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 seperate 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.

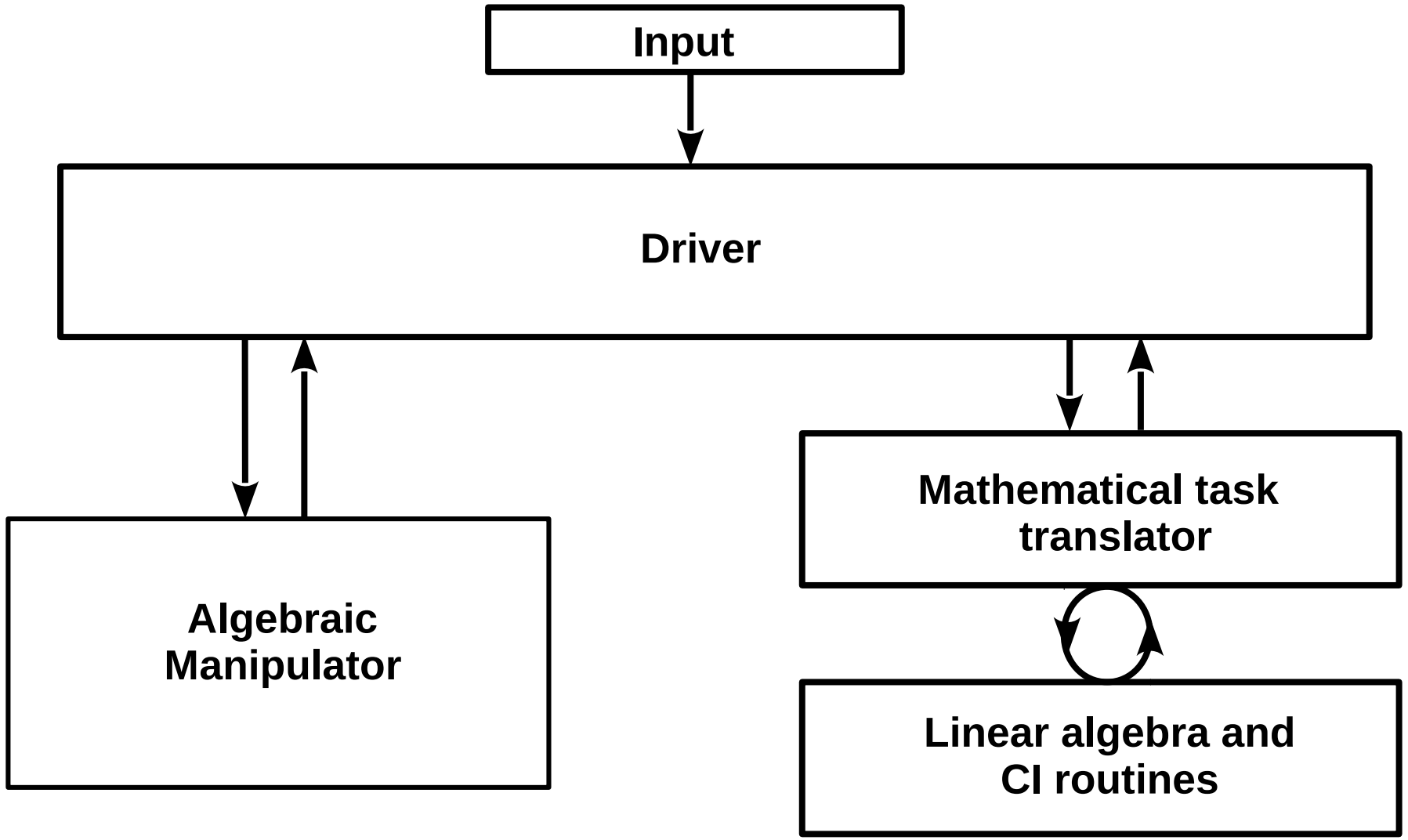
- Handles specific equation forms, e.g., find coefficients which minimize the Hylleraas functional ;

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

- Similar to code generation tools, but **no** programming necessary.

- Adapted specifically for the relativistic framework.

Program Structure



Advantages of relativistic multireference peturbation 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....

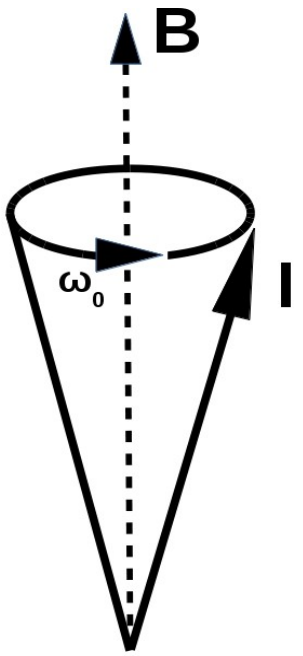


Fig. 1: Larmor precession cone.

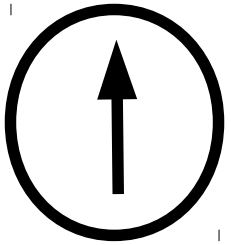


Fig 2: Nucleon.

Electron Paramagnetic Resonance (EPR)

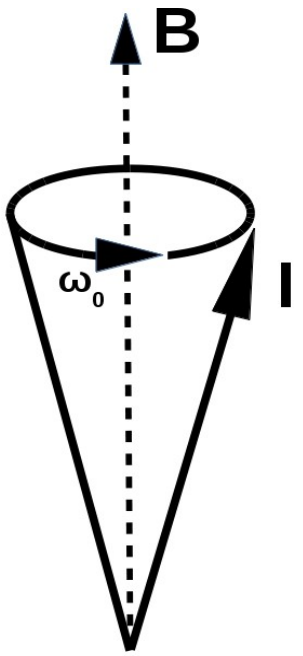
- Characterize system based on its response to an external magnetic field.
- The frequency of the Larmor precession influenced by interations with

    1) Nuclear potential

        - Hyperfine splitting
        - Spin-orbit coupling

    2) Other electrons:

        - Spin-other-orbit interaction
        - Orbit-orbit interaction



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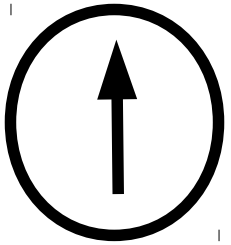


Fig 2: Electron.

Advantages of relativistic multireference peturbation 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.

quartet $\left.\begin{matrix}\Psi_0\\ \Psi_1\\ \Psi_2\\ \Psi_3\end{matrix}\right\} \epsilon_0$

doublet $\left.\begin{matrix}\Psi_4\\ \Psi_5\end{matrix}\right\} \epsilon_1$

quartet $\left.\begin{matrix}\Psi_6\\ \Psi_7\\ \Psi_8\\ \Psi_9\end{matrix}\right\} \epsilon_2$

doublet $\left.\begin{matrix}\Psi_{10}\\ \Psi_{11}\end{matrix}\right\} \epsilon_3$

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

Multireference wavefunctions

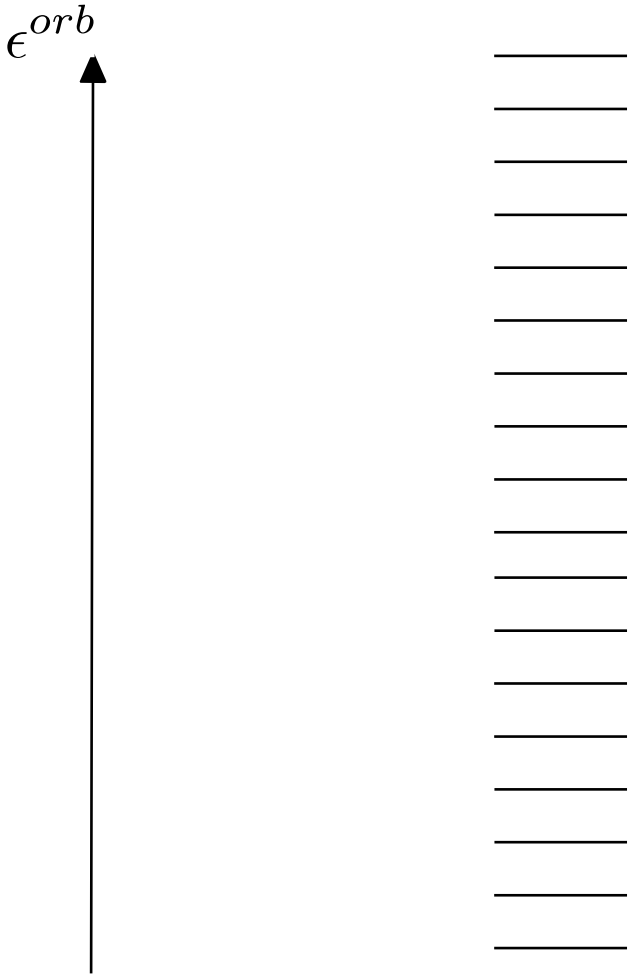
- Description of wavefunctions with spin multiplicity greater than often requires multiple determinants.
- For example, the spin-0 state in a triplet requires at least two:

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

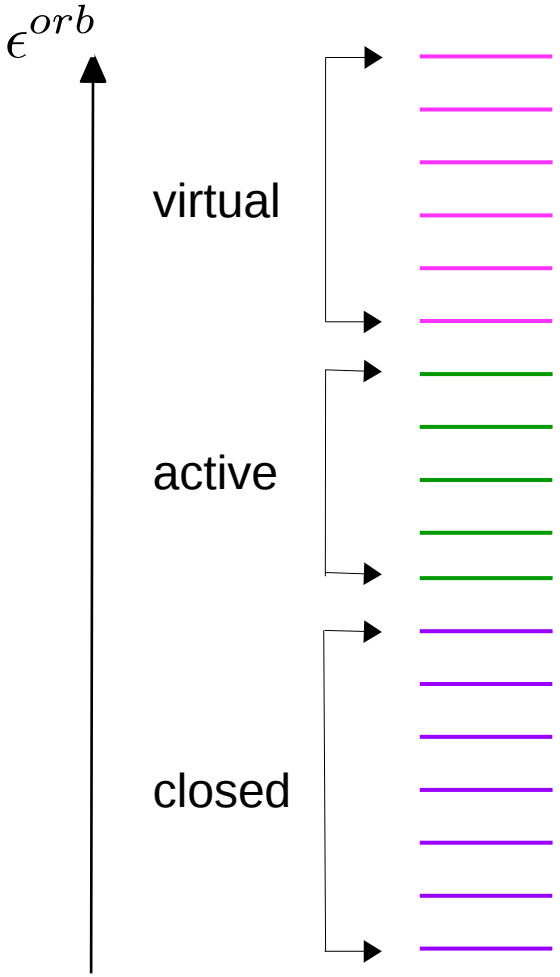
- Single determinant methods can be extremely effective, but can run into problems (e.g., spin contamination).

- Multi-determinant methods ensure we do not need to worry about this.

Single determinant method



Complete active space self-consistent field (CASSCF)



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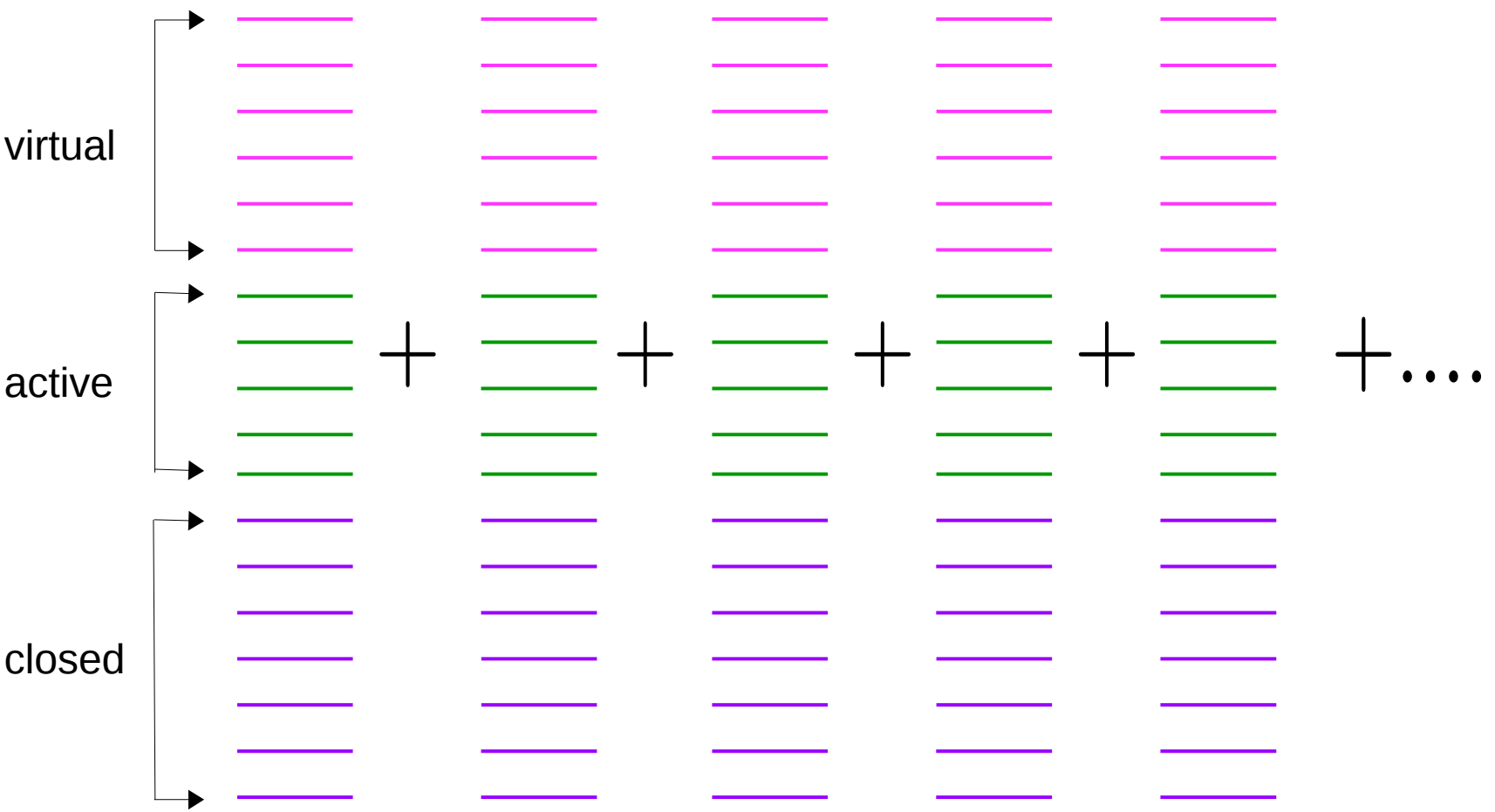

Rough interpretation of EPR parameters

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 :

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

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

$$\approx \sum_{uv} \begin{bmatrix} g^0_{uv}\boldsymbol{\sigma}_u & 0 & \dots \\ 0 & g^1_{uv}\boldsymbol{\sigma}_u & \dots \\ \dots & \dots & \dots \end{bmatrix} B_v$$

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

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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

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

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Relativistic one-electron terms

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

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Spin Multiplets in a relativitic framework

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

$$\left[\begin{array}{l}\Psi_0\\ \Psi_1\\ \Psi_2\\ \Psi_3\end{array}\right\} \epsilon_0 \qquad \left[\begin{array}{l}\Psi_4\\ \Psi_5\end{array}\right\} \epsilon_1 \qquad \left[\begin{array}{l}\Psi_6\\ \Psi_7\\ \Psi_8\\ \Psi_9\end{array}\right\} \epsilon_2 \qquad \left[\begin{array}{l}\Psi_{10}\\ \Psi_{11}\end{array}\right\} \epsilon_3 \quad \Rightarrow \quad \left[\begin{array}{l}\Psi_0\\ \Psi_1\end{array}\right\} \epsilon'_0 \qquad \left[\begin{array}{l}\Psi_2\\ \Psi_3\end{array}\right\} \epsilon'_1 \qquad \left[\begin{array}{l}\Psi_4\\ \Psi_5\end{array}\right\} \epsilon'_2 \qquad \left[\begin{array}{l}\Psi_6\\ \Psi_7\end{array}\right\} \epsilon'_3 \qquad \left[\begin{array}{l}\Psi_8\\ \Psi_9\end{array}\right\} \epsilon'_4 \qquad \left[\begin{array}{l}\Psi_{10}\\ \Psi_{11}\end{array}\right\} \epsilon'_5$$

- 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:

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

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

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

Relativistic electron-electron interactions

- Interaction of electrons is different in a relativistic framework.

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

Non-relativistic two-electron terms

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Relativistic two-electron terms

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

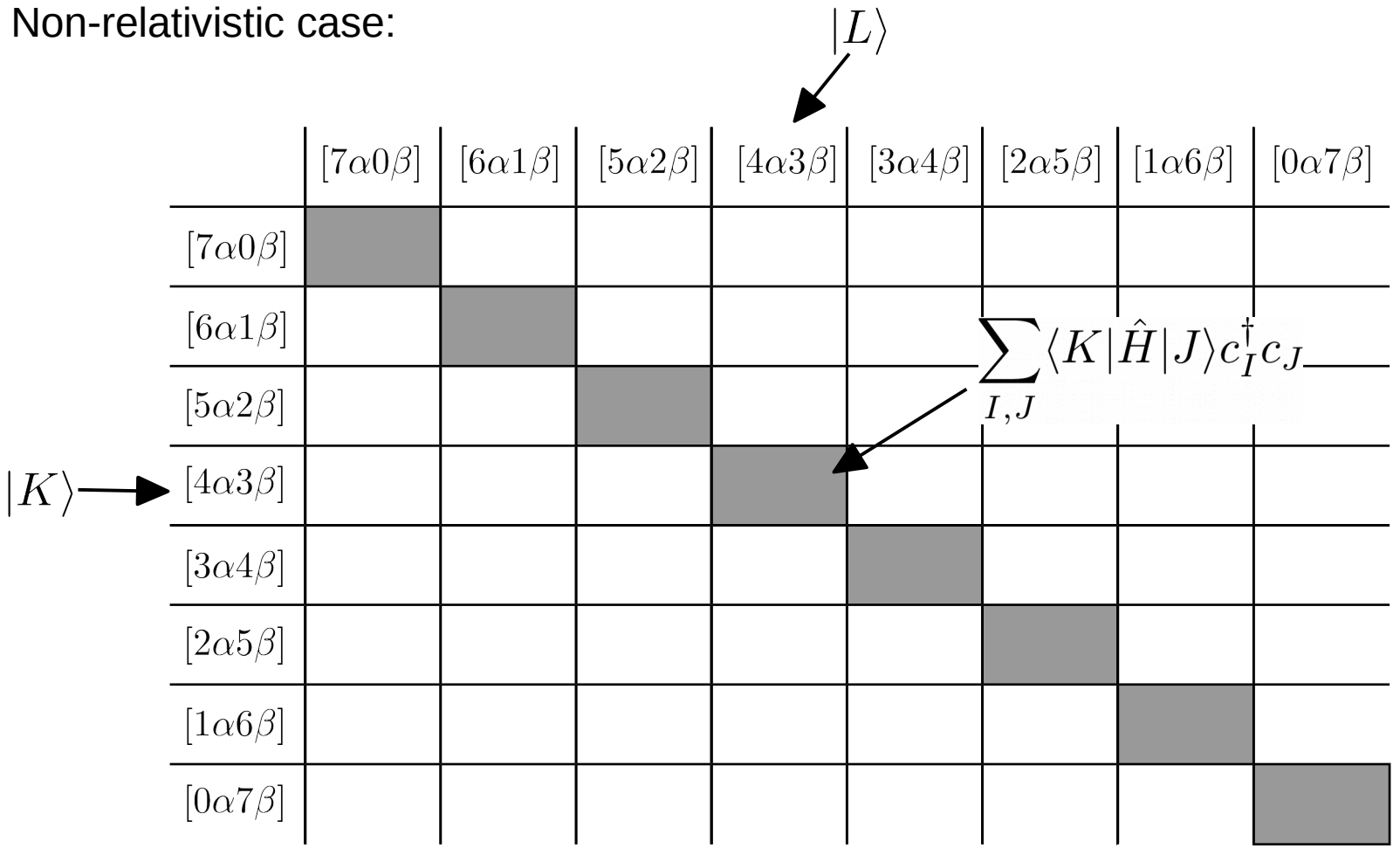
Relativistic CI-vector

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

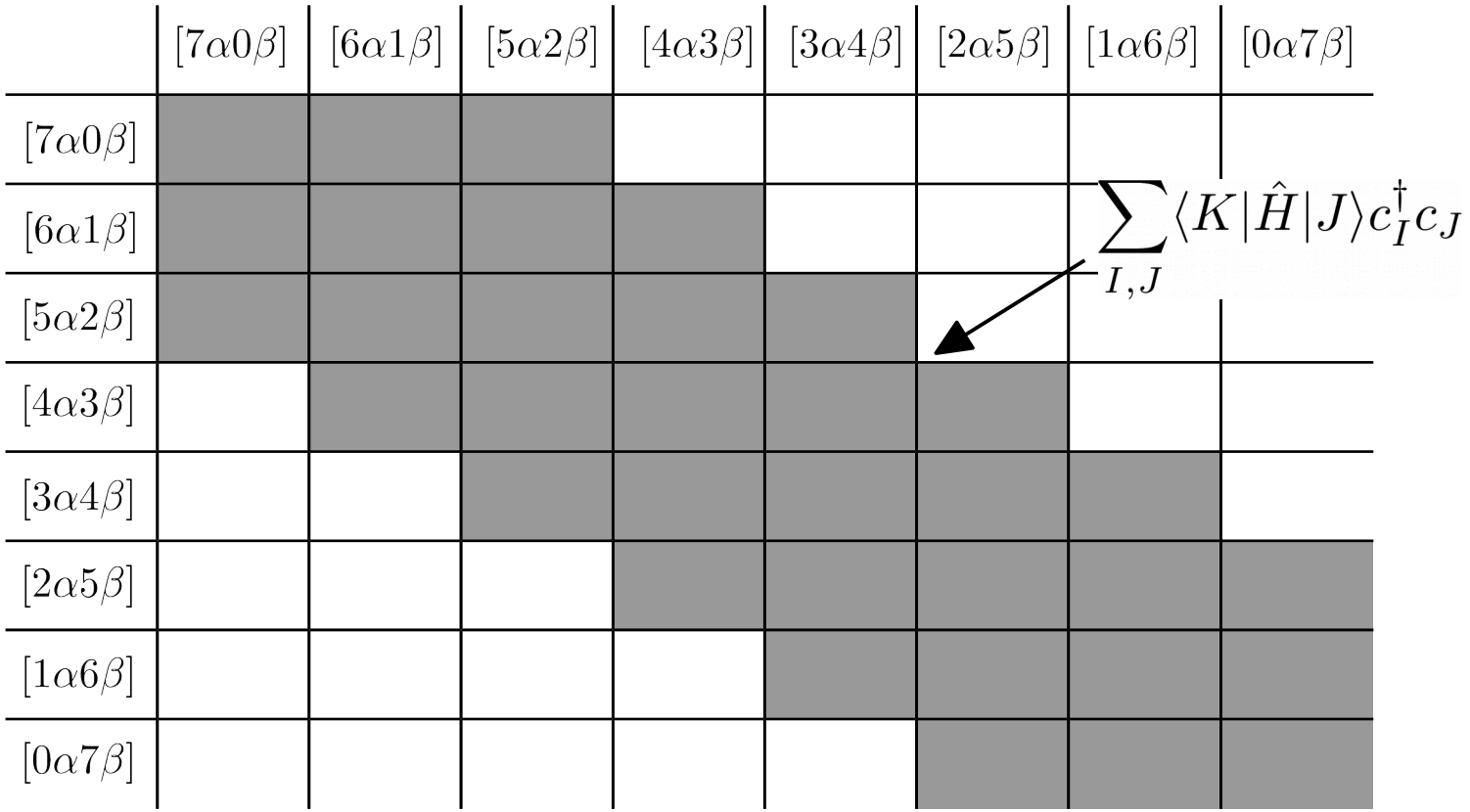
Non-interacting spin-sectors

Non-relativistic case:



Interacting between spin-sectors

Relativistic case :



Spin Multiplets in a relativitic framework

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

$$\begin{bmatrix} \hat{H}^Z_{00} & \hat{H}^Z_{01} & H^Z_{02} & \dots \\ \hat{H}^Z_{00} & \hat{H}^Z_{01} & H^Z_{02} & \dots \\ \hat{H}^Z_{00} & \hat{H}^Z_{01} & H^Z_{02} & \dots \\ \dots & \dots & \dots & \dots \end{bmatrix} \neq \sum_{uv} \begin{bmatrix} g^0_{uv}\boldsymbol{\sigma}_u & 0 & \dots \\ 0 & g^1_{uv}\boldsymbol{\sigma}_u & \dots \\ \dots & \dots & \dots \end{bmatrix} B_v$$

- 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 peturbation 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

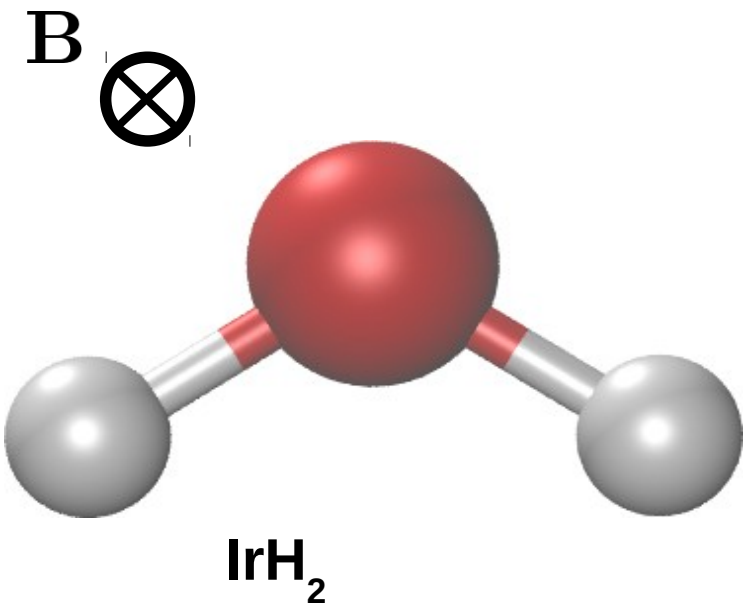
- Non-relativistic EPR parameters can be interpreted as derivatives of the energy at zero field :

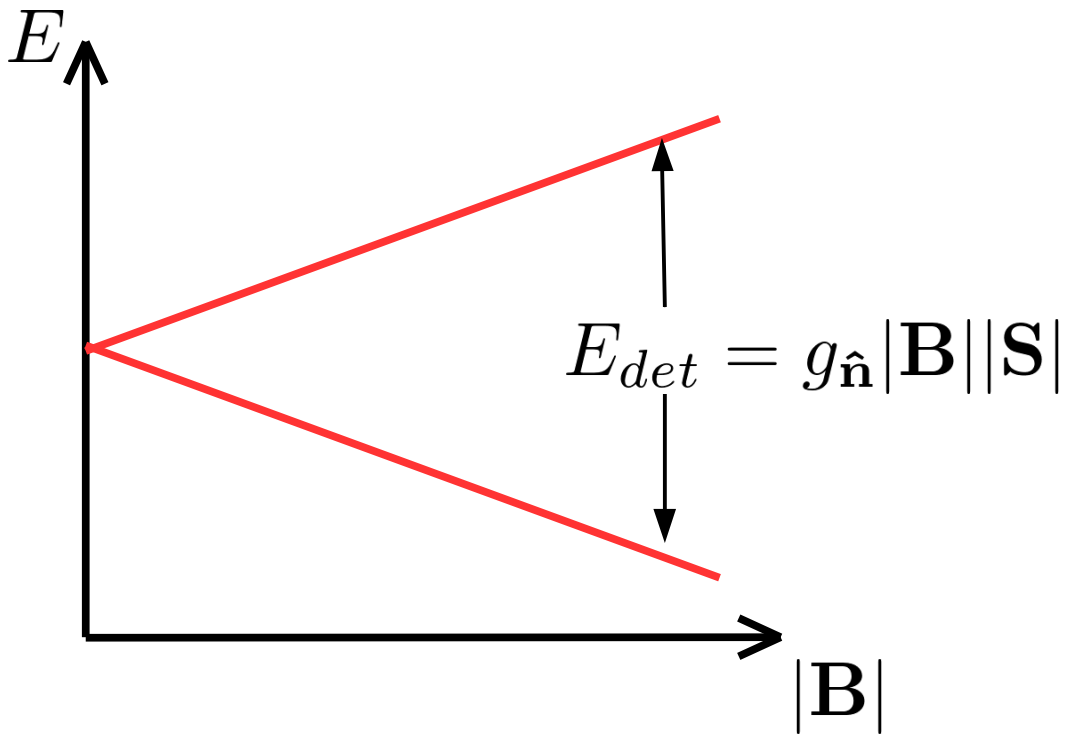
$$g_{uv} = \left. \frac{\partial^2 E}{\partial B_u \partial \langle \hat{\sigma}_v \rangle} \right|_{B_u = 0}$$

- 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



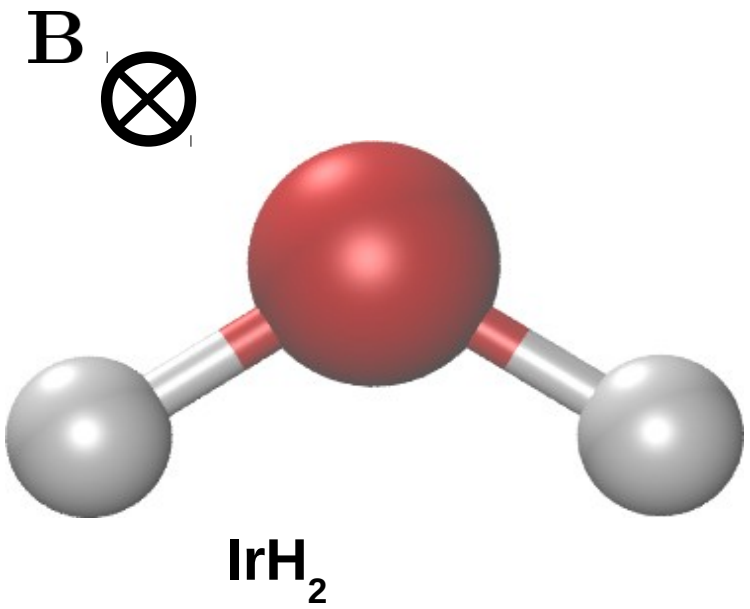


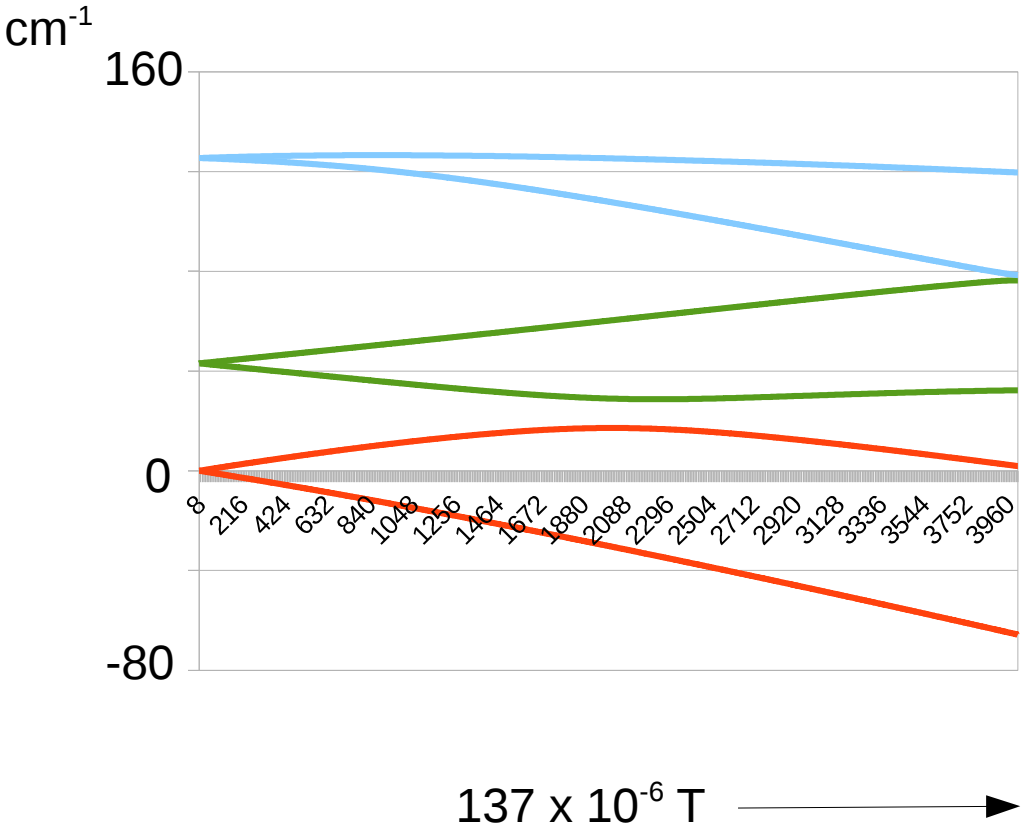
Magnetic field derivatives

- 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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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 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.

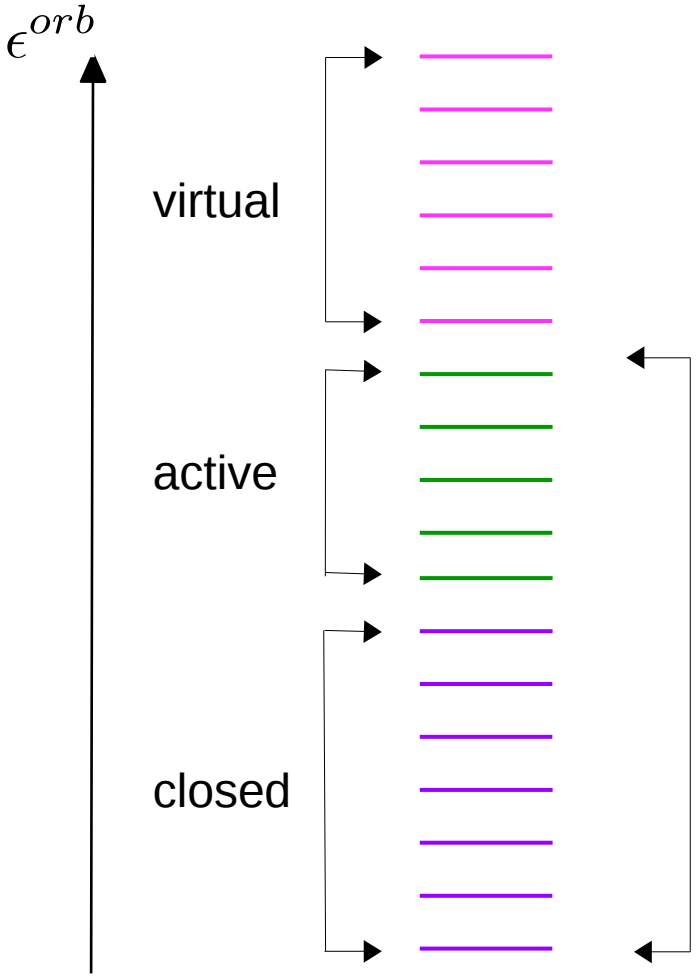
Magnetic field derivatives

- 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:

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

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

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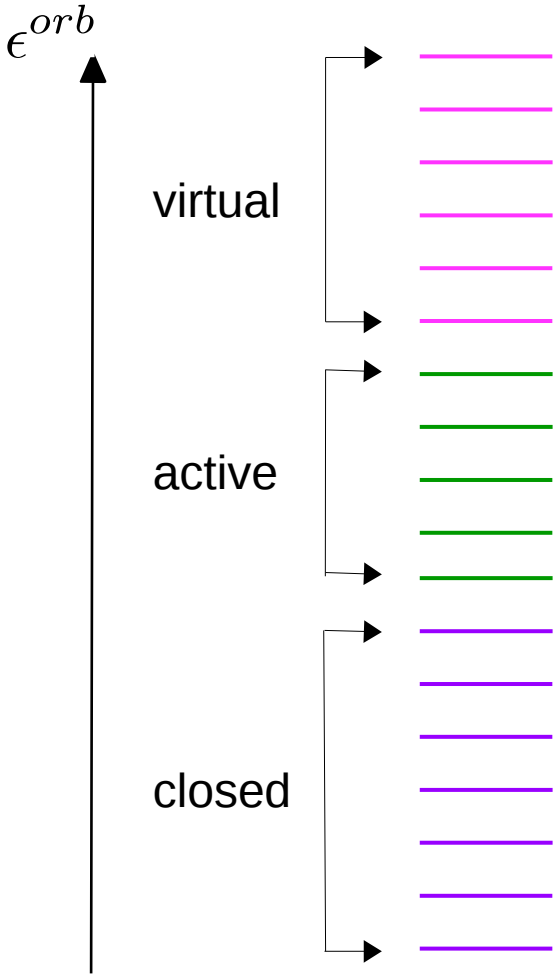
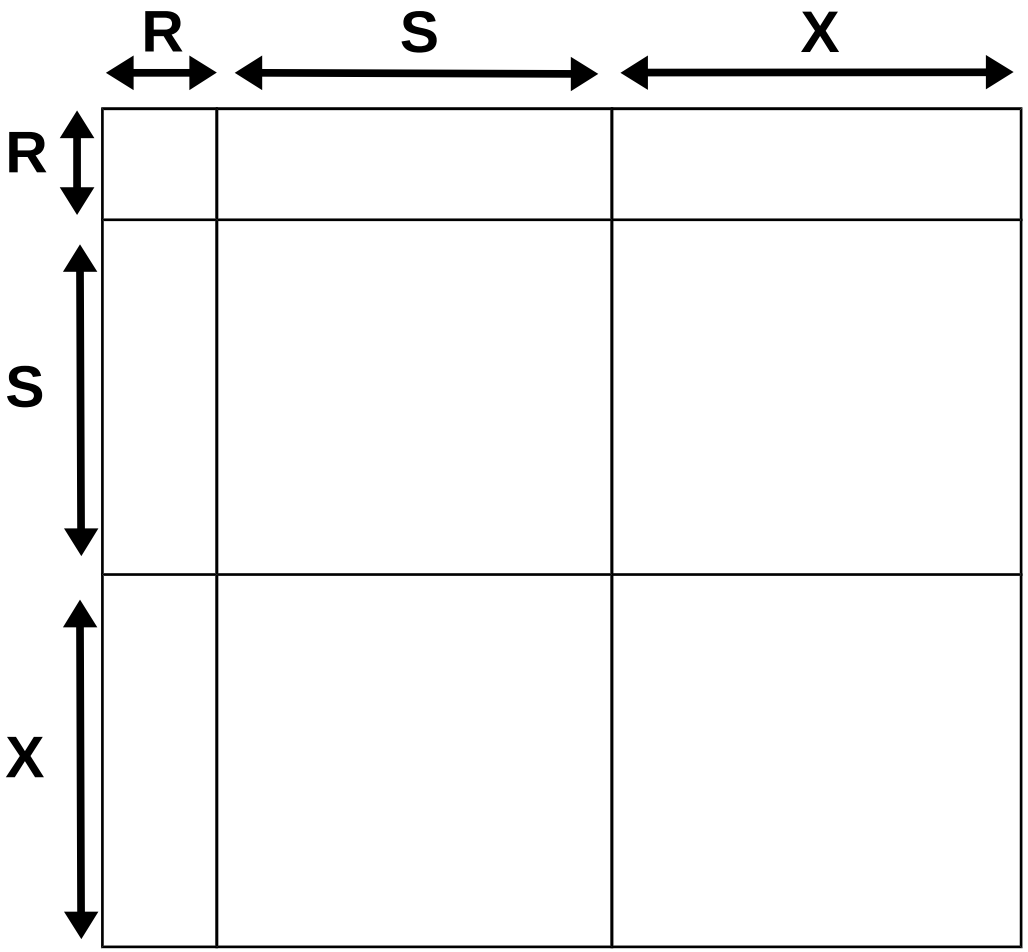


- CA space is optimized for the unperturbed Hamiltonian.
- Accurate description of a perturbation to the Hamiltonian must account for change in this space.
- Add in some determinants with excitations to orbitals in the cirtual space.

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**

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:

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

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