Calculation of Spin Orbit Coupling Effects using Stochastic Configuration Interaction Techniques

- Why is spin orbit coupling important?
  - Non-spin conserving reactions - normally forbidden
    - e.g. via Singlet-Triplet mixing

- Applications?
  - Phosphoresence
  - Dissociation
  - Photodynamic therapy
  - Semiconductors
  - Dye-sensitised solar cells

Strategy

- Good enough results with compact wavefunction. Black box?
- Get zeroth order wavefunction
  - e.g. Hartree-Fock
- Improve wavefunction
  - Monte Carlo Configuration Interaction (MCCI)
  - capture static correlation
- Get spin orbit coupling properties
  - 1^{st} order degenerate perturbation
  - Neglect higher order effects
  - Breit-Pauli Hamiltonian – effective $1e^-$ operator

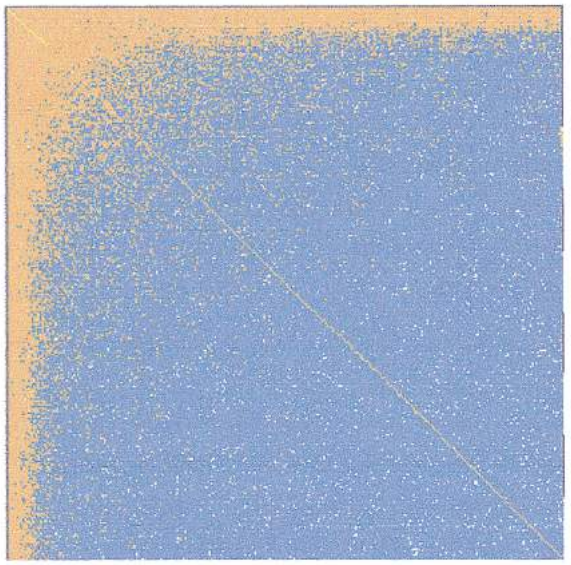
Solving the Electron Correlation Problem with CI

- Recovers electron correlation
- Expand wavefunction in basis of all possible electronic configurations
- Full Configuration Interaction
- Factorial growth in configurations with number of orbitals

$$\Psi_{\mathrm{CI}} = c_0\psi^{HF} + \overbrace{\sum_i c_i^S \psi_i^S}^{\text{Singles}} + \overbrace{\sum_j c_j^D \psi_j^D}^{\text{Doubles}} + \overbrace{\sum_k c_k^T \psi_k^T}^{\text{Triples}} + \ldots + \overbrace{\sum_l c_l^N \psi_l^N}^{N\text{-folds}}$$

Monte-Carlo Configuration Interaction

J. Comp. Phys., **1998** (146), 181.



$$C_A \left\langle \Psi_A \middle| \hat{H}_e \middle| \Psi_B \right\rangle C_B$$

Graphical representation of MCCI Matrix for HF

- Interaction matrix between configurations highly sparse.
- Only want important contributions.
- Build vector of important configurations as final wavefunction from S/D excitations from growing vector – approximate FCI.
- Single controllable parameter (towards black-box) – cutoff level.

How to Calculate Spin Orbit Coupling

- Obtain MCCI wavefunctions for all relevant states
- Use Breit-Pauli Hamiltonian for perturbation
- Calculate SOC interactions in basis of MCCI states

$$E = \left\langle \Phi_\mu \left| \hat{H} + \hat{H}^{SO} \right| \Phi_\nu \right\rangle$$

$$\hat{H}^{SO} = \frac{1}{2c^2} \sum_{i=1}^{Elec} \sum_{K=1}^{Nuc} \frac{Z_K [\hat{r}_{iK} \times \hat{p}(i)]}{r_{iK}^3} \bullet \hat{s}(i) - \frac{1}{c^2} \left\{ \sum_{i \neq j}^{Elec} \frac{[\hat{r}_{ij} \times \hat{p}(j)]}{r_{ij}^3} + \frac{1}{2c^2} \sum_{i \neq j}^{Elec} \frac{[\hat{r}_{ji} \times \hat{p}(i)]}{r_{ij}^3} \right\} \bullet \hat{s}(i)$$

- Two-electron terms provide nuclear screening for electrons.
- Neglect and introduce Z_{eff} in one-electron term.

$$Z_{eff} = \lambda_K Z_K$$

$$\left\langle \Phi_\mu \middle| \hat{H}^{SO} \middle| \Phi_\nu \right\rangle = \left\langle \Phi \middle|_\mu \hat{H}_L^{SO} \middle| \Phi_\nu \right\rangle \left\langle \Phi_\mu \middle| \hat{H}_S^{SO} \middle| \Phi_\nu \right\rangle$$

$$\hat{H}_L^{SO} = -\sum_{i=1}^{Elec} \sum_{K=1}^{Nuc} \frac{\lambda_K Z_K [\hat{r}_{iK} \times \hat{p}(i)]}{r_{iK}^3}$$

Integrals of this operator provided by Molpro in MO basis. **My code needs to provide the scaling detailed in red and convert integrals to correct format for MCCI.**
MolSOC for heterodiatomics.

$$\hat{H}_S^{SO} = -\sum_{i=1}^{Elec} \frac{1}{2c^2} \hat{s}(i)$$

My code needs to provide integrals of this operator in x, y and z directions

- Form matrix in basis of electronic states and diagonalise

$$H^{SO} = \begin{pmatrix} H_{AA} & H_{AB} & \cdots \\ H_{BA} & H_{BB} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

- Each matrix element is:

$$H^{SO}_{ab} = \left\langle \Phi_a \middle| \hat{H}^{SO} \middle| \Phi_b \right\rangle$$

- But each electronic state is a linear combination of electronic configurations

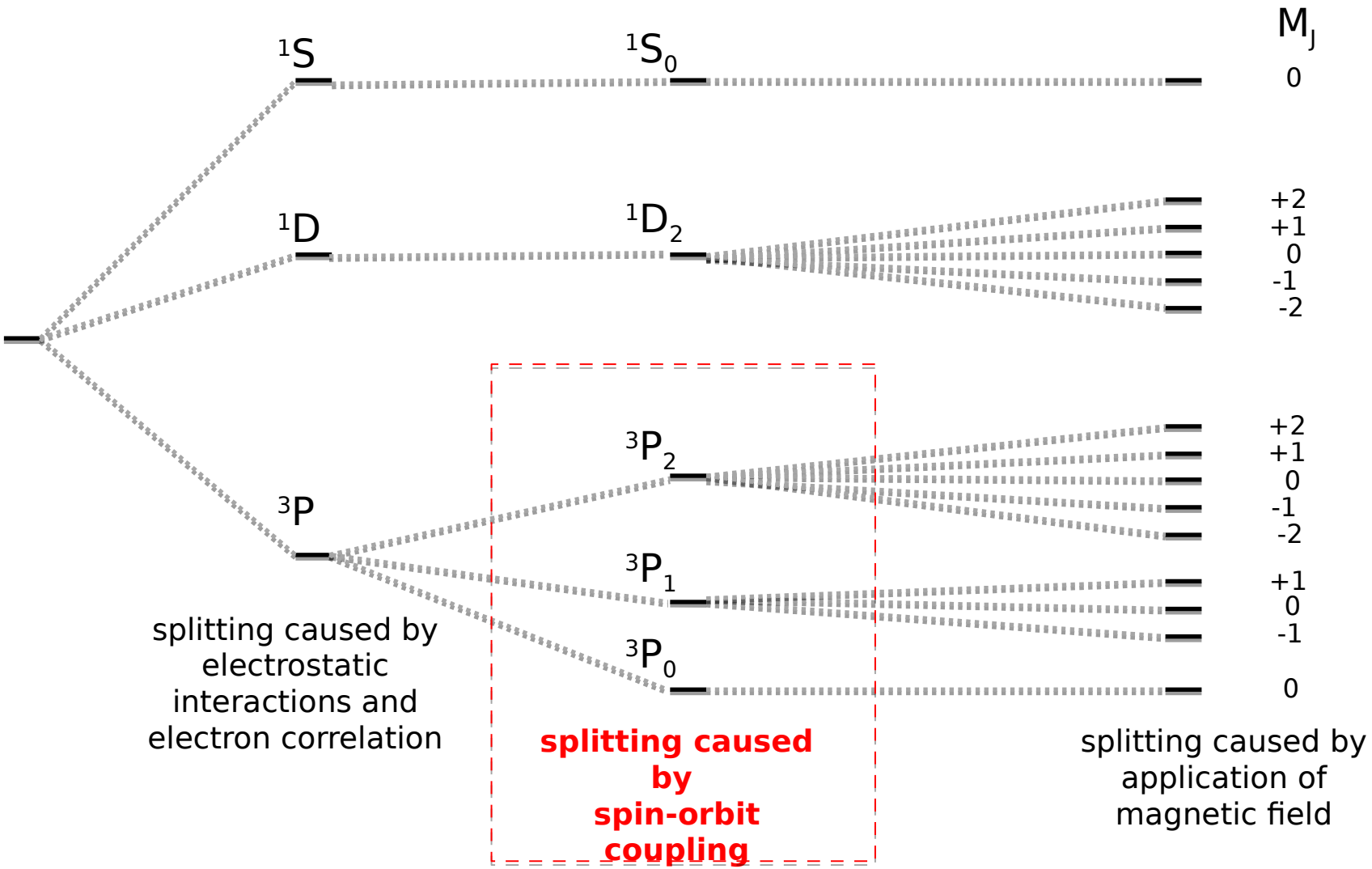
$$\left|\Phi\right\rangle = \sum_{v}^{Configs} \left|\Psi_v\right\rangle$$

- And each electronic configuration is antisymmetrised product of molecular orbitals

$$\left|\Psi\right\rangle = \frac{1}{\sqrt{N!}} \sum_{n=1}^{N!} (-1)^{p_n} \mathrm{P}_n \left| \chi_i \chi_j \chi_k \cdots\cdots \chi_l \right\rangle$$

Proof of concept

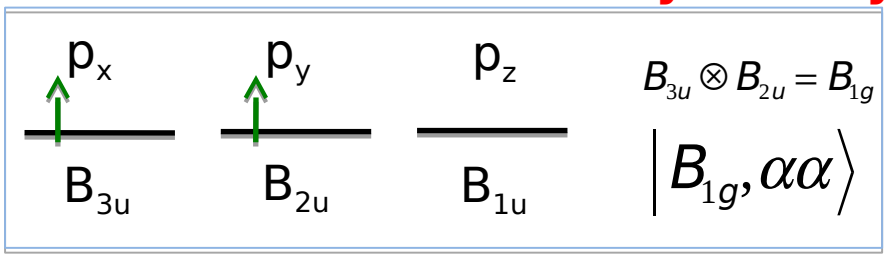
Carbon Atom (p^2)

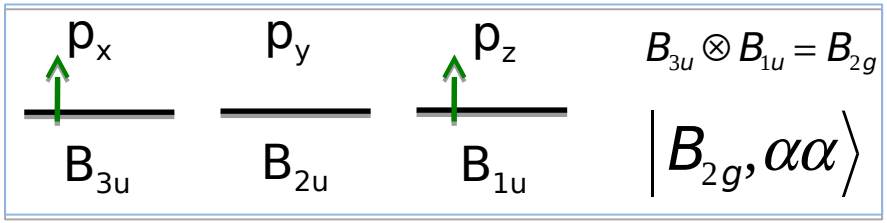


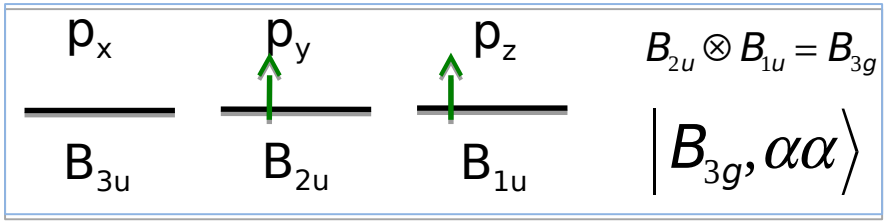
Required MCCI wavefunctions for ^{3}P ground state of C atom

Triplet M_s = +1

Overall Symmetry

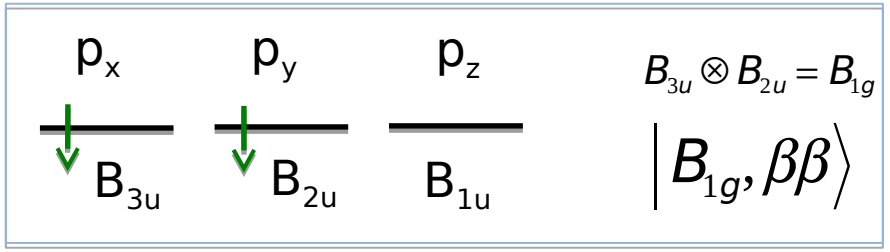


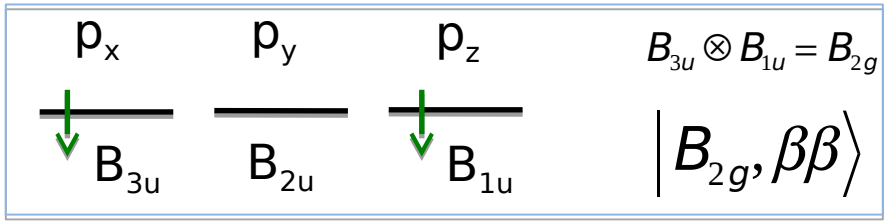


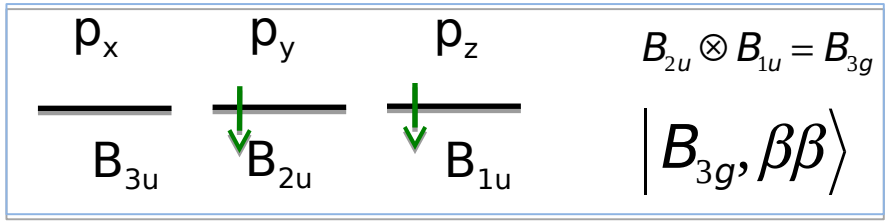


Triplet M_s = -1

Overall Symmetry



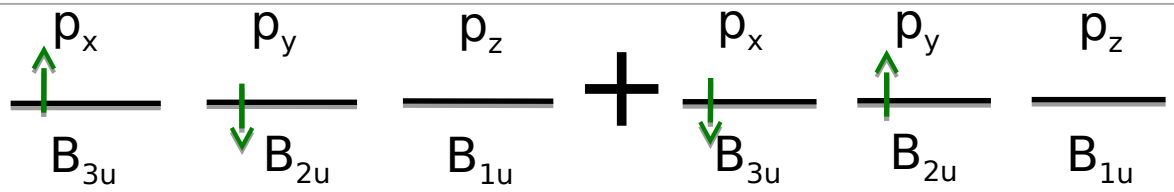




Required MCCI wavefunctions for ^{3}P ground state of C atom

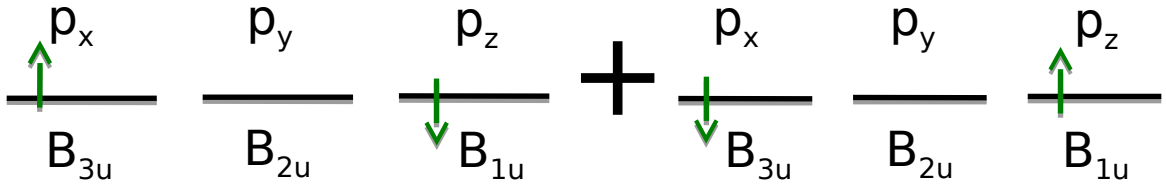
Triplet $M_s = 0$

Overall Symmetry



$$B_{3u} \otimes B_{2u} = B_{1g}$$

$$\left| B_{1g}, \alpha\beta + \beta\alpha \right\rangle$$



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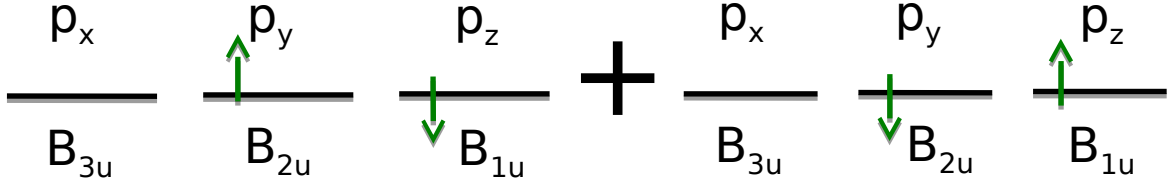

$$B_{2u} \otimes B_{1u} = B_{3g}$$

$$\left| B_{3g}, \alpha\beta + \beta\alpha \right\rangle$$

Results for ^{3}P ground state of carbon atom; *cc-pVQZ and cutoff = 0.0001*

$$H^{SO}_{Carbon} = \begin{pmatrix} 0.00 & 0.00 & 0.00 & 0.00 & -10.07i & 0.00 & 0.00 & +10.13 & 0.00 \\ 0.00 & 0.00 & 0.00 & +10.13i & 0.00 & -10.07i & -10.07 & 0.00 & -10.13 \\ 0.00 & 0.00 & 0.00 & 0.00 & -10.13i & 0.00 & 0.00 & -10.07 & 0.00 \\ 0.00 & -10.13i & 0.00 & 0.00 & 0.00 & 0.00 & -14.29i & 0.00 & 0.00 \\ +10.07i & 0.00 & +10.13i & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & +10.07i & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & +14.29i \\ 0.00 & -10.07 & 0.00 & +14.29i & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\ +10.13 & 0.00 & -10.07 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.00 & -10.13 & 0.00 & 0.00 & 0.00 & -14.29i & 0.00 & 0.00 & 0.00 \end{pmatrix}$$

- Diagonalise this matrix to get eigenvalues
  - one eigenvalue of -28.57 cm^{-1}
  - three eigenvalues of -14.29 cm^{-1}
  - five eigenvalues of +14.29 cm^{-1}
- Multiplet width 42.86 cm^{-1} (exp. 43.41 cm^{-1})
- Spin orbit coupling constant +14.29 cm^{-1} (exp. +14.47 cm^{-1})

Species	Δ_{so} (MCCl)	Δ_{so} (exp.)	ζ (MCCl)	ζ (exp.)	ζ (MRCl)
B	14.12	15.29	+9.41	+10.19	+9.75
C	42.86	43.41	+14.29	+14.47	+12.96
O	206.12	226.98	-68.71	-75.66	-76.07
F	403.51	404.14	-269.01	-269.39	-262.17
Si	192.94	223.16	+64.31	+74.39	+60.84
S	517.37	573.64	-172.46	-191.21	-170.33
Cl	829.93	882.34	-553.28	-588.23	-529.89
OH	124.78	139.21	-124.78	-139.21	-124.71
C_2	25.40	15.25	-25.40	-15.25	-27.68
CN	47.09	52.64	-47.09	-52.64	-51.64
NO	110.30	123.16	+110.30	+123.16	N/A

Species	Basis Set	Cutoff	Num SDs	FCI SDs	Fraction
B	cc-pVQZ	0.0005	1170	3.9×10^{7}	3×10^{-5}
C	cc-pVQZ	0.0001	5372	5.1×10^{8}	1×10^{-5}
O	cc-pVQZ	0.0001	11,053	9.1×10^{10}	1×10^{-7}
F	cc-pVQZ	0.0005	3126	1.2×10^{12}	3×10^{-9}
Si	cc-pVDZ	0.0001	1922	8.1×10^{8}	2×10^{-6}
S	cc-pVDZ	0.0001	3119	1.5×10^{9}	2×10^{-6}
Cl	cc-pVQZ	0.0005	5247	2.8×10^{19}	2×10^{-16}
OH	cc-pVDZ	0.0001	11,156	4.5×10^{7}	2×10^{-4}
C_2	cc-pVDZ	0.0001	42,845	1.2×10^{11}	4×10^{-7}
CN	cc-pVDZ	0.0001	60,775	4.5×10^{11}	1×10^{-7}
NO	cc-pVDZ	0.0001	61,311	3.7×10^{12}	2×10^{-8}

Conclusions, Future Work

- Proof of concept established.
- Apply MCCI to singlet-triplet interactions
  - Preliminary calculations on O_2 molecule.
  - Interaction between $X^3\Sigma_g^-$ and $b^1\Sigma_g^+$ shows spin orbit matrix element 160 cm^{-1} cf. 177 cm^{-1} from multiconfig. response theory results.
- Demonstrate generality of technique to a range of problems
- Apply MCCI to larger molecules

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