

# **A tool for property calculations using multireference wavefunctions**

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Theory group meeting  
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# MRPTool Outline



- In most software, each property has a separate implementation.

**Problem :** If you want a property which is not implemented... tough luck!

- A significant issue when using multireference 4-component methods; there aren't many programs around.

**Solution :** Write a generic framework for applying perturbation theory to 4-component multireference wavefunctions.



# MRPTool Outline

- No specific properties programmed; the user inputs algebraic expressions;

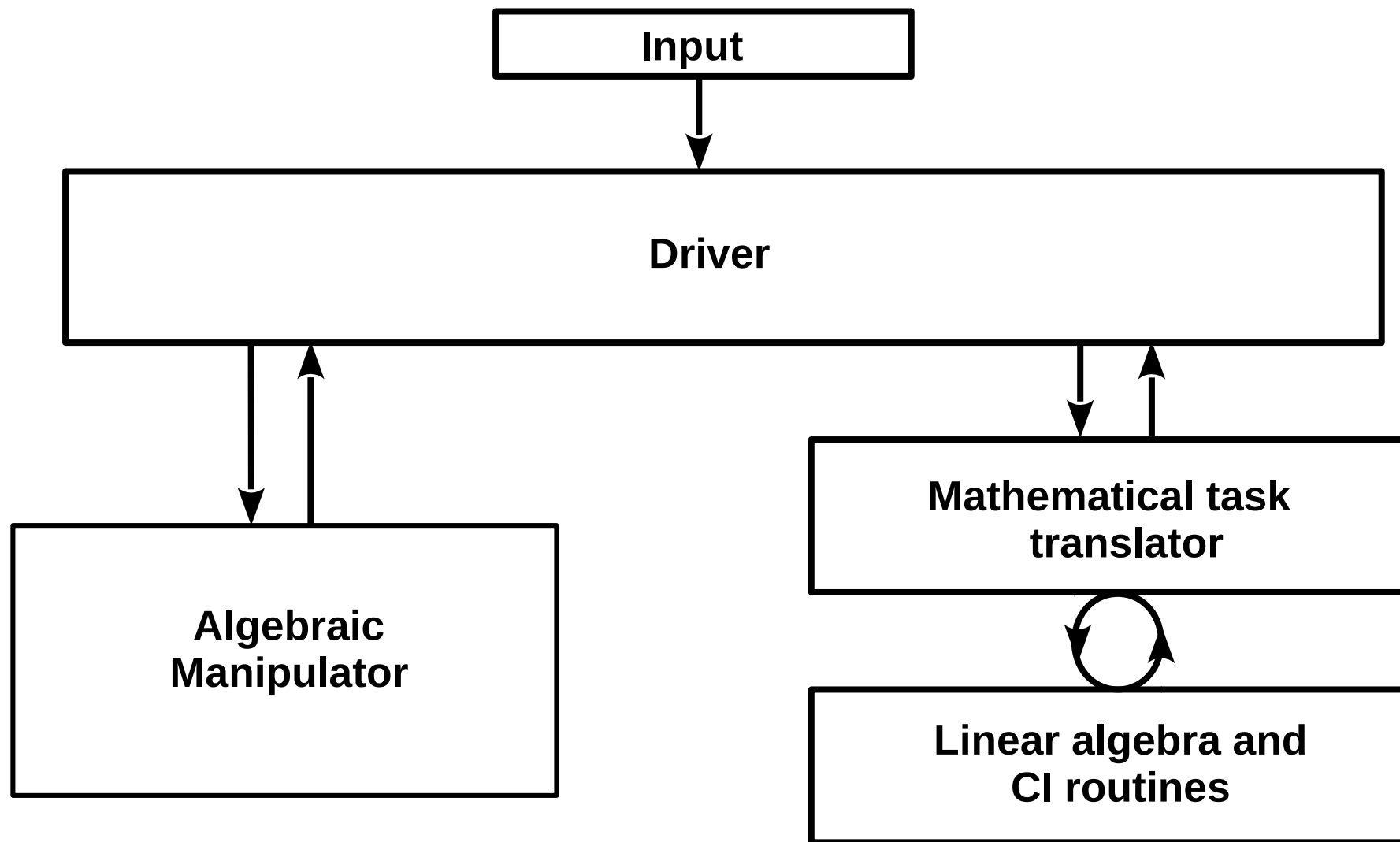
$$\sum_n^N \langle \Psi_n | \hat{X} \hat{Y} \hat{Z} | \Psi_m \rangle - \sum_p \langle \Psi_l | \hat{W}_p | \Psi_q \rangle$$

- Specify states, orbital indexes, operators, symmetries.
- Handles specific equation forms, e.g., find coefficients which minimize the Hylleraas functional ;

$$\sum_n^N \langle \Psi_n | \hat{X} \hat{Y} \hat{Z} | \Psi_m \rangle - \sum_p \langle \Psi_l | \hat{W}_p | \Psi_q \rangle$$

- Similar to code generation tools, but **no** programming necessary.
- Adapted specifically for the relativistic framework.

# Program Structure



# Advantages of relativistic multireference perturbation theory



**Why do we need multireference methods and not, e.g., DFT ?**

- *Better suited for degenerate cases.*
- *Clearer treatment of spin.*

**Why should we bother with computationally expensive 4-component relativistic methods?**

- *2-electron spin-orbit effects.*
- *Core spectroscopy for heavy elements.*

**Why do we need this flexibility?**

- *Expressions are hard to implement by hand.*
- *Wish to test theories.*

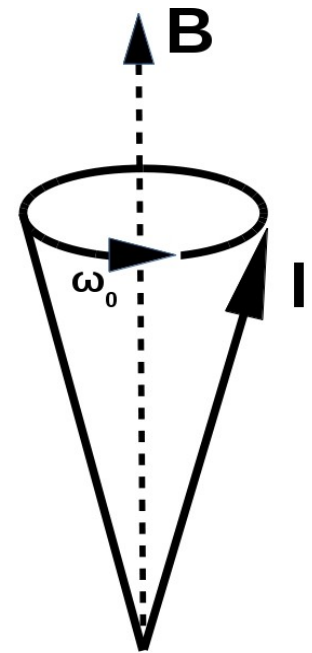
**Why do we need to do extended multistate perturbation theory?**

- *CASSCF alone is often not enough.*

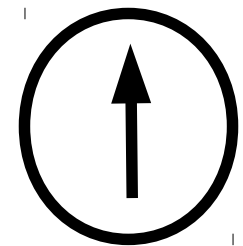
# Nuclear Magnetic Resonance (NMR)



- Characterize system based on its response to an external magnetic field.
- Electron spins will precess about the magnetic field.
- This is the Larmor precession, it is what experiments measure.
- The frequency of the Larmor precession influenced by
  - 1) Nuclear isotope.
  - 2) Electron-nuclear interactions.
  - 3) Nuclear-nuclear interactions.
  - 4) And many others....



**Fig. 1:** Larmor precession cone.

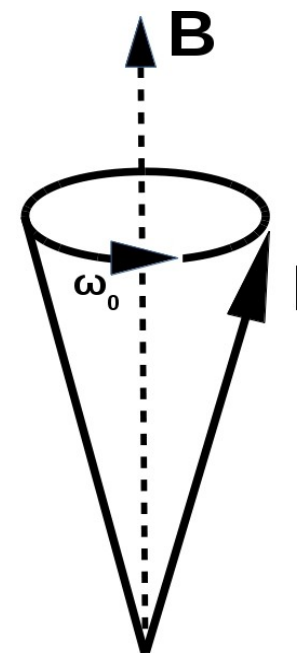


**Fig 2:** Nucleon.

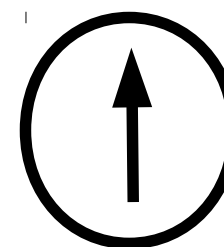
# Electron Paramagnetic Resonance (EPR)



- Characterize system based on its response to an external magnetic field.
- The frequency of the Larmor precession influenced by interactions with
  - 1) Nuclear potential
    - Hyperfine splitting
    - Spin-orbit coupling
  - 2) Other electrons:
    - Spin-other-orbit interaction
    - Orbit-orbit interaction



**Fig. 1:** Larmor precession cone.



**Fig 2:** Electron.

# Advantages of relativistic multireference perturbation theory



## Why do we need multireference methods and not, e.g., DFT ?

- *Better suited for degenerate cases.*
- *Simpler treatment of high spin multiplets.*

## Why should we bother with computationally expensive 4-component relativistic methods?

- *2-electron spin-orbit effects.*
- *Core spectroscopy for heavy elements.*

## Why do we need this flexibility?

- *Expressions are hard to implement by hand.*
- *Wish to test theories.*

## Why do we need to do extended multistate perturbation theory?

- CASSCF alone is often not enough.



# Spin Multiplets



- In the non-relativistic case, the eigenstates of the Hamiltonian can be divided up into several degenerate spin-multiplets.

$$\begin{array}{lcl}
 \text{quartet} & \left[ \begin{array}{c} \Psi_0 \\ \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \hline \end{array} \right] & \left. \vphantom{\begin{array}{c} \Psi_0 \\ \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \hline \end{array}} \right\} \epsilon_0 \\
 \text{doublet} & \left[ \begin{array}{c} \Psi_4 \\ \Psi_5 \\ \hline \end{array} \right] & \left. \vphantom{\begin{array}{c} \Psi_4 \\ \Psi_5 \\ \hline \end{array}} \right\} \epsilon_1 \\
 \text{quartet} & \left[ \begin{array}{c} \Psi_6 \\ \Psi_7 \\ \Psi_8 \\ \Psi_9 \\ \hline \end{array} \right] & \left. \vphantom{\begin{array}{c} \Psi_6 \\ \Psi_7 \\ \Psi_8 \\ \Psi_9 \\ \hline \end{array}} \right\} \epsilon_2 \\
 \text{doublet} & \left[ \begin{array}{c} \Psi_{10} \\ \Psi_{11} \end{array} \right] & \left. \vphantom{\begin{array}{c} \Psi_{10} \\ \Psi_{11} \end{array}} \right\} \epsilon_3
 \end{array}$$

- A magnetic field will split the energies of the states in the multiplet.
- The frequency of the Larmor precession is determined by the transitions between different states in the multiplet.

# Multireference wavefunctions

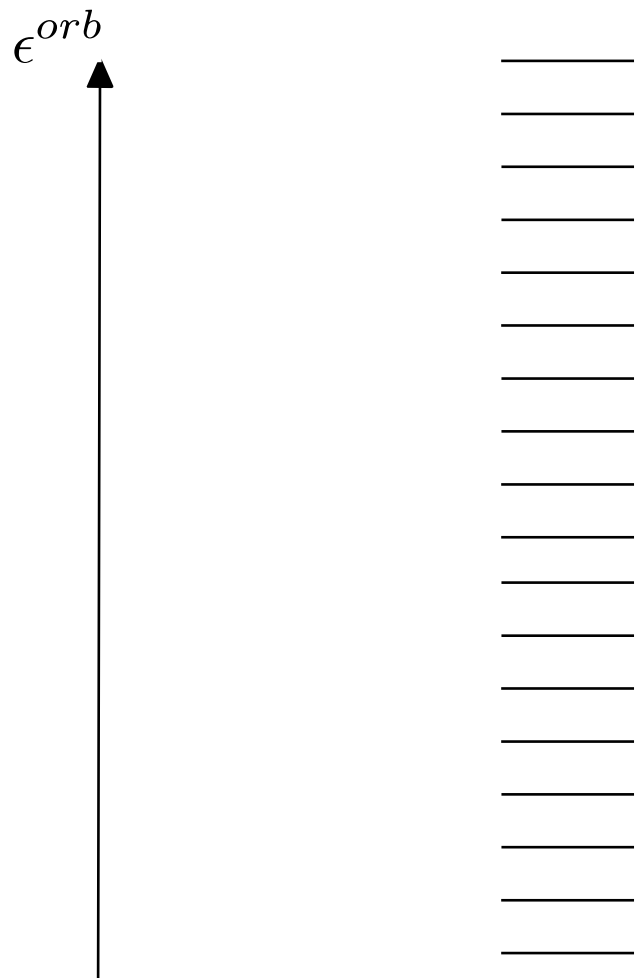


- Description of wavefunctions with spin multiplicity greater than often requires multiple determinants.
- For example, the spin-0 state in a triplet requires at least two:

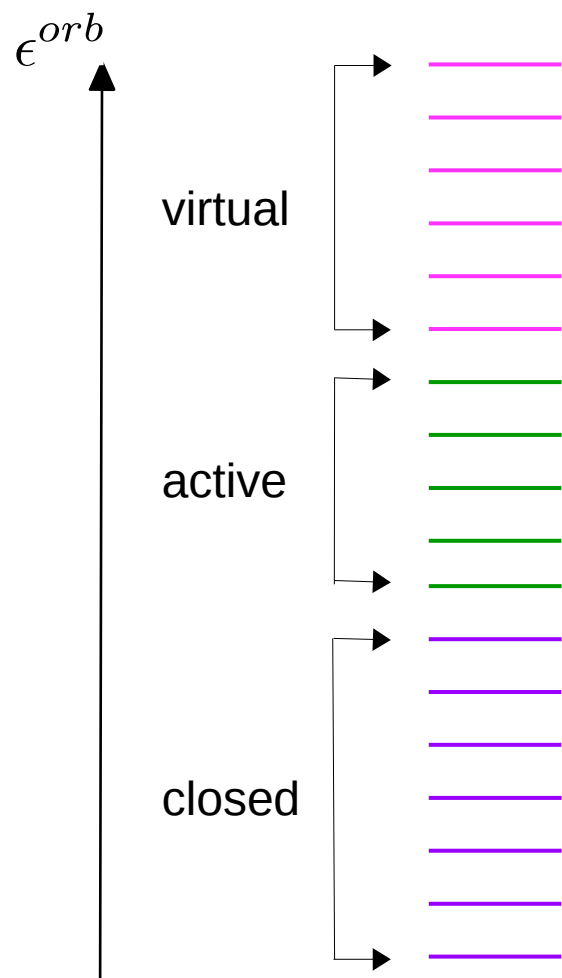
$$|\Psi_0\rangle = |\phi_{+\frac{1}{2}}\rangle + |\phi_{-\frac{1}{2}}\rangle$$

- Single determinant methods can be extremely effective, but can run into problems (e.g., spin contamination).
- Multi-determinant methods ensure we do not need to worry about this.

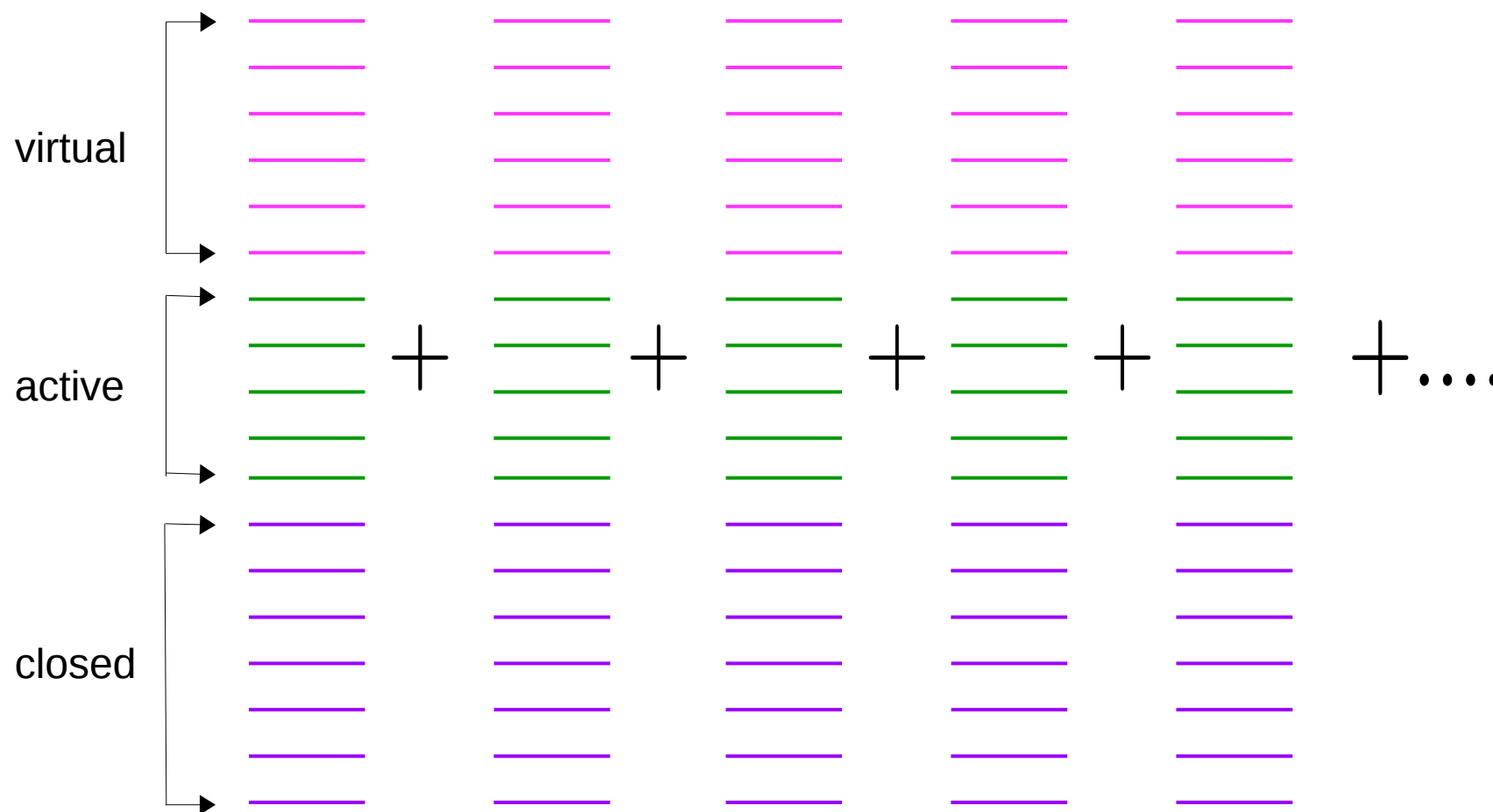
# Single determinant method



# Complete active space self-consistent field (CASSCF)



# Complete Active Space Self-Consistent Field



# Rough interpretation of EPR parameters



The Hamiltonian of system in the presence of a constant magnetic field can be written as the sum of a field free Hamiltonian and the Zeeman Hamiltonian :

$$\hat{H} = \hat{H}^{ff} + \hat{H}^Z$$

The time-evolution of a wavefunction due to the magnetic field can be approximated by:

$$\Psi(t) = e^{i\hat{H}^Z t} \Psi(0)$$

The Zeeman-Hamiltonian can be parameterized as :

$$\hat{H}^Z = \sum_{uv} g_{uv} B_u \hat{\sigma}_v$$

The coefficients,  $g_{uv}$ , parameterize the time evolution of the wavefunction, and hence the Larmour precession.

# Rough interpretation of EPR parameters



Obtain  $g_{uv}$  from the representation of the Hamiltonian in the eigenstates of the field free Hamiltonian :

$$\begin{bmatrix} \hat{H}_{00}^Z & \hat{H}_{01}^Z & H_{02}^Z & \dots \\ \hat{H}_{00}^Z & \hat{H}_{01}^Z & H_{02}^Z & \dots \\ \hat{H}_{00}^Z & \hat{H}_{01}^Z & H_{02}^Z & \dots \\ \dots & \dots & \dots & \dots \end{bmatrix} = \sum_{uv} \begin{bmatrix} \sigma_{u,00} & \sigma_{u,01} & \sigma_{u,02} & \dots \\ \sigma_{u,10} & \sigma_{u,11} & \sigma_{u,12} & \dots \\ \sigma_{u,20} & \sigma_{u,21} & \sigma_{u,22} & \dots \\ \dots & \dots & \dots & \dots \end{bmatrix} B_v g_{uv}$$

If the magnetic field is small, this matrix is roughly block diagonal:

$$\approx \sum_{uv} \begin{bmatrix} g_{uv}^0 \sigma_u & 0 & \dots \\ 0 & g_{uv}^1 \sigma_u & \dots \\ \dots & \dots & \dots \end{bmatrix} B_v$$

Each of the blocks has the dimensions of one of the multiplets.

# Advantages of relativistic multireference perturbation theory



Why do we need multireference methods and not, e.g., DFT ?

*Better suited for degenerate cases.*

*Clearer treatment of spin.*

**Why should we bother with computationally expensive 4-component relativistic methods?**

- *2-electron spin-orbit effects.*
- *Core spectroscopy for heavy elements.*

Why do we need this flexibility?

*Expressions are hard to implement by hand.*

*Wish to test theories.*

Why do we need to do extended multistate perturbation theory?

*CASSCF alone is often not enough.*



# Relativistic electron-electron interactions



- Interaction of electrons is different in a relativistic framework.

$$\hat{H} = \sum_{xy} h_{xy} \hat{E}_{xy} + \frac{1}{2} \sum_{xy} v_{xy,zw} \hat{E}_{xy,zw}$$

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## Non-relativistic one-electron terms

$$h_{xy}^{(1)} = (\mathbf{p}^{(1)})^2 - \sum_A \frac{Z_A}{r_{1A}} \text{erf}(\sqrt{\epsilon_A} r_{1A})$$

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$$h_{xy}^{(1)} = c^2(\beta - I_4) + c(\boldsymbol{\alpha}^{(1)} \cdot \mathbf{p}^{(1)}) - \sum_A \frac{Z_A}{r_{1A}} \text{erf}(\sqrt{\epsilon_A} r_{1A})$$

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$$v_{xy,zw}^{(1,2)} = \frac{1}{|\mathbf{r}_{12}|} - \frac{\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2}{|\mathbf{r}_{12}|} - \frac{\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 \cdot \nabla \mathbf{r}_{12}}{2}$$

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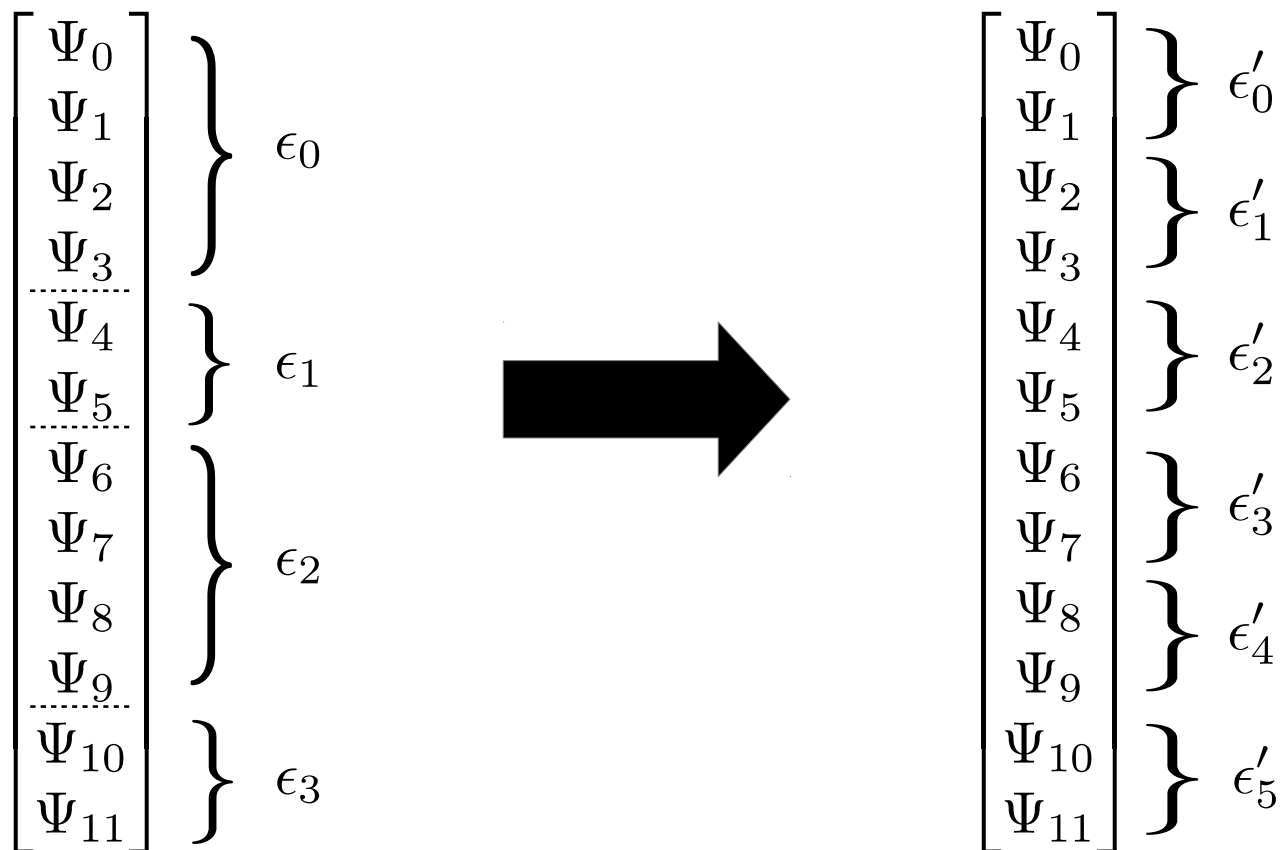
$$v_{xy,zw}^{(1,2)} = \frac{1}{|\mathbf{r}_{12}|} - \frac{\alpha_1 \cdot \alpha_2}{|\mathbf{r}_{12}|} - \frac{\alpha_1 \cdot \alpha_2 \cdot \nabla \mathbf{r}_{12}}{2}$$



# Spin Multiplets in a relativistic framework



- In systems with strong spin-orbit coupling, spin multiplets mix:



- Splitting even without a magnetic field (zero-field splitting).

# Non-relativistic CI-vector



Non-relativistic CI-vector only has determinants from a single spin sector:

$$|M\rangle = \sum_I c_{M,I} |I\rangle$$

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

Conf.	$[X\alpha Y\beta]$
$ 1\rangle$	$c_1$
$ 2\rangle$	$c_2$
...	...
...	...
...	...
...	...
$ N_{det}\rangle$	$c_{N_{det}}$

# Relativistic electron-electron interactions



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

# Non-interacting spin-sectors



Non-relativistic case:

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

$|K\rangle \rightarrow$  (points to the row index)

$|L\rangle$  (points to the column index)

$\sum_{I,J} \langle K | \hat{H} | J \rangle c_I^\dagger c_J$  (points to the matrix element at row  $[4\alpha 3\beta]$ , column  $[4\alpha 3\beta]$ )

# Interacting between spin-sectors



Relativistic case :

	$[7\alpha 0\beta]$	$[6\alpha 1\beta]$	$[5\alpha 2\beta]$	$[4\alpha 3\beta]$	$[3\alpha 4\beta]$	$[2\alpha 5\beta]$	$[1\alpha 6\beta]$	$[0\alpha 7\beta]$
$[7\alpha 0\beta]$								
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# Spin Multiplets in a relativistic framework



- The representation of magnetic field term in a basis formed from pure spin states is generally not block diagonal:

$$\begin{bmatrix} \hat{H}_{00}^Z & \hat{H}_{01}^Z & H_{02}^Z & \dots \\ \hat{H}_{00}^Z & \hat{H}_{01}^Z & H_{02}^Z & \dots \\ \hat{H}_{00}^Z & \hat{H}_{01}^Z & H_{02}^Z & \dots \\ \dots & \dots & \dots & \dots \end{bmatrix} \neq \sum_{uv} \begin{bmatrix} g_{uv}^0 \sigma_u & 0 & \dots \\ 0 & g_{uv}^1 \sigma_u & \dots \\ \dots & \dots & \dots \end{bmatrix} B_v$$

- Standard definitions of EPR parameters are not adequate for describing strong multiplet mixing.
- Off diagonal blocks will correspond to mixing of spin-multiplets, and determine the zero-field splitting.

# Spin Multiplets in a relativistic framework



- Zero-field splitting is important for EPR and paramagnetic-NMR.
- Used in determining spin-relaxation times, and identifying molecules for possible use as qubits.
- Heavily influenced by two-electron interactions, which are best\* described using Dirac-Coulomb-Breit Hamiltonian.
- Hence we would like to use 4-component multi-determinant methods.



# Advantages of relativistic multireference perturbation theory



Why do we need multireference methods and not, e.g., DFT ?

*Better suited for degenerate cases.*

*Clearer treatment of spin.*

Why should we bother with computationally expensive 4-component relativistic methods?

*2-electron spin-orbit effects.*

*Core spectroscopy for heavy elements.*

**Why do we need to do quasi-degenerate perturbation theory?**

- *Interested in state crossing.*
- *CASSCF alone is often not enough.*

*Why do we need this flexibility?*

*Expressions are hard to implement by hand.*

*Wish to test theories.*

# Magnetic fields in a relativistic framework



- Typically do not introduce magnetic fields via an extra operator.

$$\hat{H} = \hat{H}^{ff} + \hat{H}^Z$$

- Introduce via replacement of the momentum operator (minimal coupling):

$$\hat{\mathbf{p}} \rightarrow \hat{\mathbf{p}} + i\mathbf{A}$$

- This can result in changes to the form of the derivatives, and requires use of a basis which is itself dependent on the magnetic field.

# Magnetic field derivatives



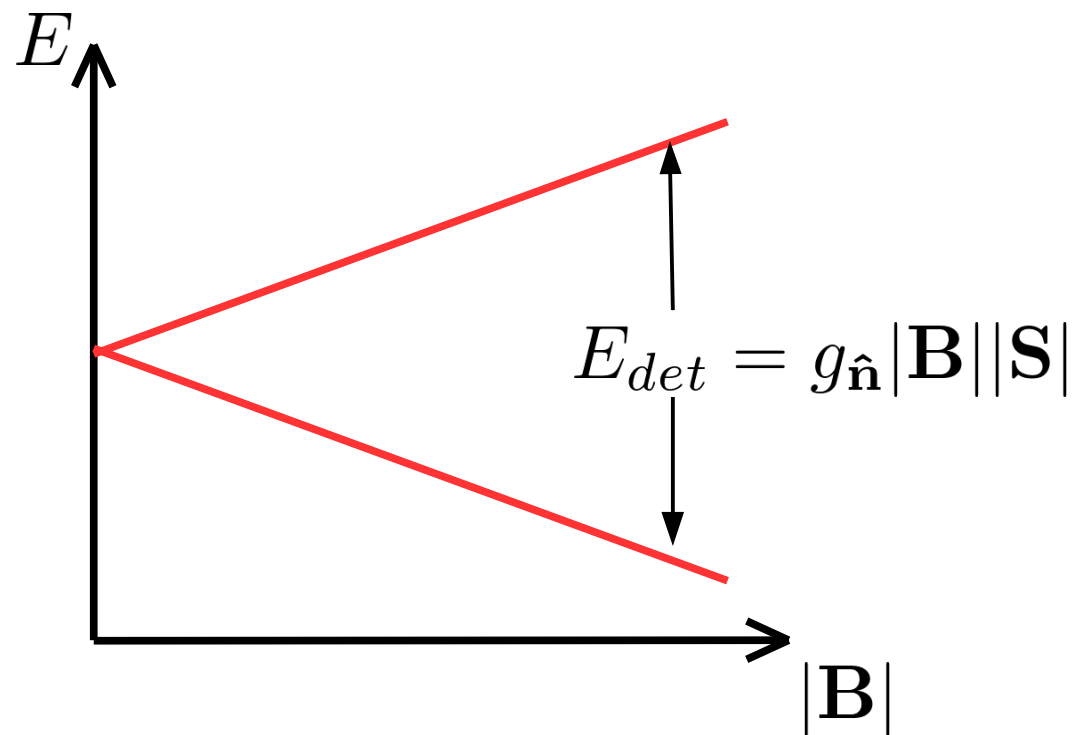
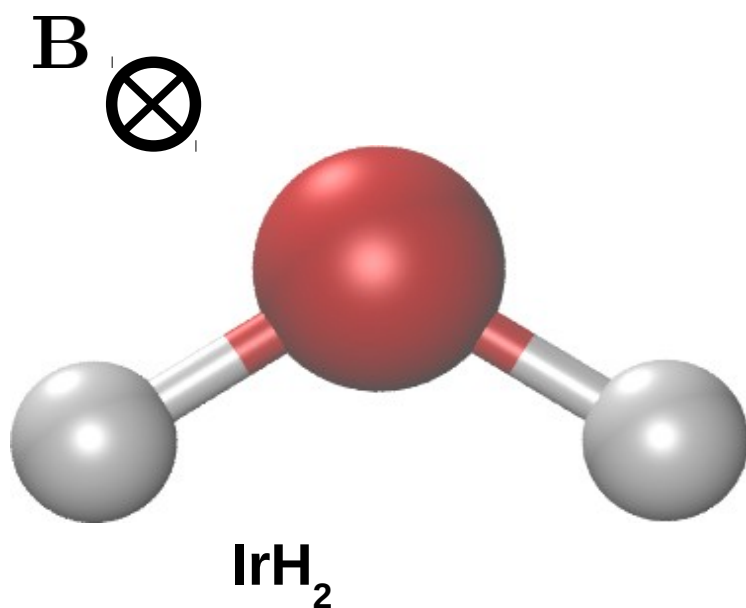
- Non-relativistic EPR parameters can be interpreted as derivatives of the energy at zero field :

$$g_{uv} = \left. \frac{\partial^2 E}{\partial B_u \partial \langle \hat{\sigma}_v \rangle} \right|_{B_u=0}$$

- The splitting is approximately linear with respect to the magnetic field.

$$g_{uv} = \left. \frac{\partial^2 E}{\partial B_u \partial \langle \hat{\sigma}_v \rangle} \right|_{B_u=0} \approx \left. \frac{\partial^2 E}{\partial B_u \partial \langle \hat{\sigma}_v \rangle} \right|_{B_u=B'}$$

# Linear Zeeman splitting



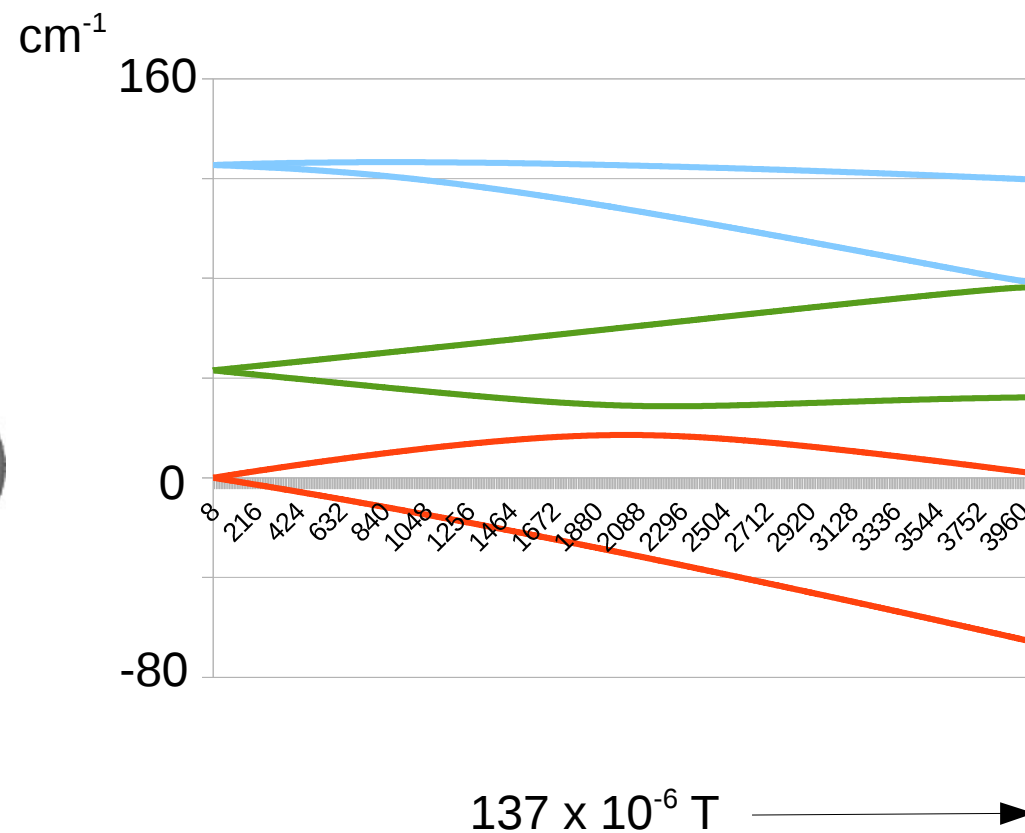
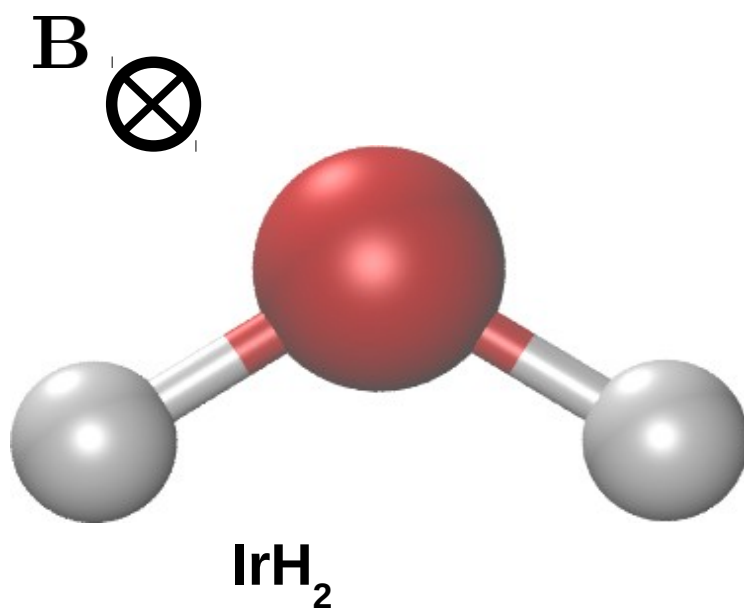
# Magnetic field derivatives



- Strong spin-orbit coupling and mixing of multiplets can result in transitions between spin states as the field increases.
- This can result in non-linear behaviour, even at low fields:

$$g_{uv} = \left. \frac{\partial^2 E}{\partial B_u \partial \langle \hat{\sigma}_v \rangle} \right|_{B_u=0} \neq \left. \frac{\partial^2 E}{\partial B_u \partial \langle \hat{\sigma}_v \rangle} \right|_{B_u=B'_u}$$

# Non-linear Zeeman splitting



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Why should we bother with computationally expensive 4-component relativistic methods?

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*Core spectroscopy for heavy elements.*

**Why do we want so much flexibility?**

- *Expressions are hard to implement by hand.*
- *Wish to new test theories, which may not work.*

Why do we need to do extended multistate perturbation theory?

*CASSCF alone is often not enough.*

# Magnetic field derivatives



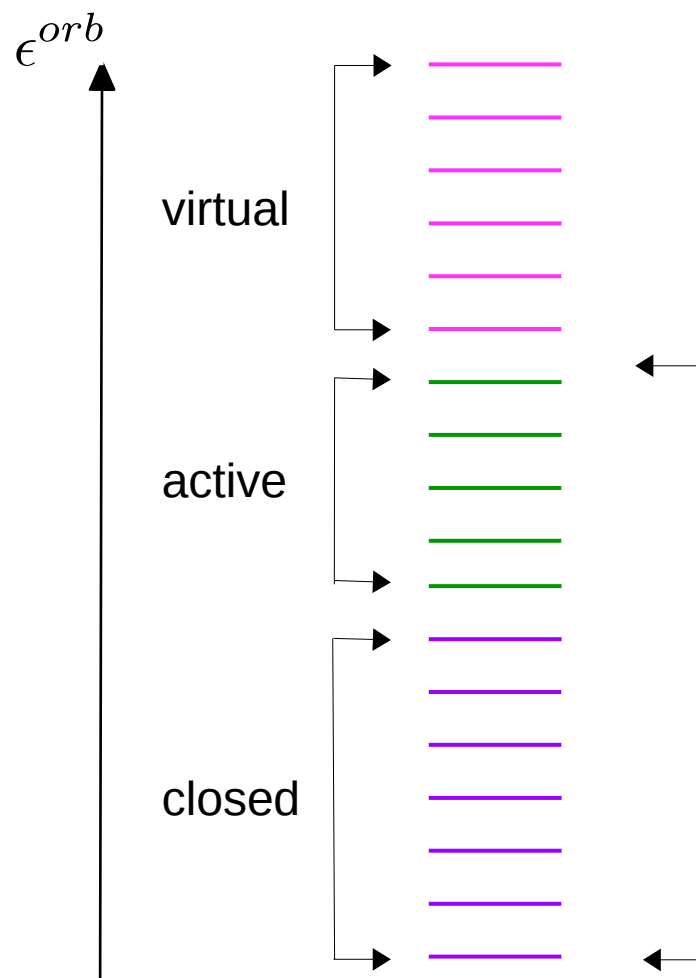
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- To probe this phenomena, we need to calculate derivative properties for finite perturbations.
- Potentially a huge number of distinct perturbations (magnitudes and directions of magnetic field).



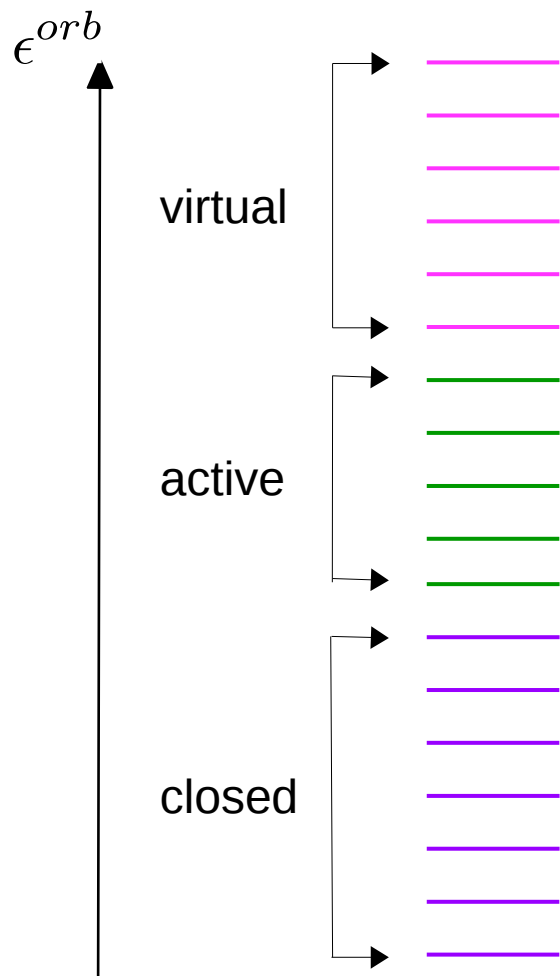
# Complete active space self-consistent field (CASSCF)



- CA space is optimized for the unperturbed Hamiltonian.
- Accurate description of a perturbation to the Hamiltonian must account for change in this space.

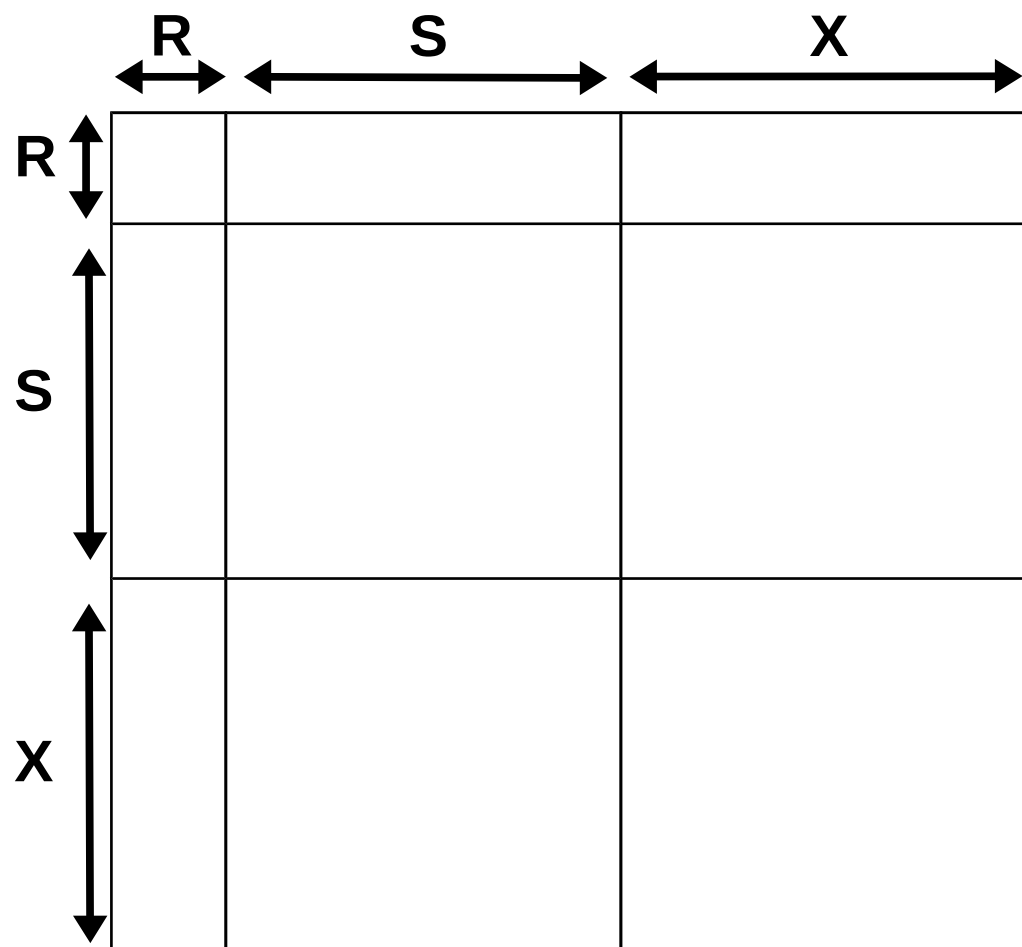
Optimized for  
unperturbed  
hamiltonian

# Complete active space self-consistent field (CASSCF)



- CA space is optimized for the unperturbed Hamiltonian.
- Accurate description of a perturbation to the Hamiltonian must account for change in this space.
- Add in some determinants with excitations to orbitals in the virtual space.

# Multi-state perturbation 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

# Primary term types



Expectation value (“full”) type terms :

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

CI-derivative type terms :

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

Excitation derivative type terms:

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

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

CI-derivative type terms :

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

Excitation derivative type terms:

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