Relativistic XMS-CASPT2 (and hyperfine splitting)

Peter John Cherry
Shiozaki group meeting
May 10th 2017

Significance of dynamic electron correlation to spin-dynamics

Single molecular magnet

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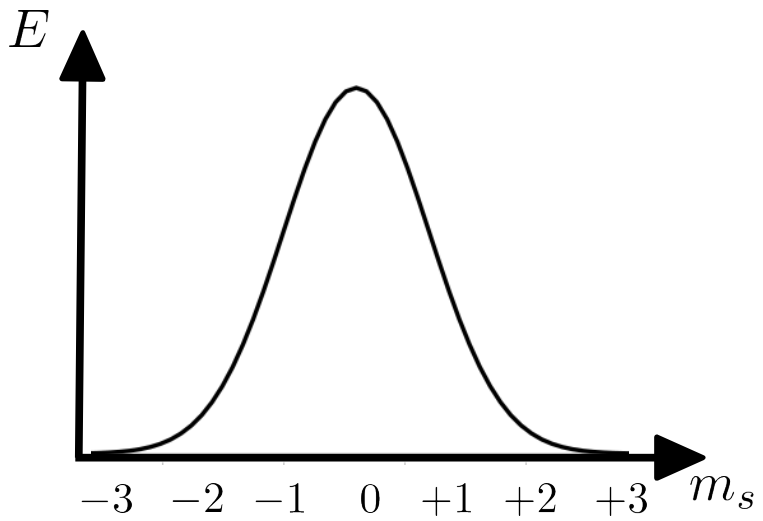

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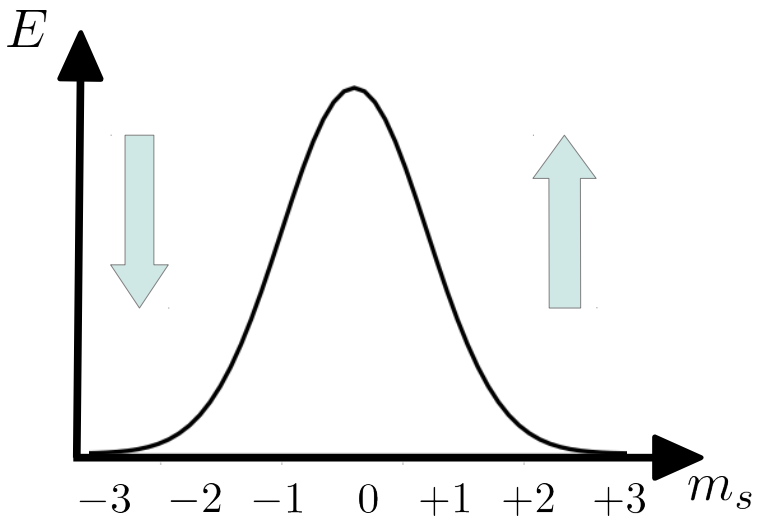

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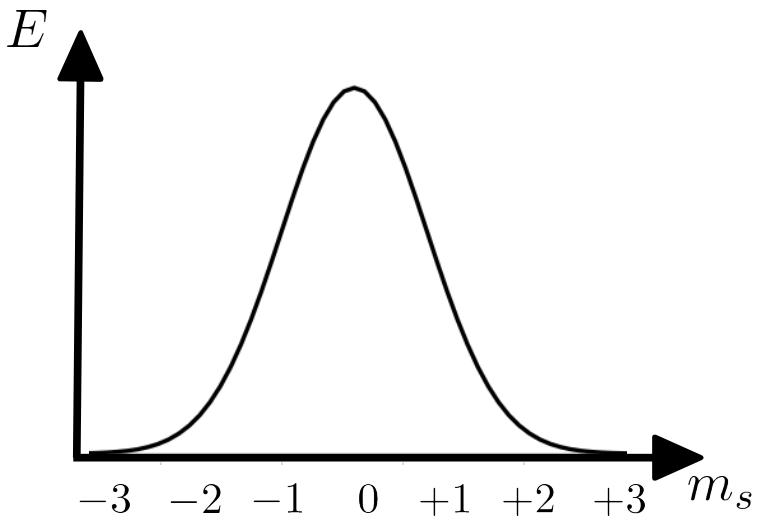
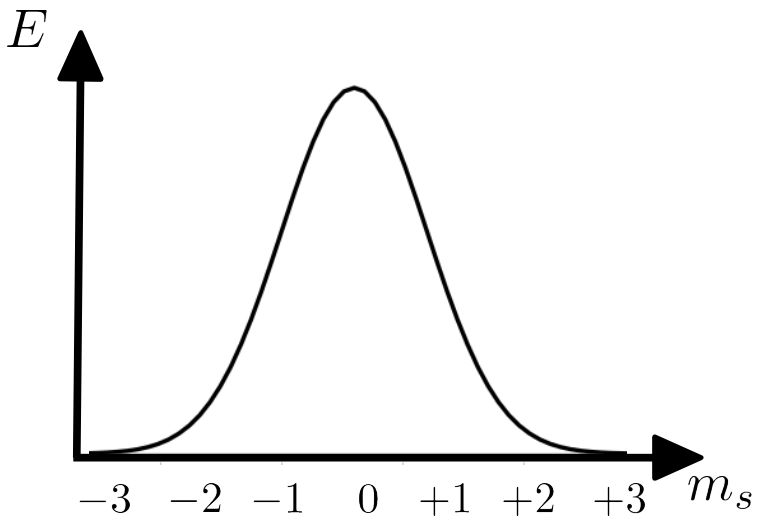


Significance of dynamic electron correlation to spin-dynamics

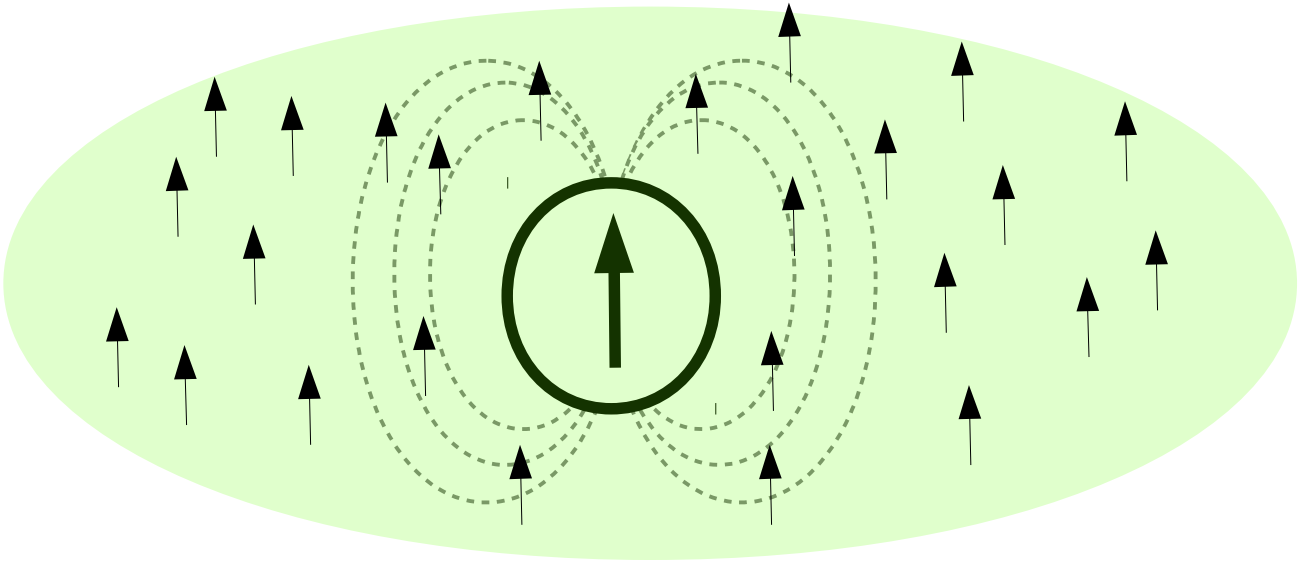
Single molecular magnet

- Aim for very slow relaxation times at high temperatures.
- Suitability can be characterized by:
  - ➔ Height of spin reversal barriers.
  - ➔ Available relaxation pathways.



Hyperfine tensors

- Interaction between the electronic magnetic moment and the nucleus.



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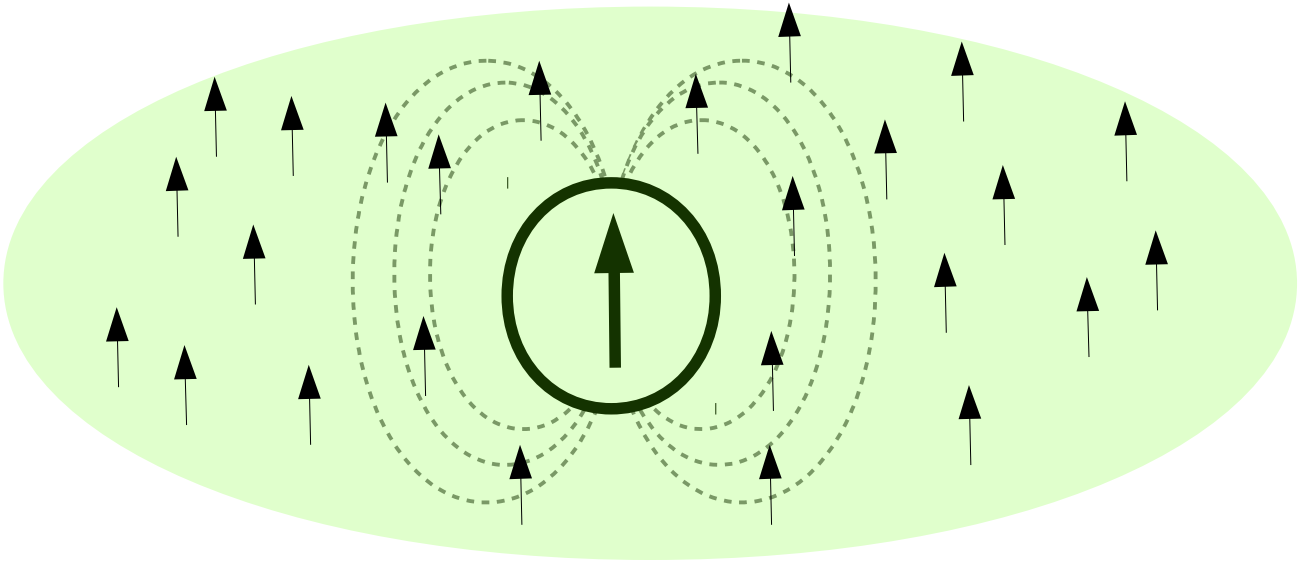

- Important in determining EPR spectra; one of the main tools for investigating single molecular magnets of most systems of interest due to presence of hydrogen.
- Typically small when compared to other effects.
- Requires very accurate spin density; small fluctuations can completely alter the results.

Hyperfine tensors

- Definition is (normally) based on energy derivatives

$$E^M_{hyp} \propto \sum_{uv}^{x,y,z} I_u A_{uv} J_v$$

$$A^M_{uv} = \frac{1}{\langle \tilde{S}_v \rangle} \frac{dE(J_v, I^M)}{dI^M_u}\bigg|_{I^M}$$

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Hyperfine splitting energy for nucleus M

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Nuclear magnetic moment vector

Total magnetization vector

Hyperfine tensors

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Component of hyperfine tensor for nucleus M

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Component of pseudospin

Hyperfine tensors

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- Typically decomposed into two main contributions:
  - Fermi contact contribution (when the spin density at nucleus is non-zero).
  - Dipolar interaction between the electronic magnetic moment and the nuclear magnetic moment.

Importance of dynamic correlation for hyperfine splitting

T. Shiozaki and T. Yanai, JCTC **12,** 4347-4351 (2016)

	$^4[V(H_2O)_6]^{2+}$	$^4[Cr(H_2O)_6]^{3+}$	$^6[Mn(H_2O)_6]^{2+}$
CASSCF(10 orb)	-0.6	-23.1	66.8
CASSCF(23 orb)	-132.7	8.9	-113.0
CASPT2(10 orb)	-232.0	45.3	-224.2
Experiment	-247	55	-245

Isotropic hyperfine coupling constants for $^4[V(H_2O)_6]^{2+}$, $^4[Cr(H_2O)_6]^{3+}$, and $^6[Mn(H_2O)_6]^{2+}$ in MHz.

XMS-CASPT2

- XMS-CASPT2 : Extended multistate complete active space second order perturbation theory.

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CASSCF wavefunction

Expansion coefficients

Determinants in active space

XMS-CASPT2

- XMS-CASPT2 : Extended multistate complete active space second order perturbation theory.
- Initial wavefunction from a CASSCF calculation:

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

- Generate new set of states by diagonalizing the state averaged Fock operator in the space formed by these states:

$$\sum_M \langle L|\hat{f}|M\rangle U_{MN} = U_{LN}\tilde{E}_N \rightarrow |\tilde{M}\rangle = \sum_N U_{MN}|N\rangle$$

XMS-CASPT2

- Define two projectors, one onto the reference space, the other onto its complement:

$$\hat{P} = \sum_{N}^{n_{cas}} |\tilde{N}\rangle\langle\tilde{N}|$$

$$\hat{Q} = 1 - \hat{P}$$

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XMS-CASPT2

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

$$|\Psi_L^{(1)}\rangle = \sum_N \hat{T}_{LN}|\tilde{N}\rangle = \sum_N \sum_\Omega \hat{E}_\Omega|\tilde{N}\rangle T_{LN}$$

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Sum over reference space

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Perturbation amplitudes

Sum over double excitations from inactive and active to virtual space

Excitation operator

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

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

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- Differentiation of which yields the amplitude equation:

$$\sum_N \langle\tilde{M}|\hat{E}_\Omega^\dagger(\hat{f} - E_L^{(0)})\hat{T}_{LN}|\tilde{N}\rangle + \langle\tilde{M}|\hat{E}_\Omega^\dagger\hat{H}_{el}|\tilde{L}\rangle = 0$$

XMS-CASPT2

- The effective Hamiltonian may then be written as:

$$\hat{H}^{(eff)}_{LL'} = \langle \tilde{L}|\hat{H}|\tilde{L}'\rangle + \frac{1}{2}\left[\langle \Psi^{(1)}_M|\hat{H}|\tilde{L}'\rangle + \langle \tilde{L}'|\hat{H}|\Psi^{(1)}_M\rangle\right] - \delta_{LL'}E_s \sum_{MN}\langle \Psi^{(1)}_M|\Psi^{(1)}_N\rangle$$

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- This is then diagonalized to find the XMS-CASPT2 energies:

$$\sum_M H^{eff}_{LM} R_{MP} = R_{LP} E^{MS}_P$$

Properties in XMS-CASPT2

- Several properties are, or can be, defined as the derivative of the energy with respect to some parameter, e.g.,

$$\frac{\delta}{\delta X} E_P^{MS}$$

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- Derivative of XMS-CASPT2 energy with respect to X will require evaluation of derivatives of :

    - Amplitudes from CASPT2.
    - Coefficients from CASSCF.
    - Atomic orbital basis functions.

Properties in XMS-CASPT2

- A Lagrangian is defined such that:

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

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Coefficients from
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Amplitudes from CASPT2

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Lagrange multipliers associated with conditions from CASSCF

Conditions from CASSCF

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$$\frac{\partial L}{\partial z_{\mu}} = 0$$

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

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

Advantages of the Lagrangian approach

- Avoids the need for differentation of $\mathbf{t}$ and $\mathbf{c}$ with respect to the perturbation.
- The equations for the Lagrange multipliers are independent of the perturbation.
- Particularly useful in geometry optimization when there is a large number of perturbations (three for each atom).
- Generic formalism which can be applied to multiple properties.

XMS-CASPT2 Lagrangian

- Minimize this Lagrangian with respect to

$$L = E_P^{MS}$$

XMS-CASPT2 energy

XMS-CASPT2 Lagrangian

- Define the Lagrangian to minimize XMSCASPT2 energy with respect to

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

Constraint from XMS-CASPT2 amplitude equation

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Constraint from XMS-CASPT2 amplitude equation

$$\hat{\lambda}_{MN} | \tilde{N} \rangle = \sum_{\Omega} \hat{E}_{\Omega} | \tilde{N} \rangle \lambda_{MN,\Omega}$$

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$$+ \frac{1}{2} Tr[\mathbf{Z}(\underbrace{\mathbf{A} - \mathbf{A}^{\dagger}}_{\text{CASSCF orbital gradient}})]$$

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CASSCF orbital gradient

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Orthogonality of orbitals

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Weight of state N used in state averaging

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Constraints on CASSCF reference coefficients $c_{N,I}$.

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Diagonalization of effective Fock matrix by inactive orbitals

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

Diagonalization of state averaged Fock operator in the reference space

XMS-CASPT2

- Solve two further equations

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  - The Lambda equation to obtain λ_{MN}.
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XMS-CASPT2 Lagrangian

- Minimize this Lagrangian with respect to

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

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

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

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

Z-vector and Lambda equations

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$$d_{xy}^{(1)}, d_{xy}^{(2)}, D_{xy,zw}^{(1)}$$

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First and second order contributions to correlated density matrices

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$$y_{I,N} = \frac{\partial L_{PT2}}{\partial c_{I,N}}$$

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$y_{I,N} = \frac{\partial L_{PT2}}{\partial c_{I,N}}$ → Derivative of the Lagrangian with respect to CASSCF reference coefficients

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$$Y_{xy} = \frac{\partial L}{\partial \kappa_{xy}}$$

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Where I am now

$y_{I,N} = \frac{\partial L_{PT2}}{\partial c_{I,N}}$ → Derivative of the Lagrangian with respect to CASSCF reference coefficients.

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Calculation of CI derivatives

- Requires evaluation of terms of this form

$$\langle \tilde{N} | \hat{\lambda}_{MN} \hat{H} | J \rangle$$

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$$|\tilde{N}\rangle = \sum_{M} |M\rangle U_{MN}$$

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- Requires evaluation of terms of this form

$$\sum_{M}\sum_{\Omega}\sum_{J}\sum_{xy}\langle I|c^{\dagger}_{\tilde{N},I}U^{\dagger}_{MN}\lambda^{\dagger}_{LN,\Omega}\hat{E}^{\dagger}_{\Omega}(h_{xy}\hat{E}_{xy}+\frac{1}{2}v_{xy,zw}\hat{E}_{xy,zw})|J\rangle$$

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$$\sum_{I} \langle I | \hat{E}_{ij,kl,mn,op}) | J \rangle c^{\dagger}_{I,\tilde{N}} A_{ij,kl,mn,op}$$

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$$\sum_I \langle I|\hat{E}_{ij,kl,mn,op})|J\rangle c^{\dagger}_{I,\tilde{N}} A_{ij,kl,mn,op}$$

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Reduced density matrix derivative

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- The $A_{ij,kl,mn,op}$ terms can be obtained from code generated using SMITH3.

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Reduced density matrix derivative

- The $A_{ij,kl,mn,op}$ terms can be obtained from code generated using SMITH3.
- The $\Gamma_{ij,kl,mn,op}$ terms requires manually written code.

Calculation of CI derivatives

- Have up to four particle excitations:

$$\sum_{ijklmn} A_{ij,kl,mn} \langle 0 | \hat{E}_{ij,kl,mn} | J \rangle = A_{ij,kl,mn} \Gamma_{ij,kl,mn}$$

$$\sum_{ijklmnop} A_{ij,kl,mn} \langle 0 | \hat{E}_{ij,kl,mn,op} | J \rangle f_{op} = \sum_{ijklmn} A_{ij,kl,mn} \tilde{\Gamma}_{ij,kl,mn}$$

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- Expressions involving many particle excitations can be rewritten as products of expressions involving single particle excitations.

- The largest contribution is of the form

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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 CI-vector

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

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

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

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

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

Calculation of CI derivatives

- Have up to four particle excitations:

$$\sum_{ijklmn} A_{ij,kl,mn}\langle 0|\hat{E}_{ij,kl,mn}|J\rangle = A_{ij,kl,mn}\Gamma_{ij,kl,mn}$$

$$\sum_{ijklmnop} A_{ij,kl,mn}\langle 0|\hat{E}_{ij,kl,mn,op}|J\rangle f_{op} = \sum_{ijklmn} A_{ij,kl,mn}\tilde{\Gamma}_{ij,kl,mn}$$

- The most computationally expensive contribution is of the form

$$\sum_{KLM}\sum_{op}\langle I|\hat{E}_{ij}|K\rangle\langle K|\hat{E}_{kl}|L\rangle\langle L|\hat{E}_{mn}|M\rangle\langle M|\hat{E}_{op}|J\rangle f_{op}$$

In the relativistic framework $|K\rangle$,$|L\rangle$ and $|M\rangle$ can belong to different spin sectors.

Interaction between spin-sectors

Interaction between determinants from different spin sectors: $\langle L|v_{xy,zw}\hat{E}_{ey,zw}|K\rangle$

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

Interaction between spin-sectors

Non-relativistic case:

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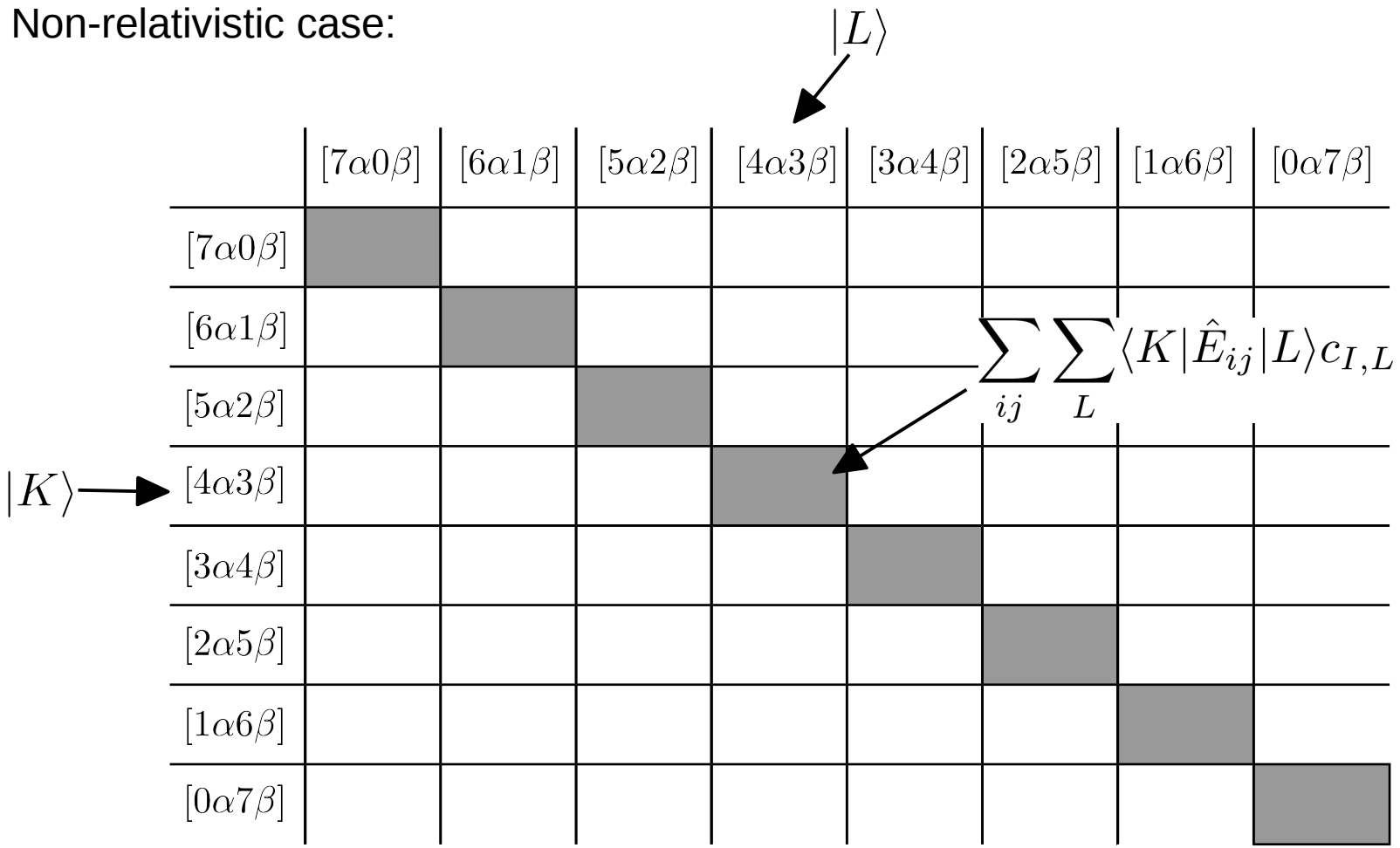
$[0\alpha 7\beta]$								

Interaction between spin-sectors

Non-relativistic case:



Interaction between spin-sectors

Maximum number of spin flips is two: $\langle I|v_{xy,zw}\hat{E}_{ey,zw}|K\rangle$

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

Interaction between spin-sectors

Can be rewritten : $\left[\sum_J \langle I|\hat{E}_{xy}|J\rangle\langle J|\hat{E}_{zw}|K\rangle - \langle I|\hat{E}_{xy}|K\rangle\delta_{yz}\right] v_{xy,zw}$

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

Interaction between spin-sectors

Different number of configurations in each spin sector!

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	$[7\alpha 0\beta]$	$[6\alpha 1\beta]$	$[5\alpha 2\beta]$	$[4\alpha 3\beta]$	$[3\alpha 4\beta]$	$[2\alpha 5\beta]$	$[1\alpha 6\beta]$	$[0\alpha 7\beta]$
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...	$c^{7,0}_{N_{det,7,0}}$	...	...	...	...	...	...	$c^{[0,7]}_{N_{det,[0,7]}}$
...		...	...	...	...	...	...	
			...	...	...	...		
		$c^{[6,1]}_{N_{det,[6,1]}}$	...	...	...	...	$c^{[1,6]}_{N_{det,[1,6]}}$	
			...	...	...	...		
			...	...	...	...		
				...	...			
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				...	...			
				...	...			
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Relativistic XMS-CASPT2

- The quantities to be evaluated are essentially the same as before:

$$A_{ij,kl,mn}\langle 0|\hat{E}_{ij,kl,mn}|J\rangle = A_{ij,kl,mn}\Gamma_{ij,kl,mn}$$

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- The quantities to be evaluated are essentially the same as before:

$$A_{ij,kl,mn}\langle 0|\hat{E}_{ij,kl,mn}|J\rangle = A_{ij,kl,mn}\Gamma_{ij,kl,mn}$$

- The main difference is the range of the summations.
- Must be careful about varying lengths of the CI-vectors when parallelizing.
- Only some terms in the Hamiltonian result in spin flips.

END

- Check basic definition is correct.
- Include definition of Hylleras functional.
- Differentiate Hylleras functional wrt T amplitudes.
- Include effective Hamiltonian slide. Say this gives us the energies.
- Improve definition of first order wavefuntion.
- Check basic terms for A and gamma are correct.
- Explain why we use the Lagrangian method: do not want to differentiate energy directly, instead define Lagrangian which must be satisfied, and which has Lagrange multipliers from which the T apmplitudes, CI coefficients and orbital coefficients can be determined.
- Check relativistic Hamiltonian is OK.
- Check constraints are correctly identified.
- Add citations.

END

- Check terms in Hmailtonian are OK.
- Cehck spin sector definitions and interaction is OK.
- Check if stuff on spin reversal barrier has been done by Ryan.

Hylleras functional

- First order terms in the perturbation expansion:

$$\hat{H}_0|\Psi^{(1)}\rangle + \hat{V}|\Psi^{(0)}\rangle = E^{(0)}|\Psi^{(1)}\rangle + E^{(1)}|\Psi^{(0)}\rangle$$

$$\langle\Psi^{(1)}|\hat{H}_0 - E_0|\Psi^{(1)}\rangle + \langle\Psi^{(1)}|\hat{V} - E^{(1)}|\Psi^{(0)}\rangle = 0$$

$$E^{(1)} = \langle\Psi^{(0)}|\hat{V}|\Psi^{(0)}\rangle$$

$$E^{(2)} = \langle\Psi^{(0)}|\hat{V}|\Psi^{(1)}\rangle$$

$$E^{(2)} = \langle\Psi^{(0)}|\hat{V}|\Psi^{(1)}\rangle + \langle\Psi^{(1)}|\hat{H}_0 - E_0|\Psi^{(1)}\rangle + \langle\Psi^{(1)}|\hat{V} - E^{(1)}|\Psi^{(0)}\rangle$$

$$\langle\Psi^{(0)}|\Psi^{(1)}\rangle = 0$$

$$E^{(2)} = 2\Re e[\langle\Psi^{(0)}|\hat{V}|\Psi^{(1)}\rangle] + \langle\Psi^{(1)}|\hat{H}_0 - E_0|\Psi^{(1)}\rangle$$

$$|\Psi_L^{(1)}\rangle = \sum_N \hat{T}_{LN}|\tilde{N}\rangle = \sum_N \sum_\Omega \hat{E}_\Omega|\tilde{N}\rangle T_{LN}$$

XMS-CASPT2

- XMS-CASPT2 : Extended multistate complete active space second order perturbation theory.
- Initial wavefunction from a CASSCF calculation:

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

- Generate new set of states by diagonalizing the Fock operator in the space formed by these states:

$$\sum_M \langle L|\hat{f}|M\rangle U_{MN} = U_{LN}\tilde{E}_N \rightarrow |\tilde{M}\rangle = \sum_N U_{MN}|N\rangle$$

XMS-CASPT2

- First-order perturbation to the wavefunction is expanded in basis of excited determinants:

$$|\Psi_L^{(1)}\rangle = \sum_N \hat{T}_{LN}|\tilde{N}\rangle = \sum_N \sum_\Omega \hat{E}_\Omega |\tilde{N}\rangle T_{LN}$$

Sum over states in CASSCF reference space

XMS-CASPT2

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$$|\Psi_L^{(1)}\rangle = \sum_N \hat{T}_{LN}|\tilde{N}\rangle = \sum_N \sum_\Omega \hat{E}_\Omega |\tilde{N}\rangle T_{LN}$$

T amplitudes

Single and double excitations between inactive, active and virtual orbitals.

Excitation operator

XMS-CASPT2

- First-order perturbation to the wavefunction is expanded in basis of excited determinants:

$$|\Psi_L^{(1)}\rangle = \sum_N \hat{T}_{LN}|\tilde{N}\rangle = \sum_N \sum_\Omega \hat{E}_\Omega |\tilde{N}\rangle T_{LN}$$

- The T amplitudes for a given state are those which satisfy

$$\sum_N \langle \tilde{M}|\hat{E}_\Omega^\dagger (\hat{f} - E_L^{(0)})\hat{T}_{LN}|\tilde{N}\rangle + \langle \tilde{M}|\hat{E}_\Omega^\dagger \hat{H}|\tilde{L}\rangle = 0$$

XMS-CASPT2

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State averaged
Fock Matrix

Zeroth order
energy of state L

XMS-CASPT2

- XMS-CASPT2 energy
  - T amplitudes.
  - Orbital rotations.
  - CI coefficients.
-

XMS-CASPT2

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

Conf.	$[7\alpha 0\beta]$	$[6\alpha 1\beta]$	$[5\alpha 2\beta]$	$[4\alpha 3\beta]$	$[3\alpha 4\beta]$	$[2\alpha 5\beta]$	$[1\alpha 6\beta]$	$[0\alpha 7\beta]$
$\|1\rangle$	...	...	...	...	...	...	...	...
	$c^{7,0}_{N_{det},7,0}$	...	...	...	...	...	...	$c^{[0,7]}_{N_{det},[0,7]}$
		...	...	...	...	...	...	
			...	...	...	...		
		$c^{[6,1]}_{N_{det},[6,1]}$	...	...	...	...	$c^{[1,6]}_{N_{det},[1,6]}$	
			...	...	...	...		
			...	...	...	...		
				...	...			
			$c^{[5,2]}_{N_{det},[5,2]}$	...	...	$c^{[2,5]}_{N_{det},[2,5]}$		
				...	...			
				...	...			
				$c^{[4,3]}_{N_{det},[4,3]}$	$c^{[3,4]}_{N_{det},[3,4]}$			

XMS-CASPT2

Solve for initial XMS-CASPT2 energy

↓

Solve for Lamda coefficients

↓

$$Y_{xy} = \frac{\partial L}{\partial \kappa_x y}$$

$$d^{(1)}_{xy}, d^{(2)}_{xy}, D^{(1)}_{xy,zw}$$

$$y_{I,N} = \frac{\partial L_{PT2}}{\partial c_{I,N}}$$

Solve Z-vector equation