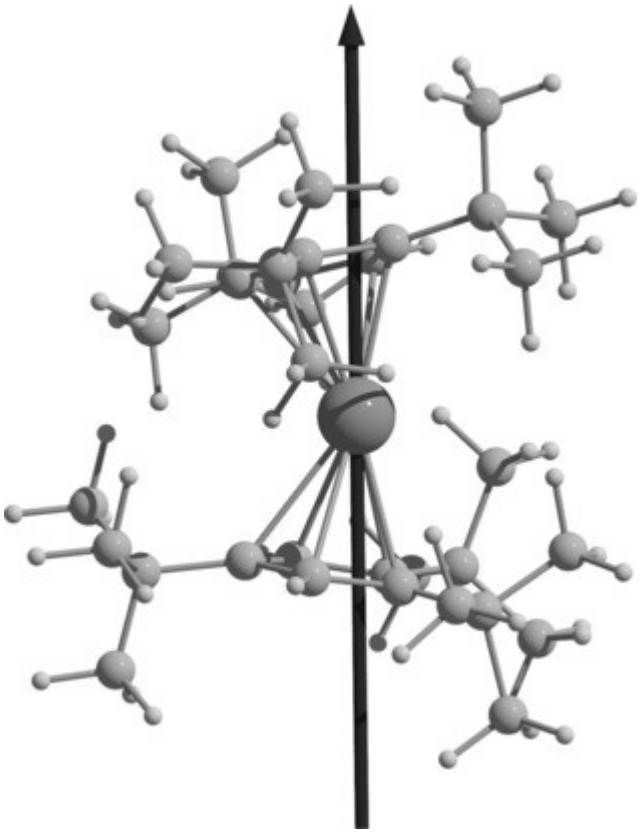

Figure 1. Dysprosium metallocene single Molecular magnet [4]

[4] F. S. Guo, B. M. Day, Y. C. Chen, M. L. Tong, A. Mansikkamäki, and R.A. Layfield, Ang. Chem. Int. Ed., 56(38), 11445-11449 (2017).

Method Requirements

- Some key challenges:
  - Near-degenerate (conical intersections following perturbation).
  - Spin-spin interactions raise questions regarding state-averaging key to some existing methods.
  - Need for derivative properties.
  - Computationally demanding.

- Tools exist, but not optimized for the four-component framework.

Longer term goals

- Several SMMs have multiple paramagnetic centres.
  - Want a tool which is applicable to tensor decomposed wavefunctions and operators.
- Want to be able to interface directly to spin-dynamics packages.
  - Enable on the fly task list construction.
- To accomplish this, began working on own program, MRPTool.

Existing tools

- Code generation widely used.
  - Tensor Contraction Engine (NWChem).
  - SMITH3 (Bagel).

- Has become a standard technique.
  - Increasingly relevant as supercomputer architectures become more complicated.
  - Not widely adopted by the majority of 4-component post-HF codes.

MRPTool Capabilities

- Should be able to :
  - Evaluate three basic terms types.
  - Combine these appropriately, and use them to solve a user-specified equation.
  - Calculate independent contributions sequentially (if computing resources require this).
  - Take advantage of symmetry and sparsity (particularly spin related symmetries).
- Extensibility is important:
  - Not tied to specific approach to storing data.
  - Can swap out tensor manipulation and FCI routines, without impacting basic functioning.

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First order CASPT2 wavefunction

- The first-order wavefunction is expanded in an internally contracted basis:

$$|\Psi^{(1)}\rangle = \hat{T}|\Psi^{(0)}\rangle = \sum_{t_0 t_1 t_2 t_3} \hat{a}^\dagger_{t_0} \hat{a}^\dagger_{t_1} \hat{a}_{t_2} \hat{a}_{t_3} |\Psi^{(0)}\rangle T_{t_0 t_1 t_2 t_3}$$

- The perturbation amplitudes minimize the Hylleraas functional for the second order energy:

$$E^{(2)} = 2\Re e \langle \Psi^{(1)}|\hat{H}_{el}|\Psi^{(0)}\rangle + \langle \Psi^{(1)}|\hat{H}^{(0)} - E^{(0)}|\Psi^{(1)}\rangle$$

Derivative properties

- The CASPT2 energy is not minimized with respect to the CASCI coefficients.
- Calculation of the derivatives of the CASCI-coefficients is very complicated, and computationally expensive.
- To avoid this, we define a Lagrangian which satisfies:

$$\frac{\partial L}{\partial X} = \frac{\delta E^{XMS}}{\delta X}$$

Lagrangian definition

- Lagrangian has the form:

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

- Satisfies the conditions:

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

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

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

Lagrangian definition

- XMS-CASPT2 Lagrangian definition:

$$L = E_P^{MS} + \sum_{LMN} \langle \tilde{M}|\hat{\lambda}^{\dagger}_{LM}(\hat{f} - E_L^{(0)} + E_s)\hat{T}_{LN}|\tilde{N}\rangle + \langle \tilde{M}|\hat{\lambda}^{\dagger}_{LM}\hat{H}|\tilde{L}\rangle$$

$$+\frac{1}{2}Tr[\mathbf{Z}(\mathbf{A} - \mathbf{A}^{\dagger})] - \frac{1}{2}Tr[\mathbf{X}(\mathbf{C}^{\dagger}\mathbf{S}\mathbf{C} - 1)]$$

$$+\sum_N W_N \Big[\sum_I z_{I,N}\langle I|\hat{H} - E_N^{ref})|N\rangle - x_N(\langle N|N\rangle - 1)\Big]$$

$$+\sum_i^{closed} \sum_j^{frozen} z_{ij}^c f_{ij} + \sum_{\substack{MN \\ M\neq N}} w_{MN}\langle M|\hat{f}|N\rangle$$

- Using MRPT2 necessitates that we have an efficient method of implementing this and similarly complicated things.

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Three basic term types

- All the terms of immediate interest can be broken down into three basic types of term :
  - **Full :**

$$\langle \Psi_M | \hat{B}\hat{C}\hat{D}.... | \Psi_N \rangle$$

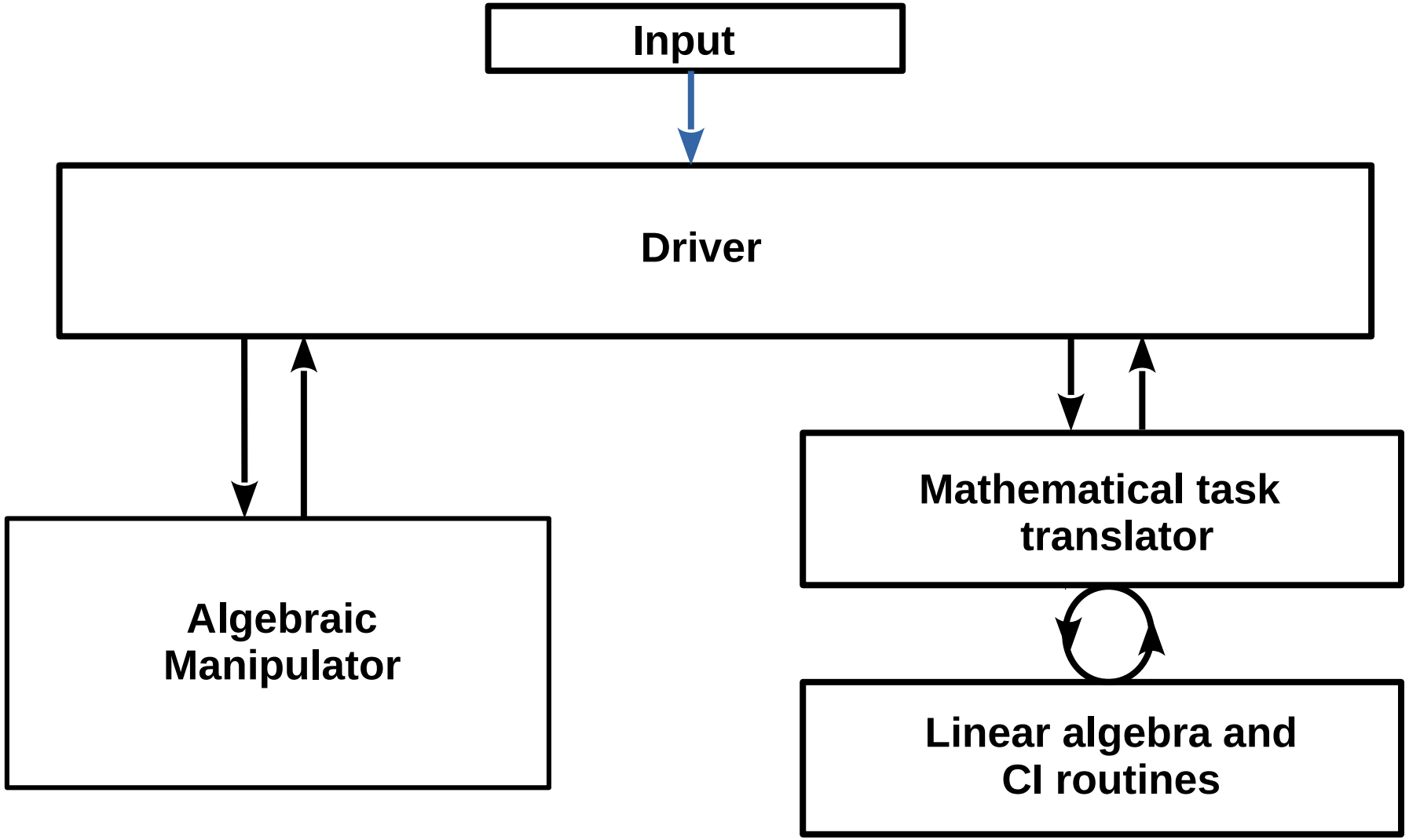
  - **Orbital Derivative :**

$$\frac{\partial}{\partial B_{b_1 b_2 \ldots}} \langle \Psi_M | \hat{B}\hat{C}\hat{D}.... | \Psi_N \rangle$$

  - **CI Derivative :**

$$\frac{\partial}{\partial c_J^N} \langle \Psi_M | \hat{B}\hat{C}\hat{D}.... | \Psi_N \rangle$$

MRPTool Structure



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“Full” term

- Simplest kind of term; “full”:

$$\langle \Psi_M | \hat{B}\hat{C}\hat{D}.... | \Psi_N \rangle$$

$$= \sum_{IJ} \sum_{\substack{b_1 b_2 \ldots \\ c_1 c_2 \ldots \\ d_1 d_2 \ldots}} c_I^{M\dagger} \langle I | \hat{B}_{b_1 b_2 \ldots} \hat{C}_{c_1 c_2 \ldots} \hat{D}_{d_1 d_2 \ldots} | J \rangle c_J^N$$

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“Orbital derivative” term

- Defined by taking the partial derivative with respect to one element of the representation of the operator in the orbital basis:

$$\frac{\partial}{\partial B_{b_1 b_2 \ldots}} \langle \Psi_M | \hat{B}\hat{C}\hat{D}.... | \Psi_N \rangle$$

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

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“CI derivative” term

- Partial derivative with respect to a CI-coefficient

$$\frac{\partial}{\partial c_J^N}\langle\Psi_M|\hat{B}\hat{C}\hat{D}....|\Psi_N\rangle$$

$$=\sum_I \sum_{\substack{c_1 c_2 \ldots \\ d_1 d_2 \ldots}} c_I^{M\dagger}\langle I|\hat{B}_{b_1 b_2 \ldots}\hat{C}_{c_1 c_2 \ldots}\hat{D}_{d_1 d_2 \ldots}|J\rangle c_J^N$$

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Term Evaluation

- Four stages:
  - Algebraic task list generation.
  - Task list translation.
  - Computational task list generation.
  - Computational task list execution.

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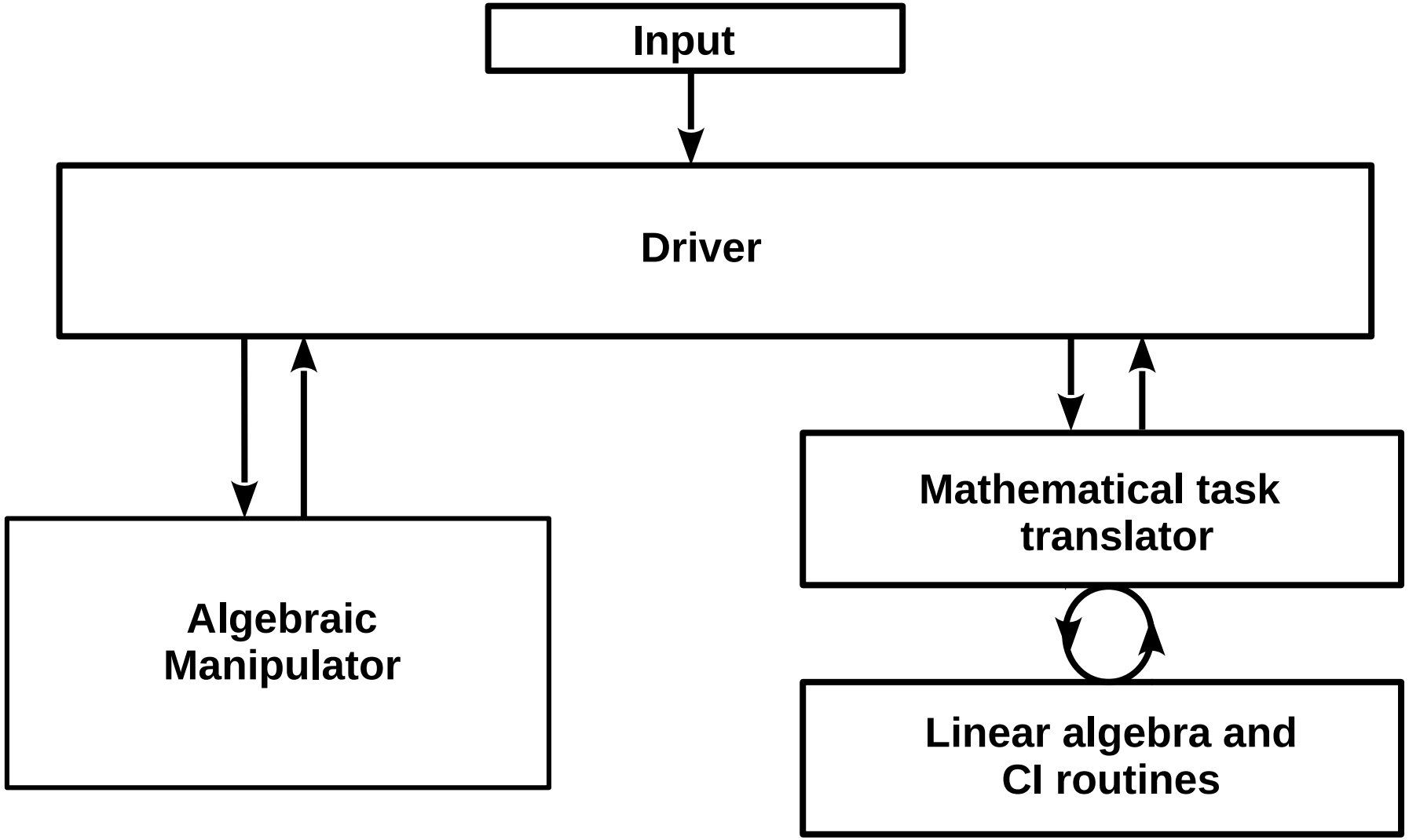

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Term Evaluation

- A typical term may require summation over **core**, **active** and **virtual** indices (**general** indices):

$$\sum_{I} \sum_{\mathbf{wxyz}} \sum_{\mathbf{ij}} \sum_{\mathbf{mnop}} \langle I|\hat{a}_{\mathbf{w}}\hat{a}_{\mathbf{x}}\hat{a}^{\dagger}_{\mathbf{y}}\hat{a}^{\dagger}_{\mathbf{z}}\hat{a}^{\dagger}_{\mathbf{i}}\hat{a}_{\mathbf{j}}\hat{a}^{\dagger}_{\mathbf{m}}\hat{a}^{\dagger}_{\mathbf{n}}\hat{a}_{\mathbf{o}}\hat{a}_{\mathbf{p}}|J\rangle c_J^N \lambda^{\dagger}_{\mathbf{wxyz}} f_{\mathbf{ij}} T_{\mathbf{mnop}}.$$

- Sum over general indices is rewritten as a sum over active indices :

$$= \sum_{\mathbf{abcdef}} \Gamma^{I}_{\mathbf{abcdef}} A_{\mathbf{abcdef}} + \sum_{\mathbf{abcd}} \Gamma^{I}_{\mathbf{abcd}} A'_{\mathbf{abcd}}$$

$$+ \sum_{\mathbf{ab}} \Gamma^{I}_{\mathbf{ab}} A''_{\mathbf{ab}} + A'''$$

$$\Gamma^{I}_{\mathbf{abcdefg}} = \langle I|a^{\dagger}_{\mathbf{a}} a^{\dagger}_{\mathbf{b}} a^{\dagger}_{\mathbf{c}} a_{\mathbf{d}} a_{\mathbf{e}} a_{\mathbf{f}}|J\rangle c_J$$

- Significantly reduces the dimension of the problem.

Evaluation stages

- Number of techniques employed to obtain an efficient task list, including:
  - Merging of tensor terms.
  - Operator reordering (e.g., Wicks theorem).
  - Block decomposition.
  - Block annihilation.
  - Operator reordering sequences.
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A-tensor definition

- Each A-tensor is defined by the original operators, $\hat{\lambda}$, $\hat{f}$, and $\hat{T}$, and a set, X, of contraction indices and factors:

$$A_{abcd} = \sum_{x}^{x \in X} \sum_{efghkl} \delta_{ef}\delta_{gh}\delta_{kl}\lambda^{\dagger}_{wxyz} f_{ij} T^{\dagger}_{mnop}$$

$$X = \{(\{(a_1, b_1), (c_1, d_1), (e_1, f_1)\}, s_1), (\{(a_2, b_2), (c_2, d_2), (e_2, f_2)\}, s_2), ...\}$$

- Each contribution, A^x, to the A-tensor is obtained by performing a recursive sequence of operations:

$$A^x_{abcd} = B(A^x_{abcdefgh}, (g, h)) =$$

$$= B(B(A^x_{abcdefgh}, (g, h)), (e, f)) = B(B(B(A^x_{abcdefgh}, (g, h)), (e, f)), (c, d))$$

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Non-relativistic CI-vector

- The wavefunction is described by a linear combination of determinants :

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

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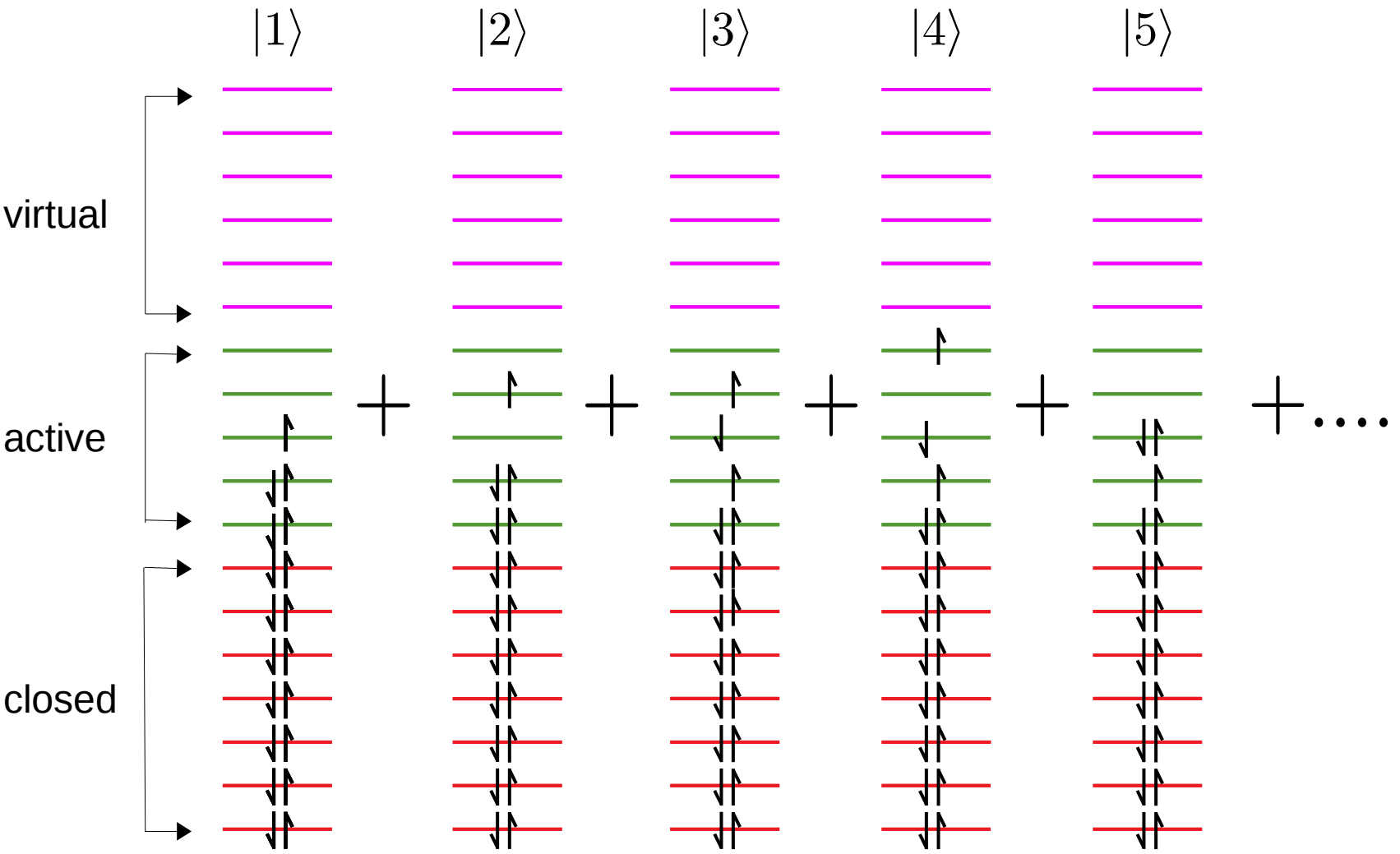
$\|1\rangle$	c_1
$\|2\rangle$	c_2
...	...
...	...
...	...
...	...
$\|N_{det}\rangle$	$c_{N_{det}}$

Active determinants



Electron number constraints

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- Both I and J are are active determinants belonging to the same spin sector:

$$n^I_{core} = n^J_{core} \qquad \Delta n_{core} = 0$$
$$n^I_{active} = n^J_{active} \qquad \Delta n_{active} = 0$$
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- This fact is exploited (via Wick's theorem) to pair up all "non-active" indexes.

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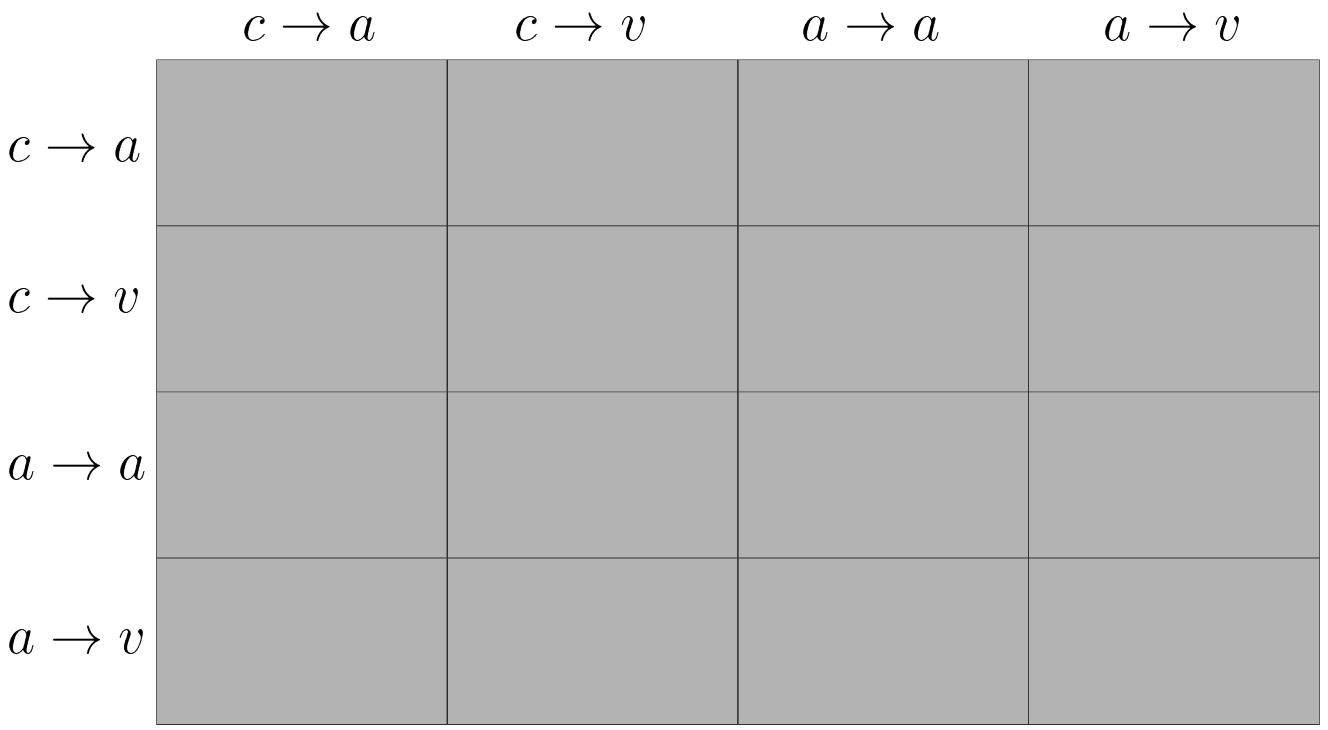
Block Decomposition

- CASPT2 amplitudes, $T_{(mo),(np)}$, and Lagrange multipliers, $\lambda_{(wy)(xz)}$



Possible transitions

$$closed \to active$$
$$closed \to virtual$$
$$active \to active$$
$$active \to virtual$$

Block Decomposition

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	$c \rightarrow a$	$c \rightarrow v$	$a \rightarrow a$	$a \rightarrow v$
$c \rightarrow a$	b_1	b_5	b_9	b_{13}
$c \rightarrow v$	b_2	b_6	b_{10}	b_{14}
$a \rightarrow a$	b_3	b_7	b_{11}	b_{15}
$a \rightarrow v$	b_4	b_8	b_{12}	b_{16}

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Block Decomposition

- State averaged Fock operator f_{ij}

	c	a	v
c	b_1	b_4	b_8
a	b_2	b_6	b_7
v	b_3	b_5	b_9

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Term/Block annihilation

- Split up the operators into sub-blocks, and loop over all combinations of blocks:

$$\sum_{I} \sum_{\mathbf{wxyz}} \sum_{\mathbf{ij}} \sum_{\mathbf{mnop}} \langle I|\hat{a}_{\mathbf{w}}\hat{a}_{\mathbf{x}}\hat{a}^{\dagger}_{\mathbf{y}}\hat{a}^{\dagger}_{\mathbf{z}}\hat{a}^{\dagger}_{\mathbf{i}}\hat{a}_{\mathbf{j}}\hat{a}^{\dagger}_{\mathbf{m}}\hat{a}^{\dagger}_{\mathbf{n}}\hat{a}_{\mathbf{o}}\hat{a}_{\mathbf{p}}|J\rangle c_J^N \lambda^{\dagger}_{\mathbf{wxyz}} f_{\mathbf{ij}} T_{\mathbf{mnop}}.$$

$$= \sum_{J} \sum_{\mu} \sum_{\nu} \sum_{\zeta} \langle I|(\hat{\lambda}^{b^{\lambda}_{\mu}}_{wxyz})^{\dagger} \hat{f}^{b^{f}_{nu}}_{ij} \hat{T}^{b^{T}_{\zeta}}_{mnop}|J\rangle c_J$$

- Several block combinations will vanish.

Term/Block Annihilation

- Determine range shift numbers for each block, e.g.,

$$T^{b_2^T} \rightarrow \Delta n_c = -2, \quad \Delta n_a = +1, \quad \Delta n_v = +1$$

$$\lambda^{b_4^\lambda} \rightarrow \Delta n_c = -1, \quad \Delta n_a = 0, \quad \Delta n_v = +1$$

$$f^{b_6^f} \rightarrow \Delta n_c = 0, \quad \Delta n_a = 0, \quad \Delta n_v = 0$$

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- Combine blocks, and determine the combined range shift number :

$$(\hat{\lambda}^{b_4^\lambda})^\dagger \hat{f}^{b_6^f} \hat{T}^{b_2^T} \rightarrow \Delta n_c = -1, \quad \Delta n_a = +1, \quad \Delta n_v = 0$$

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Block Constraints

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$\|1\rangle$	c_1
$\|2\rangle$	c_2
...	...
...	...
...	...
...	...
$\|N_{det}\rangle$	$c_{N_{det}}$

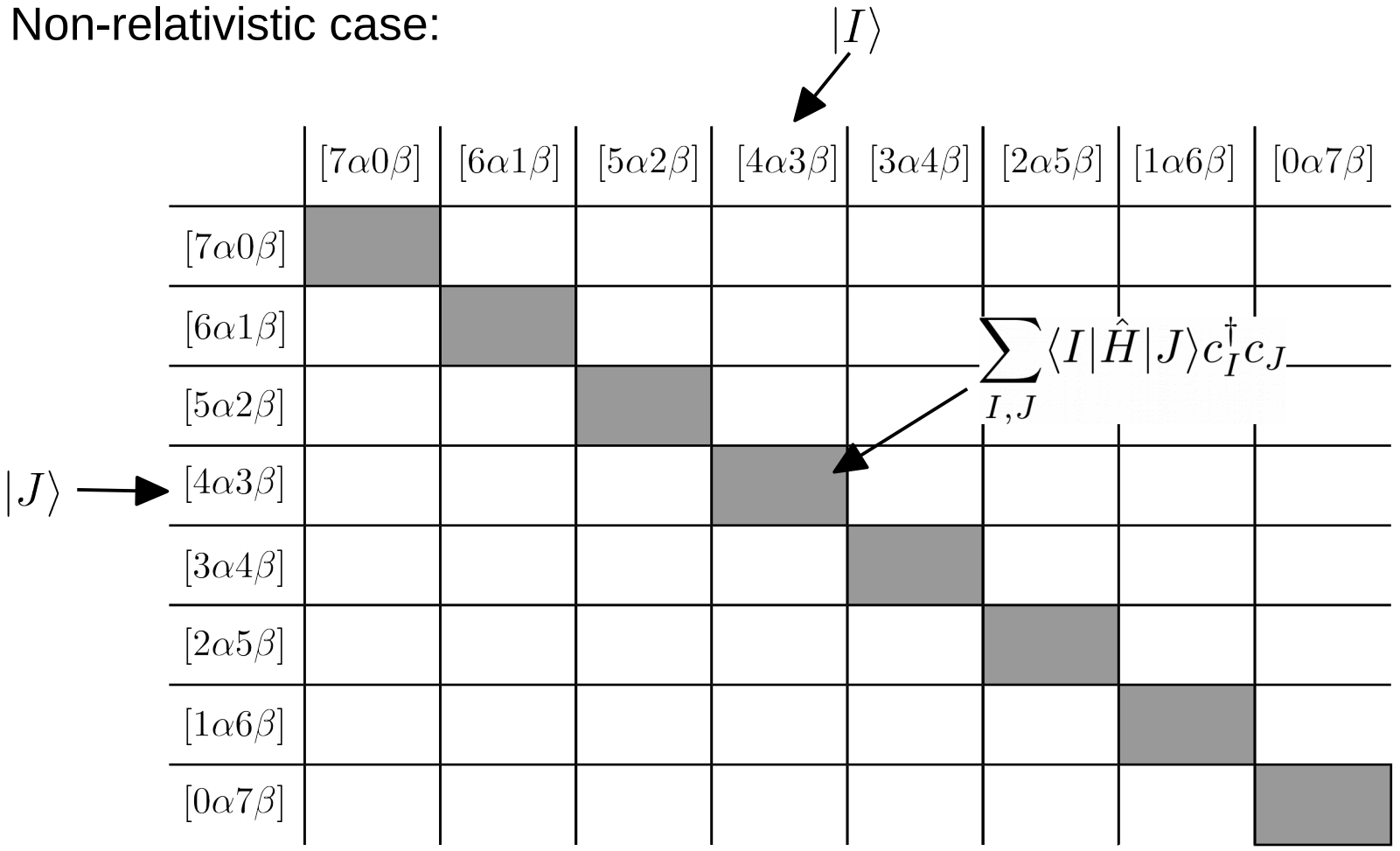
Relativistic CI-vector

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

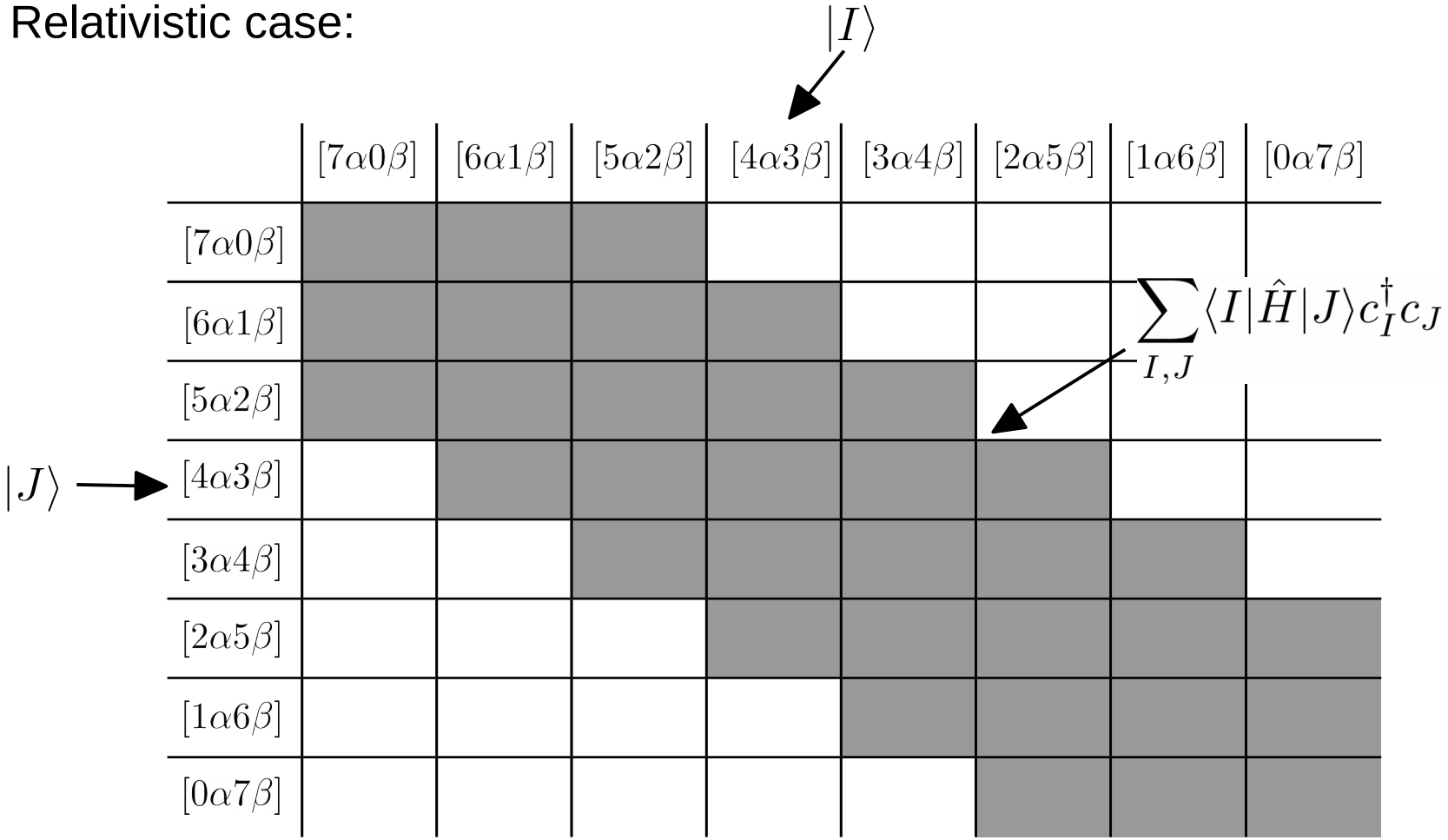
Non-interacting spin-sectors

Non-relativistic case:



Interacting spin-sectors

Relativistic case:



Relativistic CI-vector

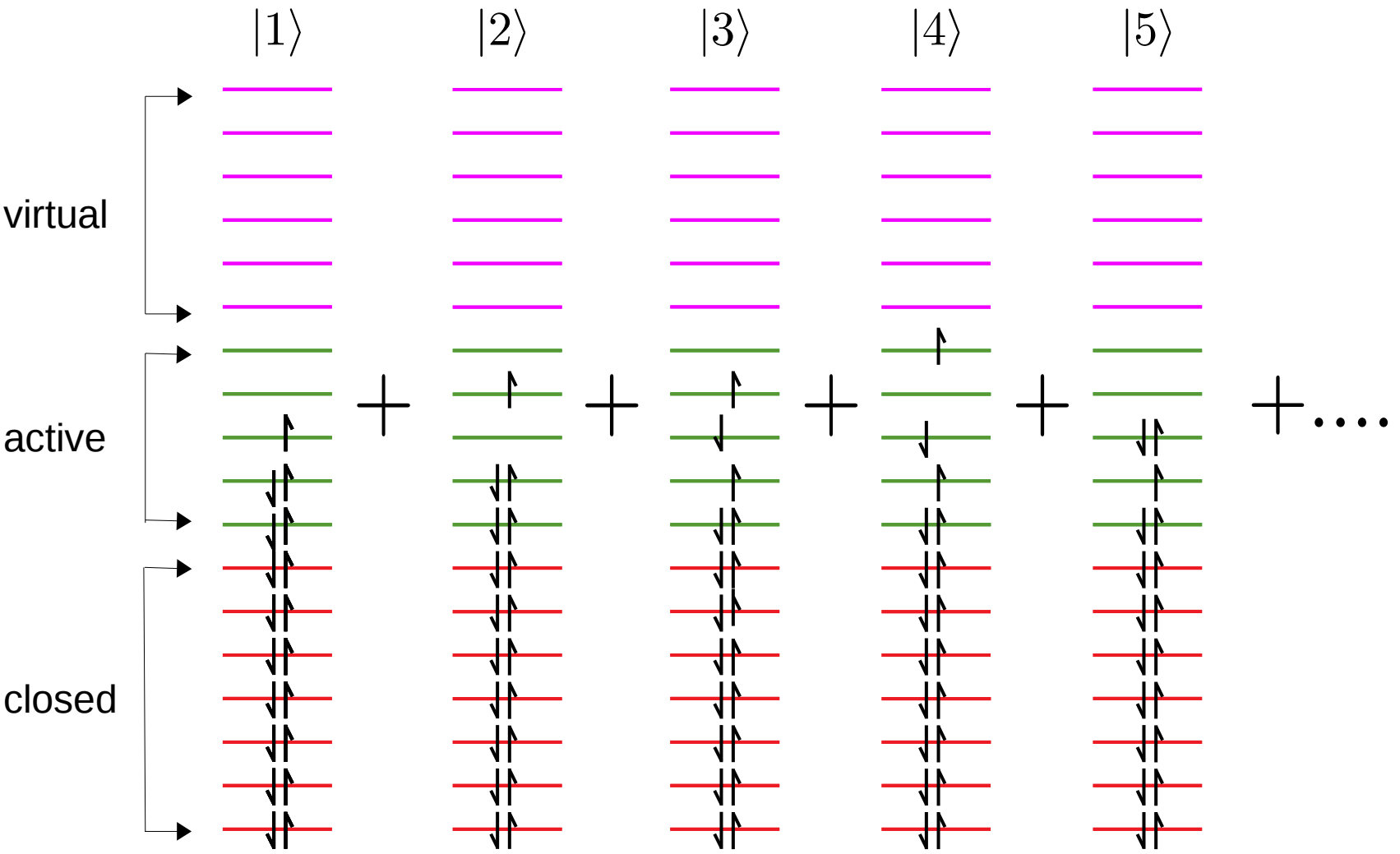
Spin-orbit coupling terms results in contributions from determinants in different spin sectors:

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

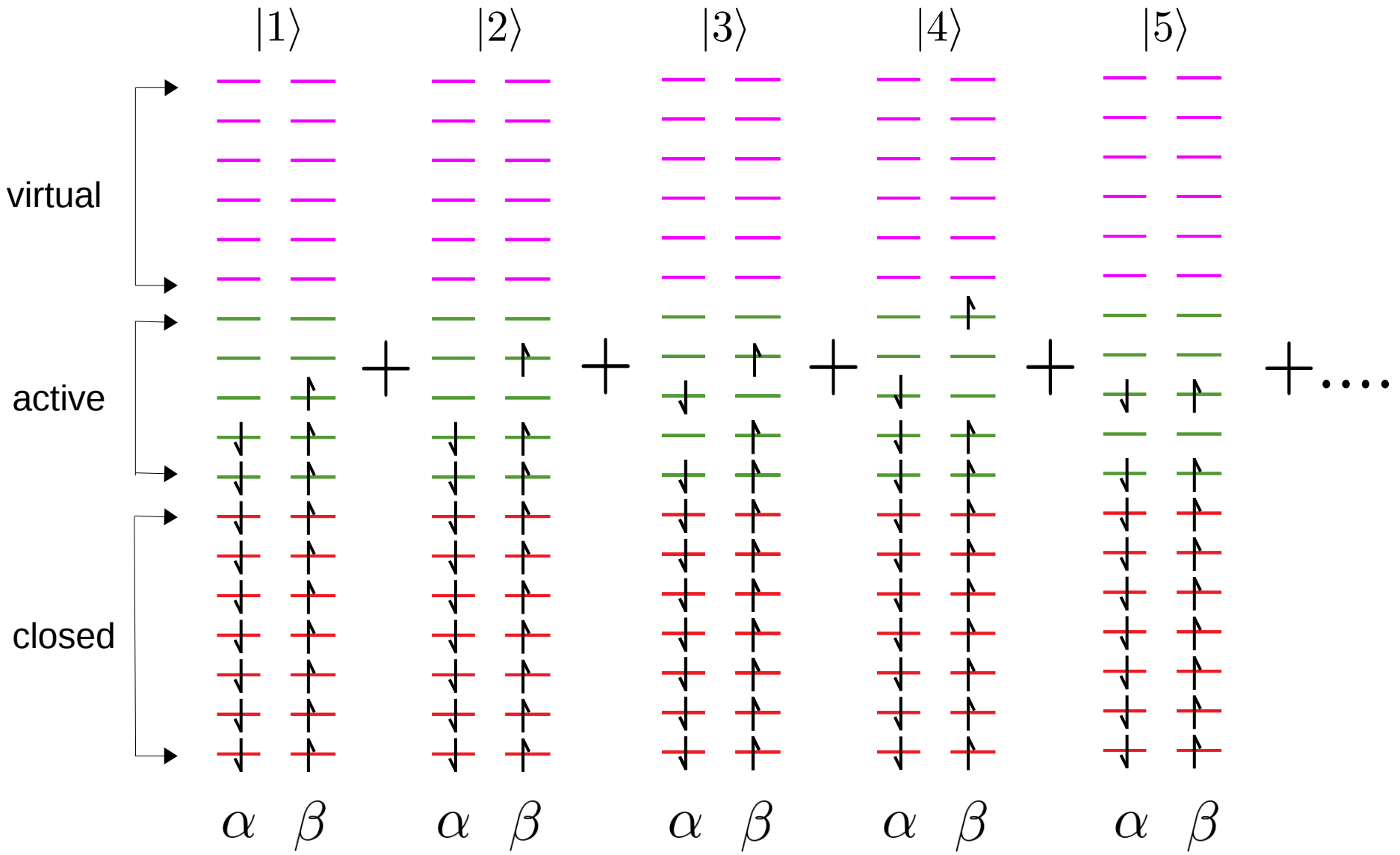
Block decomposition

- Split up **core**, **active** and **virtual** indices into up and down spins; **core** and ***core***, **active** and ***active*** , **virtual** and ***virtual*** :

Active determinants



Active determinants



Block constraints

- Split up **core**, **active** and **virtual** indices into up and down spins; **core** and ***core***, **active** and ***active*** , **virtual** and ***virtual*** :

$$\Delta n_{\mathbf{c}} = \Delta n_{\overline{\mathbf{c}}} = 0$$

$$\Delta n_{\mathbf{v}} = \Delta n_{\overline{\mathbf{v}}} = 0$$

$$-3 < \Delta n^{I}_{\mathbf{a}} < 3 \qquad -3 < \Delta n^{I}_{\overline{\mathbf{a}}} < 3$$

- Spin sector transitions are possible.

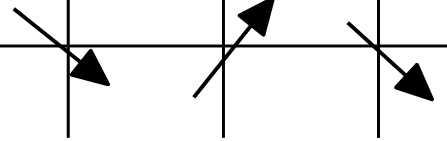
Evaluation stages

- Number of techniques employed to obtain an efficient task list, including:
  - Merging of tensor terms.
  - Operator reordering (e.g., Wicks theorem).
  - Block decomposition.
  - Term/Block annihilation.
  - Operator reordering sequences.
  - Limited tensor decomposition.

Reordering techniques

- Reorder creation and annihilation operators so as to push terms out of the active space:

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



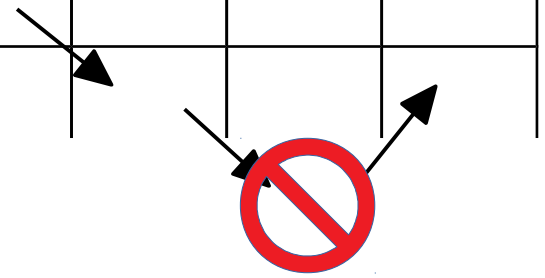
$$\sum_{KL} \langle I|\beta_k^\dagger \alpha_l|K\rangle\langle K|\alpha_i^\dagger \beta_j|L\rangle\langle L|\beta_m^\dagger \alpha_n|J\rangle =$$

$$= \begin{cases} 0 & \text{if} \quad i \neq n \quad \text{and} \quad i \neq k \\ \pm 1 & \text{otherwise} \end{cases}$$

Reordering techniques

- Reorder so as to “push” the wavefunction out of the active space.

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



$$\sum_{KL} \langle I|\alpha_i^\dagger \beta_j|K\rangle\langle K|\beta_k^\dagger \alpha_l|L\rangle\langle L|\beta_m^\dagger \alpha_n|J\rangle = 0$$

Reordering sequence

- Pass through multiple different reorderings so as to eliminate as many blocks as possible.
- Eliminates several higher order terms at the expense of creating more lower order ones.
  - First Order : Normal order (+++---).
  - Second Order : Anti-normal order (---+++).
  - Third Order : Alternating order (+-+-+-).

- Normal order and anti-normal order purge different block combinations.
- Note that “pairing” of non-active indexes never occurs; all non-active indexes are eradicated through range shift constraints.
- Alternating order aids with symmetry, and efficient calculation of higher order terms.

Alternating ordering

- Final sequence of expressions to evaluate may be :

$$\frac{\partial}{\partial c_I^M}\langle\Psi_M|\hat{H}\hat{T}|\Psi_N\rangle$$

$$= \sum_J \sum_{ijklmn} \Gamma^I_{ijklmn} A'''_{ijklmn} + \sum_J \sum_{ijkl} \Gamma^I_{ijkl} A''_{ijkl}$$

$$+ \sum_J \sum_{ij} \Gamma^I_{ij} A'_{ij} + A$$

- Where

$$\Gamma^I_{ijklmn} = \sum_{JKL} \langle I|a_i^\dagger a_j|K\rangle\langle K|a_k^\dagger a_l|L\rangle\langle L|a_m^\dagger a_n|J\rangle c_J$$

Contraction of Γ and $\mathbf{A}$

- Perform contraction in two steps:

$$\sum_{\sigma_3} \sum_{ijklmn} \Gamma^{IJ\sigma_3}_{ij,kl,mn} A^{\sigma_3}_{ij,kl,mn} c_J = \sum_{\sigma_1} \sum_{ij} \sum_{K} \Gamma^{IK\sigma_1}_{ij} \tilde{\Gamma}^{K\sigma_1}_{ij}$$

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

- Where σ_3 is shorthand for a spin-transition block, e.g.,

$$\sigma_1 : (\alpha\beta) \qquad \sigma_2 : (\alpha\alpha\beta\alpha)$$

$$\sigma_3 = \sigma_1 \otimes \sigma_2 : (\alpha\beta\alpha\alpha\beta\alpha)$$

Summary

- Developing a tool for multireference perturbation theory calculations.
- Targeted at 4-component methods, and tensor decomposed wavefunctions.
- Heavy emphasis on block symmetry and sparsity.
- Separation of computational and algebraic manipulation routines to facilitated rapid implementation of new task list generation.
- System specific task list generation to enable task list regeneration during dynamics calculations.

Summary

- Developing a tool for multireference perturbation theory calculations.
- Targeted at 4-component methods, and tensor decomposed wavefunctions.
- Heavy emphasis on block symmetry and sparsity.
- Seperation of computational and algebraic manipulation routines to facilitated rapid implementation of new task list generation.
- System specific task list generation with a view to interfacing with dynamics programs.

Code is available on my github account!

https://github.com/peterjohncherry/bagel_mrptool_devel

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CAREER: Theories for Magnetic Properties of Lanthanide and Actinide Complexes

END

External determinants