UNIVERSITY OF WATERLOO
FACULTY OF SCIENCE
Department of Chemistry

Benchmark of Model Magnetic Systems

Siyuan Wu
Faculty of Science
Department of Chemistry

Outline

Introduction

- Magnetism
- Artificial systems
- Spin-orbit coupling

Methodology

- Multireference Configuration Interaction (MRCI) in Molpro package
- Multireference Equation-of-motion (MREOM) in ORCA packge

Results

Conclusion

Introduction to Magnetism

In general, magnetism is a class of physical phenomena that are associated with magnetic field.

More than 2500 years ago, the first definite description of magnetism that magnetite (Fe_3O_4) attracts iron was described.
It has since grown into a major topic in the context of science.

Applications:

Compass, Horseshoe Magnet, Motors, Wireless, Television, Consumer electronics…

Motivation of Research Project

Calculated energy levels for systems of having multiple magnetic sites.

- Perform *ab initio* accurate calculations
- Extract magnetic coupling parameters from the calculations

Long term Goal (not discussed today):

- Calculate thermal energies and magnetization for large systems.

Model Magnetic Systems

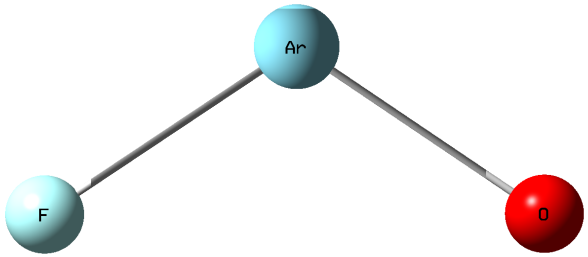
Introduce some artificial magnetic systems: ArFO, ArF2.

They cannot be made experimentally.

F, O atoms are open-shell atoms and have unpaired electrons. Each of it is Considered as a magnetic site.

Argon atom acts as spacer.

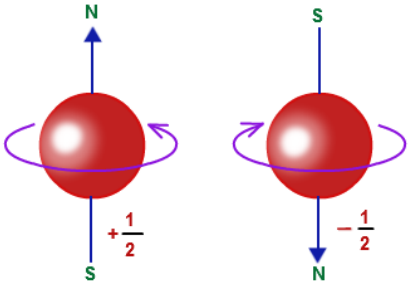
ArFO can be considered as a magnetic Dimer.



Spin-orbit coupling

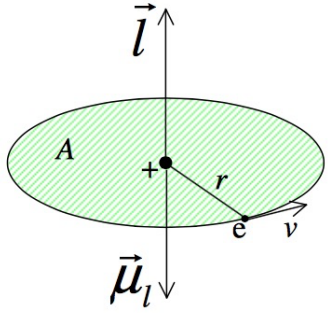
Electron spin:

- Spin of an electron makes it a magnet.
- An intrinsic angular momentum with quantum number s=1/2.



Orbit motion of the electron:

- An electron moving around the nucleus also makes a magnet.



These two magnetic moments can interact (**spin-orbit coupling**) and lead to energy splitting.

Symbolism for Atomic States

L: orbital angular momentum quantum number
L=0 -> S, 1 = P, 2 = D, 3 = F

M_L: orbital magnetic quantum number (Σm_l)
$2L+1$ possible values, M_L = -L, -L+1 … L-1, L

S: total spin quantum number

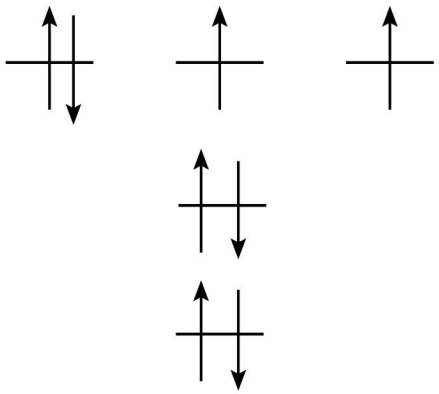
M_S: spin magnetic quantum number (Σm_s)
$2S+1$ possible values, M_S = -S, -S+1 … S-1, S

J: total angular quantum number
$J = L+S, L+S-1, \ldots, |L-S|$
2J+1 values, M_J = -J,-J+1 …, J-1, J

Term Symbol Form: ${}^{2S+1}\{L\}_J$ *(Considering spin-orbit coupling)*

Atomic Term Symbol for Oxygen

Oxygen: $1s^2 2s^2 2p^4$



L= 1x2+0-1=1
S= 3x1/2-1/2=1
2L+1=2x1+1=3
2S+1=2x1+1=3
J=2,1,0

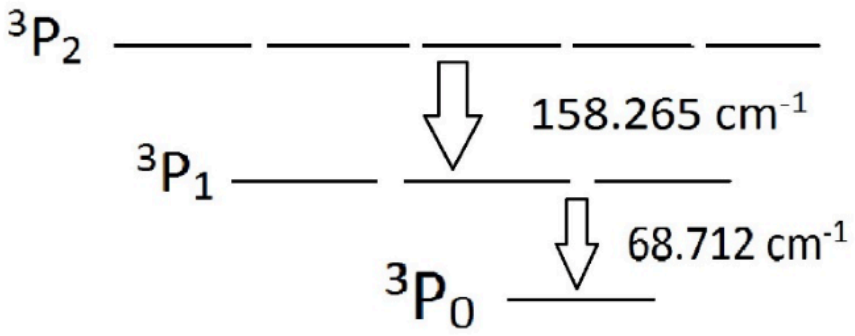
Without SOC:

3x3=9 degenerate states

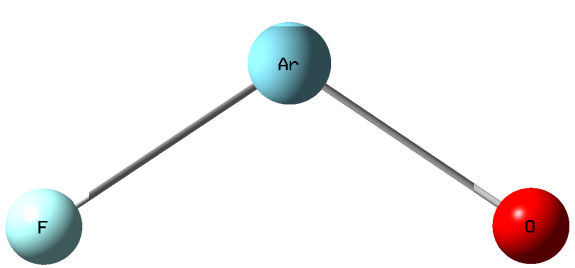
With SOC:

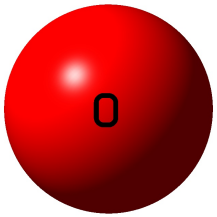
$^3P_2$(5 states), $^3P_1$(3 states), $^3P_0$(1 state)

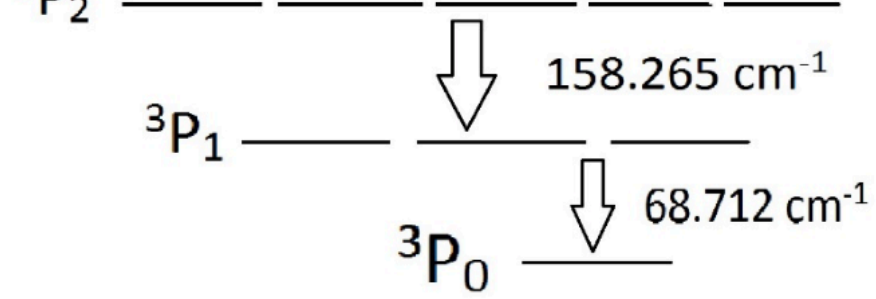
Low-lying States energies from NIST:

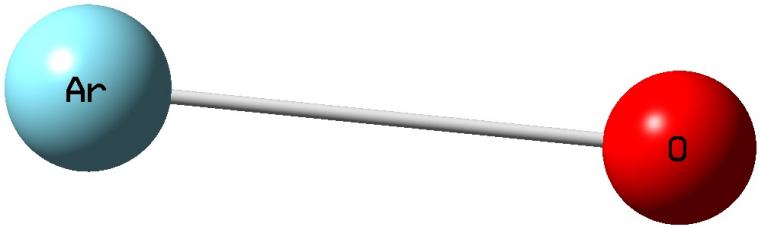


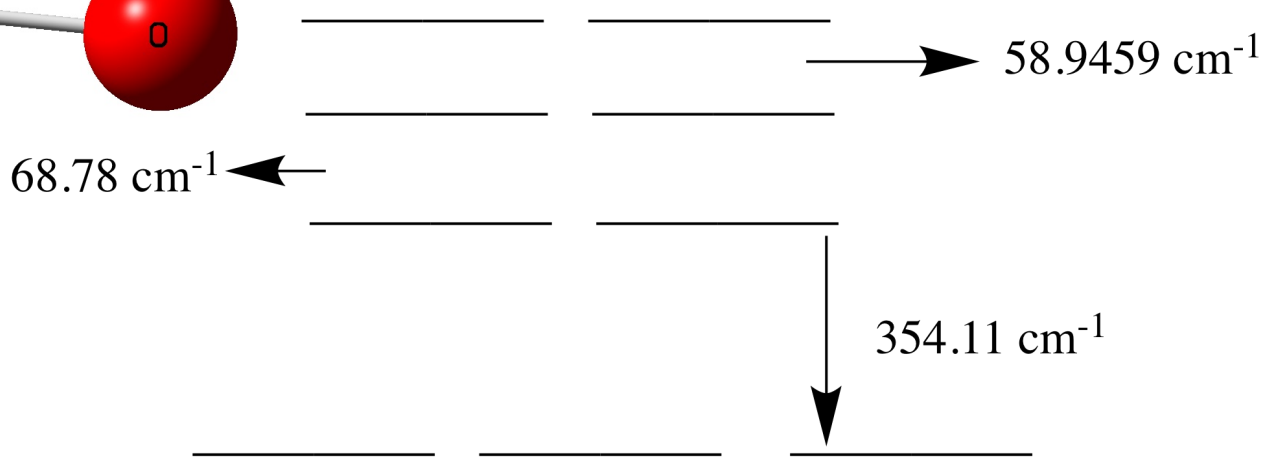
Magnetic Dimer ArFO



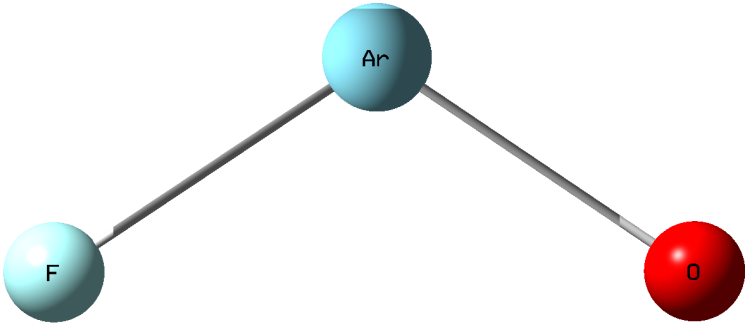


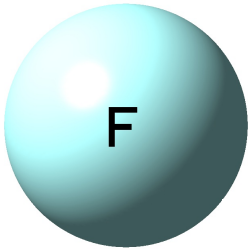


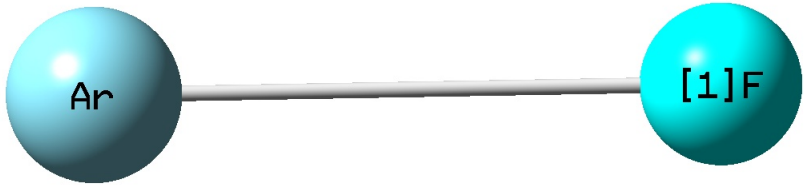


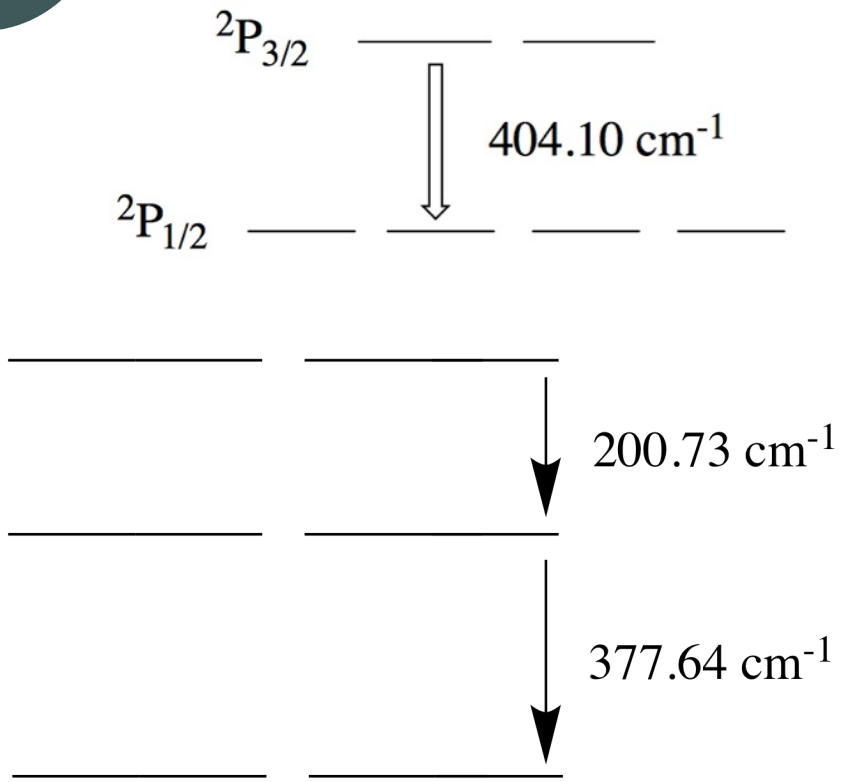


Magnetic Dimer ArFO





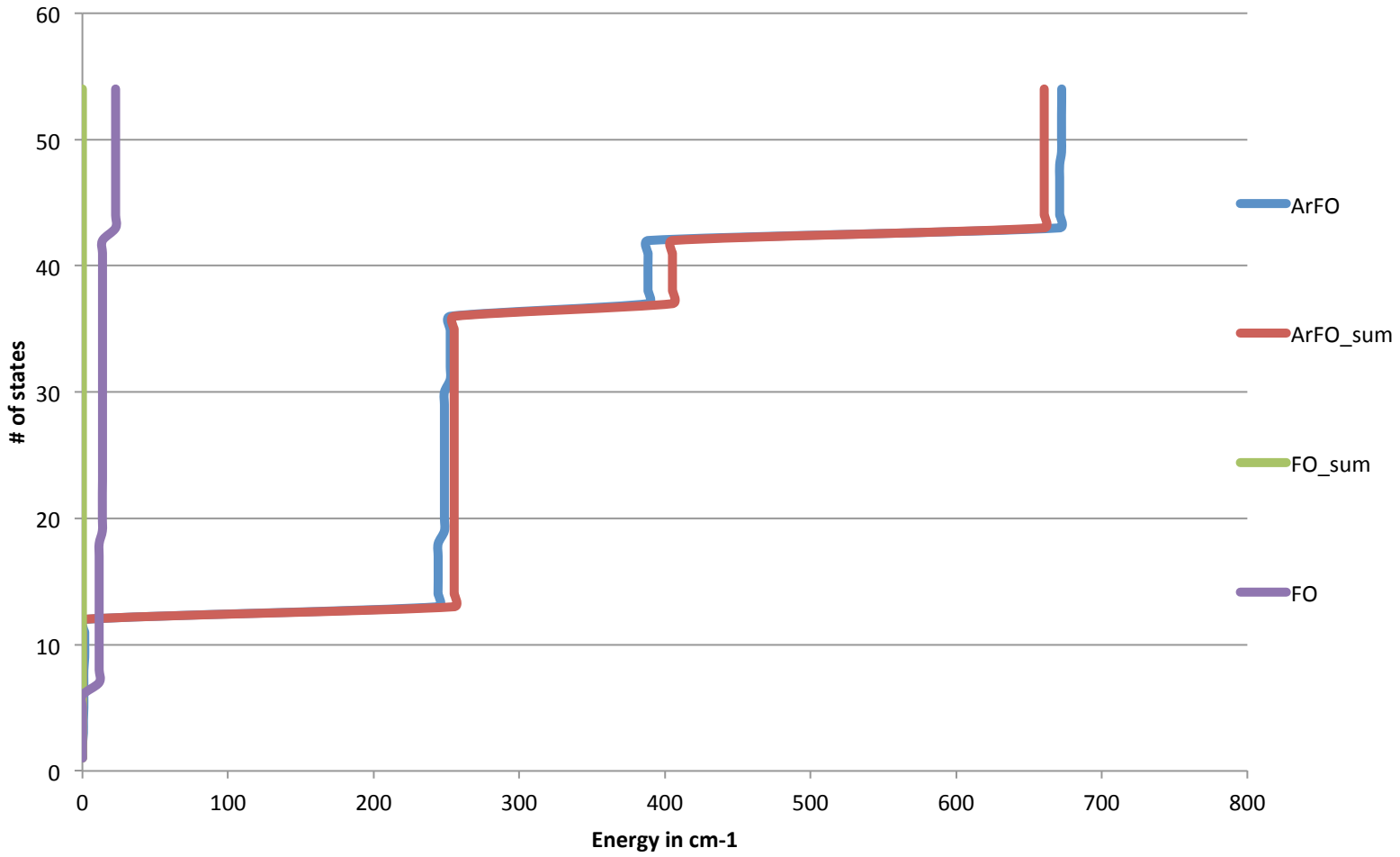




Energy Comparison between Interacting and Non-interacting for ArFO and FO

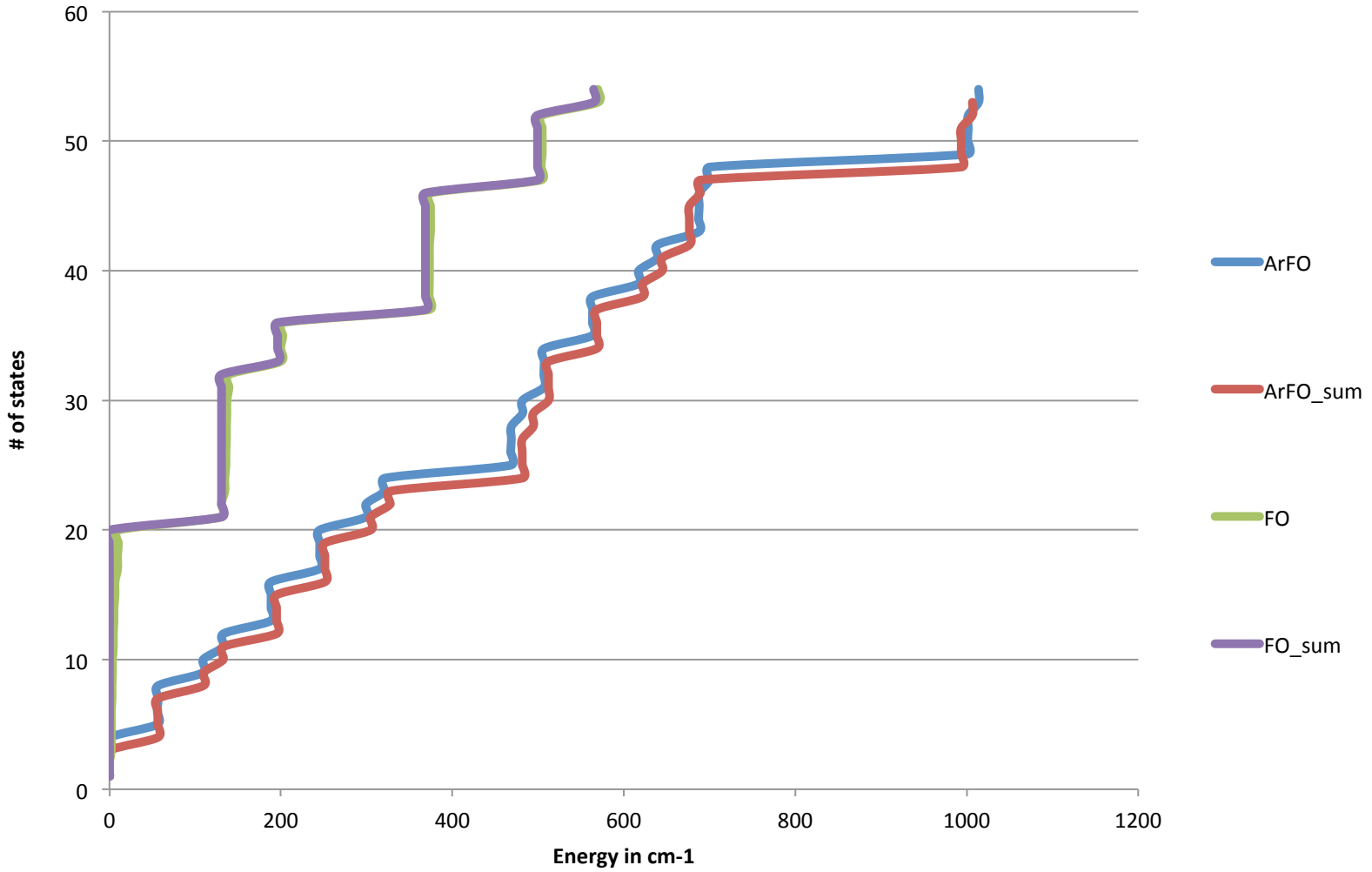
Without spin-orbit coupling: Low-lying States: (6)(9)=54

E_ArFO_sum = E_ArO + E_ArF E_FO_sum = E_F + E_O



Energy Comparison between Interacting and Non-interacting for ArFO and FO

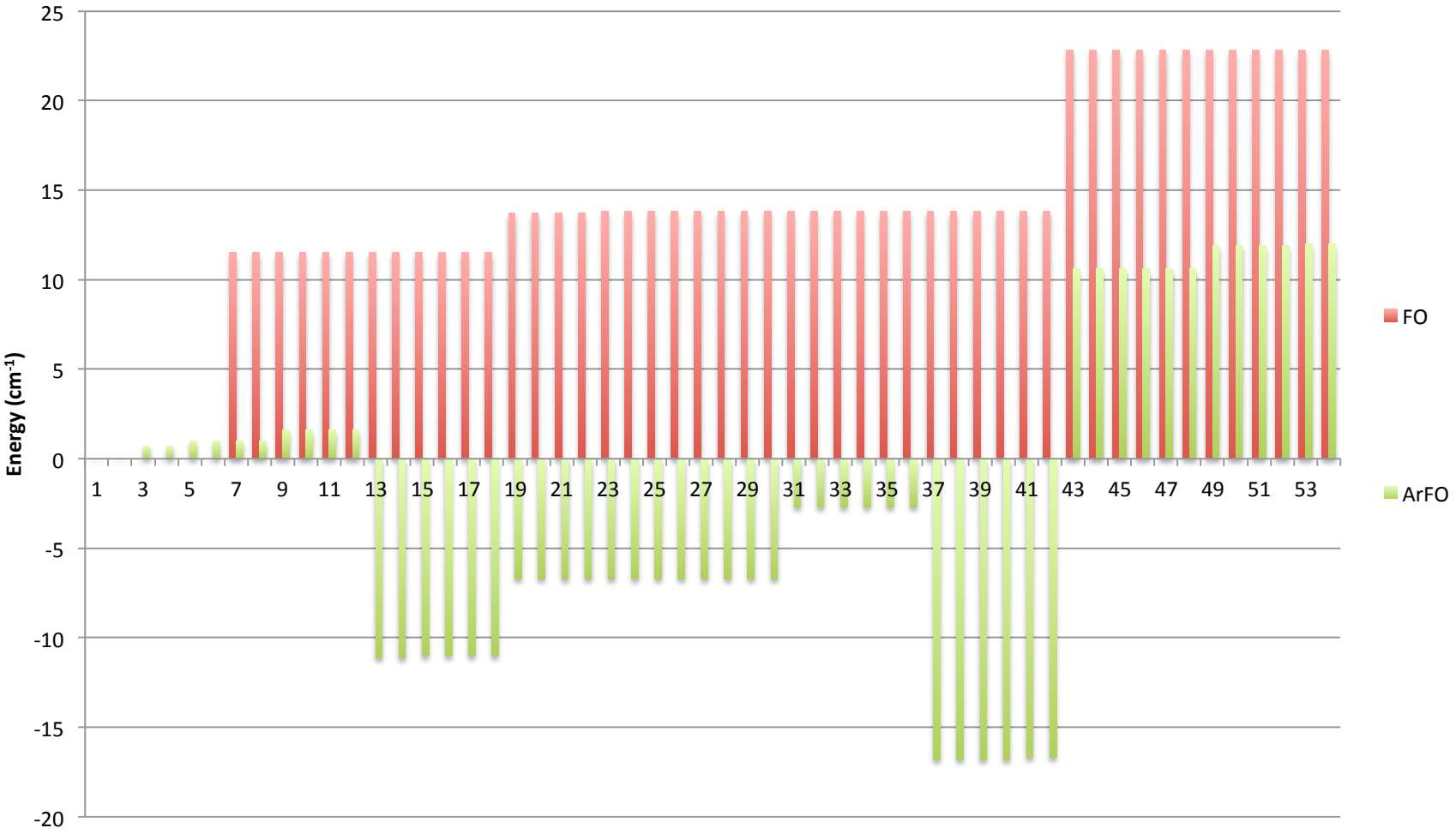
With spin-orbit coupling:



Energy difference between Interacting and Non-interacting for ArFO and FO

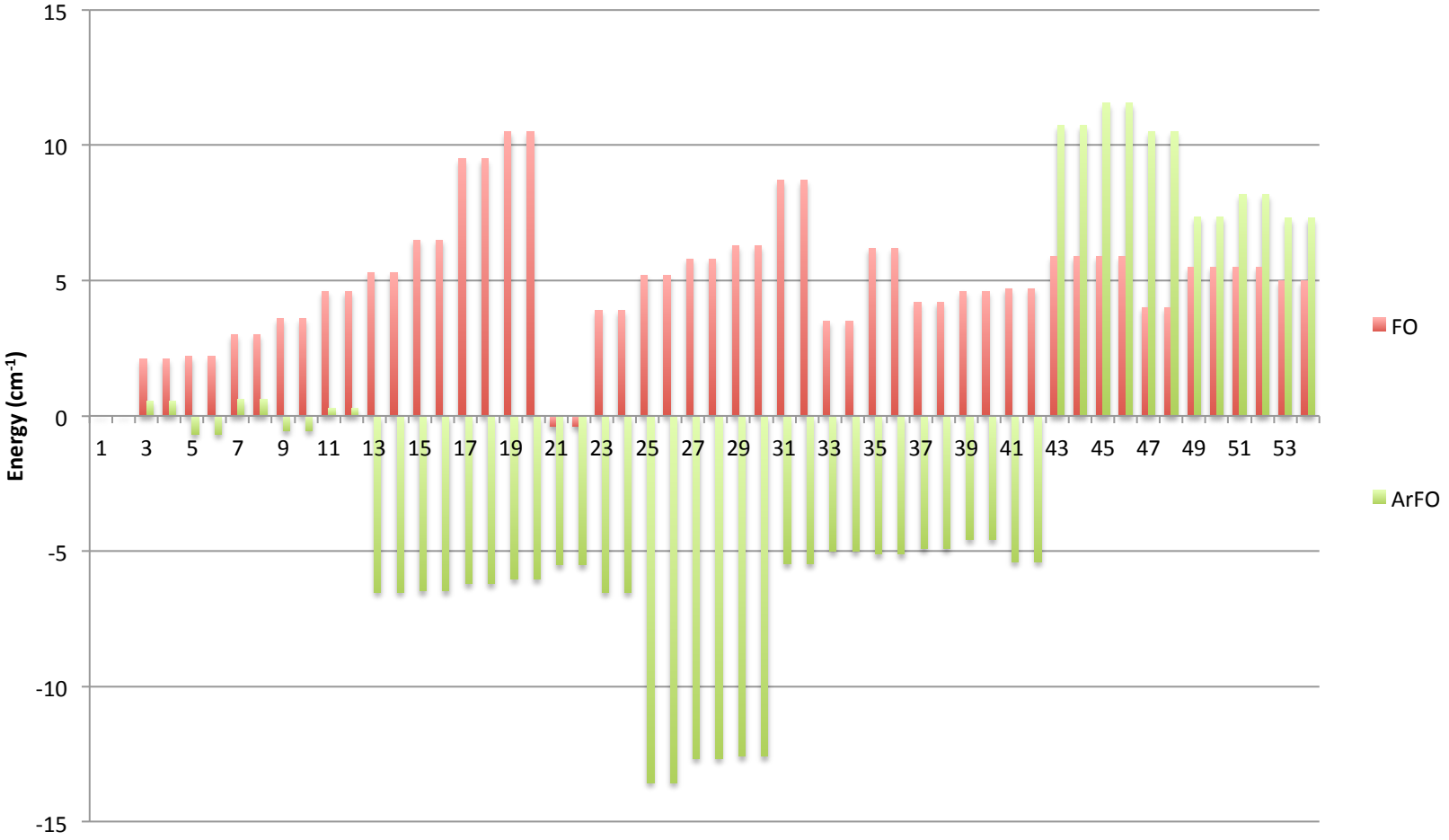
Without spin-orbit coupling:

Energy difference: E_ArFO − E_ArFO_sum
E_FO − E_FO_sum



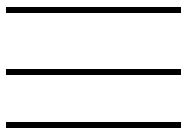
Energy Comparison between Interacting and Non-interacting for ArFO and FO

With spin-orbit coupling:



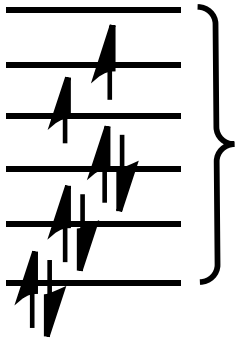
Complete Active Space

$$|\Psi_{CAS}\rangle = \sum_a C_a |\Psi_a\rangle$$ a collection of all the possible electronic configurations

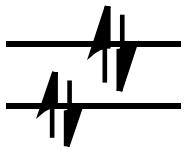


Virtual Space
a, b, c

CASSCF: optimize orbitals and coefficients such that E_{CAS} is minimal



Active Space
x, y, z



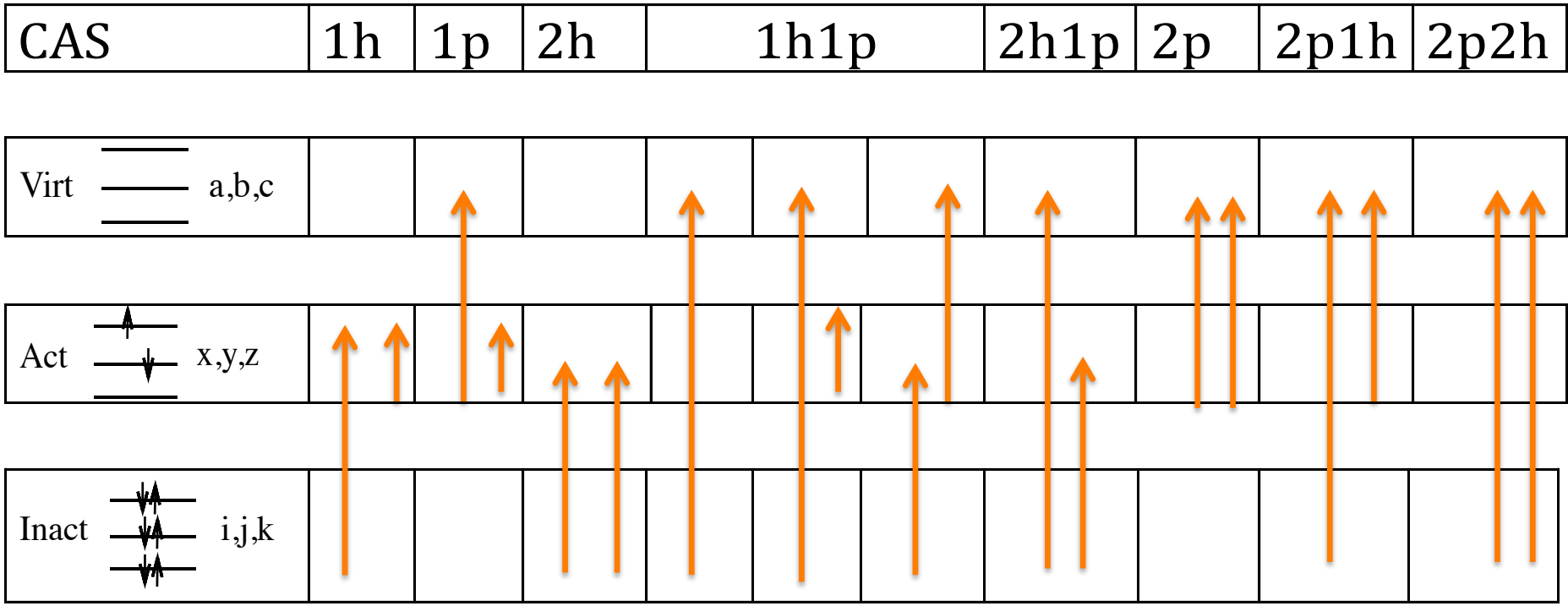
Occupied Space
i, j, k

CASSCF is analog of HF for multireference systems.

MRCI

$$|\Psi\rangle = \sum_a C_a |\Psi_a\rangle + \sum_{\lambda \neq a} C_\lambda |\Psi_\lambda\rangle$$

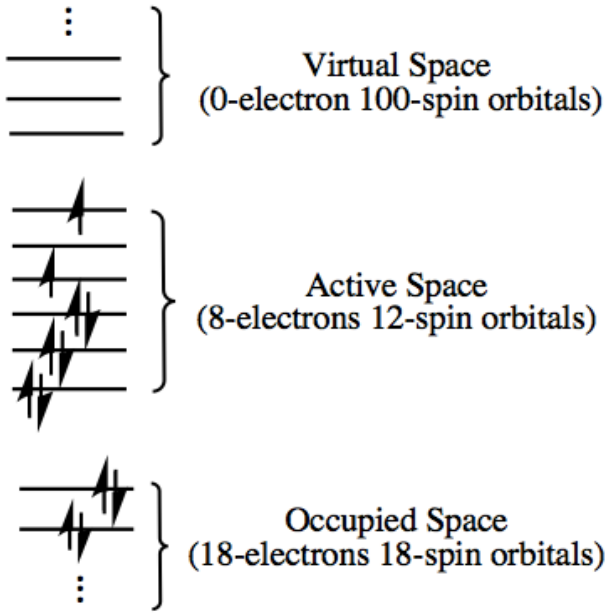
$|\Psi_{CAS}\rangle$



All single and double excitations out of the CAS $< \psi | H | \psi >$

MRCI: computationally very expensive

Co^+ : $3d^8 4s^0$ ($3d^7 4s^1$, $3d^7 4p^1$…)



Set 100 spin orbitals as the virtual space.

Combination of CAS orbitals: C_{12}^{8} = 495

Variational parameters: up to 10^8

Excitations	1h	1p	1h1p	2h	2p	1h2p	1p2h	2h2p
Diagonalization Space	18	100	18×100	$\binom{18}{2}$	$\binom{100}{2}$	$18\times\binom{100}{2}$	$100\times\binom{18}{2}$	$\binom{100}{2}\times\binom{18}{2}$
D.S.×|CAS⟩	8910	5×10^4	9×10^5	8×10^4	2×10^6	4×10^7	8×10^6	4×10^8

MRCI with Davison Correction

Separated system A, B

$$^{A}\Psi_{CID} = {}^{A}\Psi_{HF} + {}^{A}\Psi_{D}$$

$$^{B}\Psi_{CID} = {}^{B}\Psi_{HF} + {}^{B}\Psi_{D}$$

Interacted system AB

$$^{A+B}\Psi_{\mathrm{CID}} = {}^{A}\Psi_{\mathrm{CID}}\,{}^{B}\Psi_{\mathrm{CID}}$$

$$= ({}^{A}\Psi_{HF} + {}^{A}\Psi_{D})({}^{B}\Psi_{HF} + {}^{B}\Psi_{D})$$

$$= {}^{A+B}\Psi_{HF} + {}^{A+B}\Psi_{D} + {}^{A}\Psi_{D}\,{}^{B}\Psi_{D}$$

$$^{A}\Psi_{CID}\,{}^{B}\Psi_{CID} \neq {}^{A+B}\Psi_{CID}$$

The missing energy (quadruple excitation) gives rise to size inconsistency.

Davidson Correction: $\Delta E_{DC} = (1 - C_0{}^2)E_{corr}(CID)$

The CI calculation with Davidson correction is called the CI+Q method.

Internally contracted MRCI VS Uncontracted MRCI

Uncontracted MRCI:

$$|\Psi_{MRCI}\rangle = \sum_{a} C_a |\Psi_a\rangle + \sum_{\lambda \neq a} C_\lambda |\Psi_\lambda\rangle$$

Innternally MRCI:

$$\hat{C}_1 = \sum_{p,q \in exc} C_p^q \hat{E}_q^p \qquad \hat{C}_2 = \sum_{p,q,r,s \in exc} C_{pq}^{rs} \hat{E}_{rs}^{pq}$$

$$|\Psi_{IC-MRCI}\rangle = (1 + \hat{C}_1 + \hat{C}_2)|\Psi_{CAS}\rangle$$

Always minimize: $< \psi \mid H \mid \psi >$

MRCI: n_{exc} x n_{ref} dimensions

IC-MRCI: n_{exc} + n_{ref} dimensions

Much smaller if n_{rel} is larger

MREOM

Transformation concept:

Starting point: $\hat{H}|\Psi\rangle = E|\Psi\rangle$ Original Schrödinger equation

Transformation:

$$\begin{aligned} \hat{H}UU^{-1}|\Psi\rangle &= E|\Psi\rangle \\ U^{-1}\hat{H}UU^{-1}|\Psi\rangle &= EU^{-1}|\Psi\rangle \qquad \hat{\tilde{H}} = U^{-1}\hat{H}U \\ \hat{\tilde{H}}U^{-1}|\Psi\rangle &= EU^{-1}|\Psi\rangle \qquad |\phi\rangle = U^{-1}|\Psi\rangle \\ \hat{\tilde{H}}|\phi\rangle &= E|\phi\rangle \end{aligned}$$

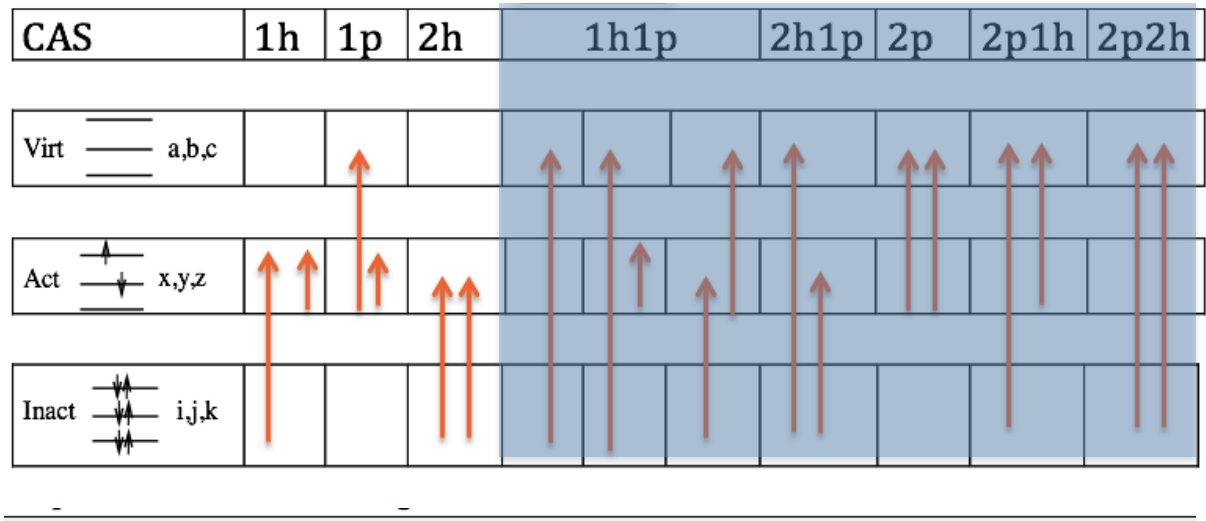
Any operator U can be used to transform. Different eigenstates but same eigenvalue.

MREOM: perform similarity transformations of the second quantized Hamiltonian

Transformation Strategy Continued…

$$|\Psi\rangle = \sum_a C_a|\Psi_a\rangle + \sum_{\lambda\neq a} C_\lambda|\Psi_\lambda\rangle$$

$$|\Psi_{CAS}\rangle$$



$$\hat{G} = \{e^{(\hat{S}+\hat{X}+\hat{D})}\}^{-1}\bar{H}\{e^{(\hat{S}+\hat{X}+\hat{D})}\}$$

$$\langle\Phi_X|\hat{G}|\Phi_\lambda{}^{CAS}\rangle = 0$$

Hamiltonian amplitudes that couple determinants in the CAS to determinants (e.g., 1p1h , 2p1h excitations) vanish.

Acronym	Operator	Operator Components	Excitation Type
T	$\hat{T}_1$	$t_a^x E_x^a + t_a^i E_i^a$	1p, 1h1p
	$\hat{T}_2$	$t_{ab}^{xy} E_{xy}^{ab} + t_{ab}^{ix} E_{ix}^{ab} + t_{ab}^{ij} E_{ij}^{ab}$	2p, 2p1h, 2p2h
S	$\hat{S}_1$	$s_a^x E_x^a + s_a^i E_i^a$	1p,1h1p
	$\hat{S}_2$	$s_{ax}^{ij} E_{ij}^{ax}$	2h1p
X	$\hat{X}_2$	$x_{ay}^{xj} E_{xj}^{ay}$	1h1p
D	$\hat{D}_2$	$d_{ay}^{ix} E_{ix}^{ay}$	1h1p
U	$\hat{U}_2$	$u_{xy}^{ij} E_{ij}^{xy}$	2h
NI	…	$E_i^x, E_{iz}^{xy}, E_{xy}^{az}$	1h,1p

Diagonalization Concept

Final step:

Diagonalize G, the final Hamiltonian over the remaining configurations (1h,1p,2h).

G	CAS	1h	1p	2h	1h1p	2h1p	…2p
CAS	A						
1h							
1p							
2h	C~0						
1h1p							
2h1p							
…2p							

Efficient!

Excitations	1h	1p	1h1p	2h	2p	1h2p	1p2h	2h2p
Diagonalization Space	18	100	18×100	$\binom{18}{2}$	$\binom{100}{2}$	$18\times\binom{100}{2}$	$100\times\binom{18}{2}$	$\binom{100}{2}\times\binom{18}{2}$
D.S.×|CAS⟩	8910	5×10^4	9×10^5	8×10^4	2×10^6	4×10^7	8×10^6	4×10^8

Features of Methodology

MRCI (Multireference Configuration Interaction)

- Widely cited as accurate method
- Computationally expensive
- Not Size-consistent

MREOM (Multireference Equation-of-motion Methodology)

- More effective compared to MRCI calculation
- Size-consistent
- Less well tested for accuracy

Questions:

Is MREOM accurate enough for magnetic systems?

How to include SOC with MREOM ? (variations are possible)

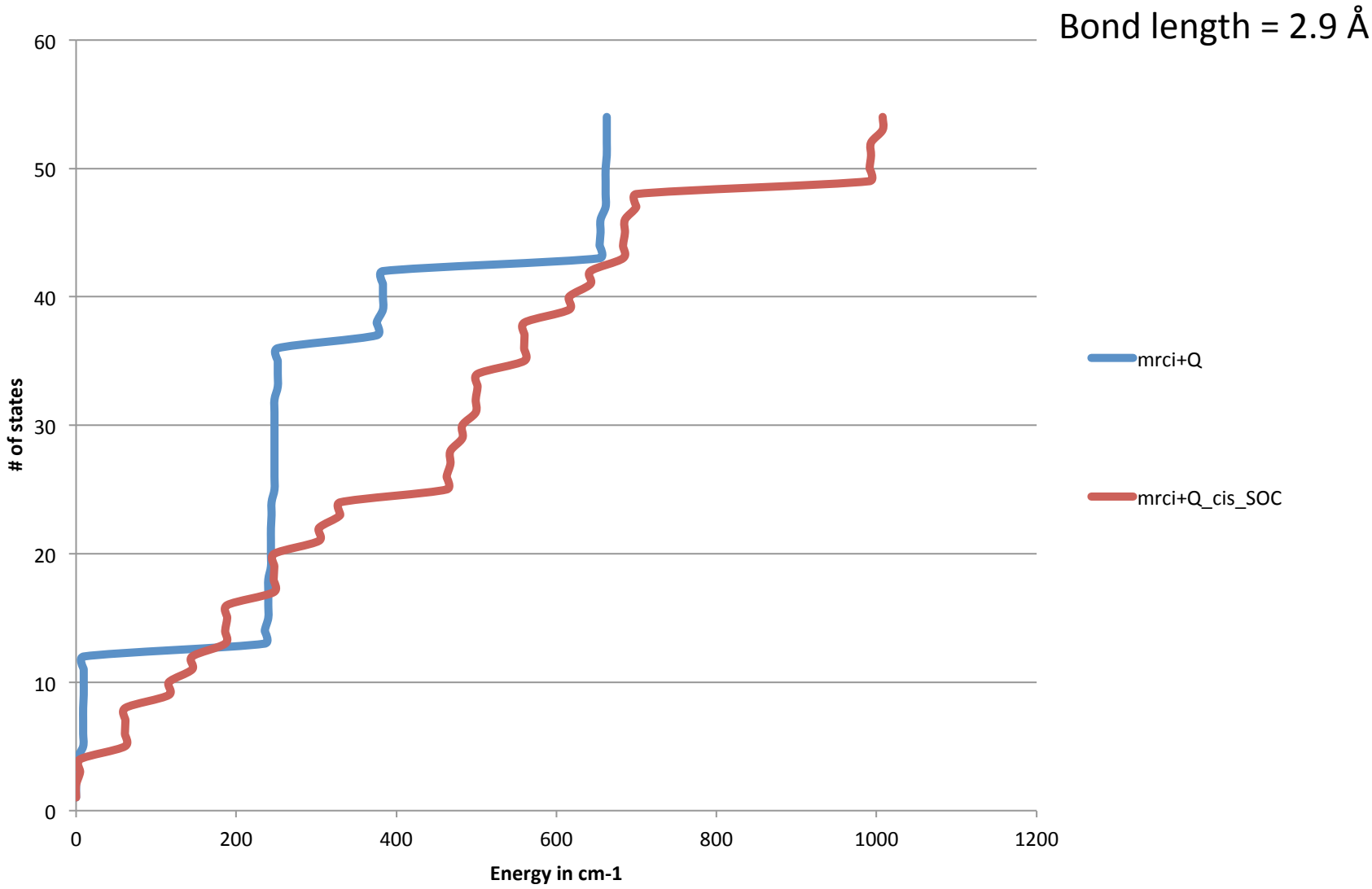
Means of Analysis

Two computational packages (Molpro, ORCA) will be employed to study:

- Statistical Mechanical properties, such as heat capacity under spin-orbit coupling level and no spin-orbit coupling level. (accuracy)
- Behavior for the two-body delta energies(E_dimer- sum of E_monomer) with the change of bond length under spin-orbit coupling level and no spin-orbit coupling level.
- Do two-body delta energies go to zero at large bond distance? (size-consistency)

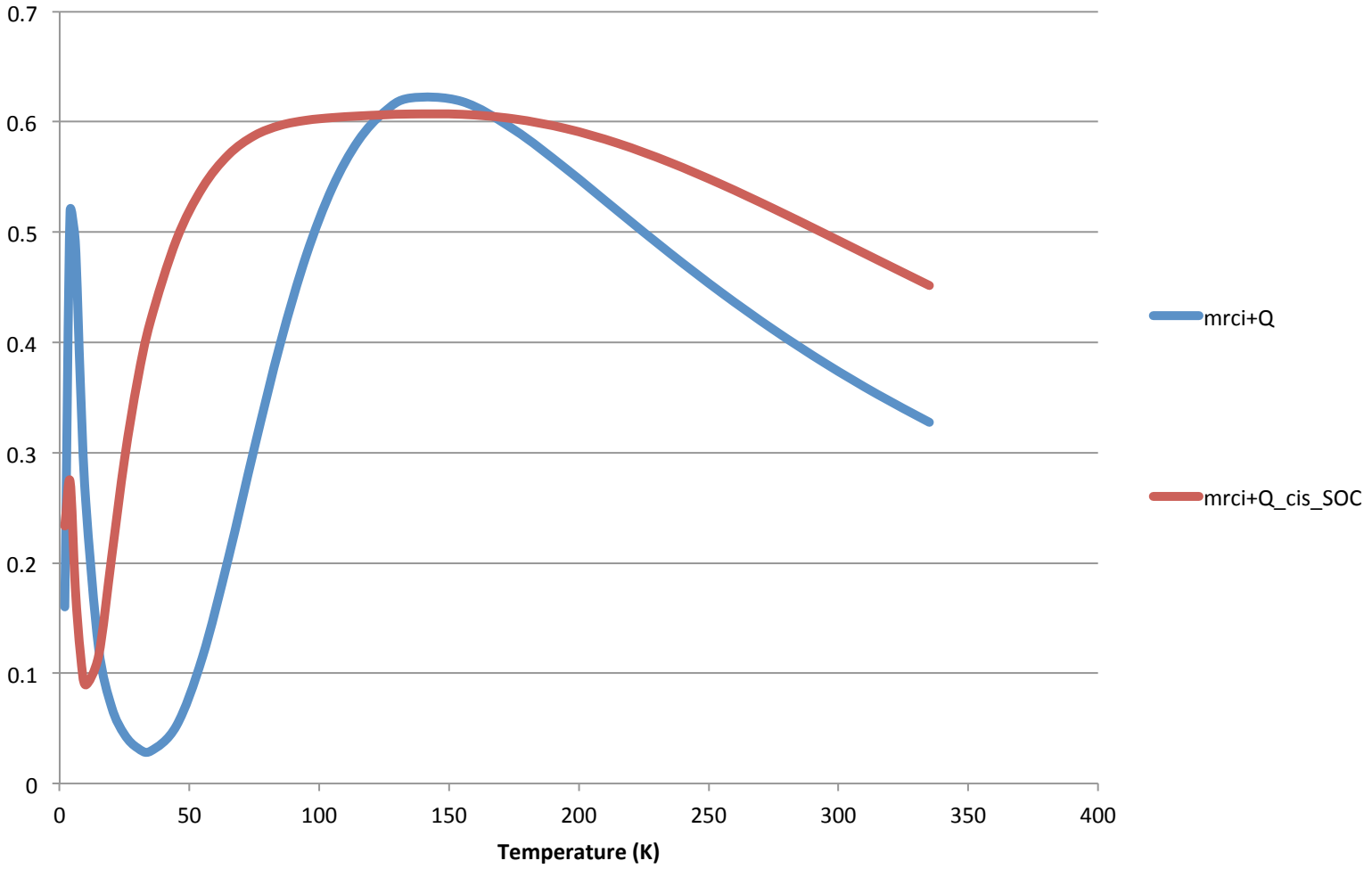
Results

Energy comparison of mrci+Q_cis_SOC with mrci+Q for ArFO



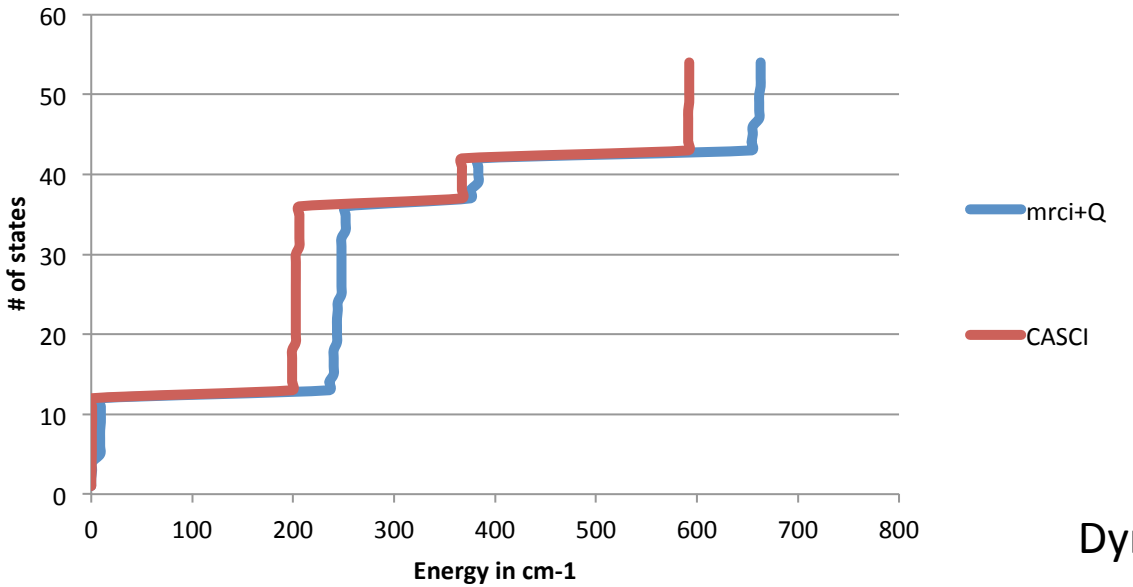
Heat capacity comparison of mrci+Q_cis_SOC with mrci+Q for ArFO

Bond length = 2.9 Å



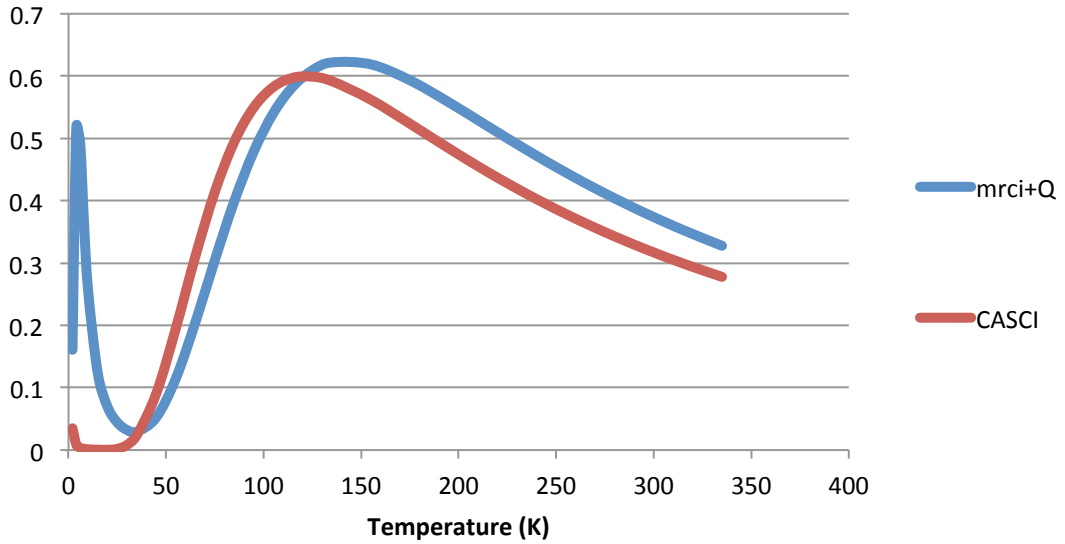
Stat-mech properties comparison of CASCI and MRCI+Q without SOC for ArFO

States E:



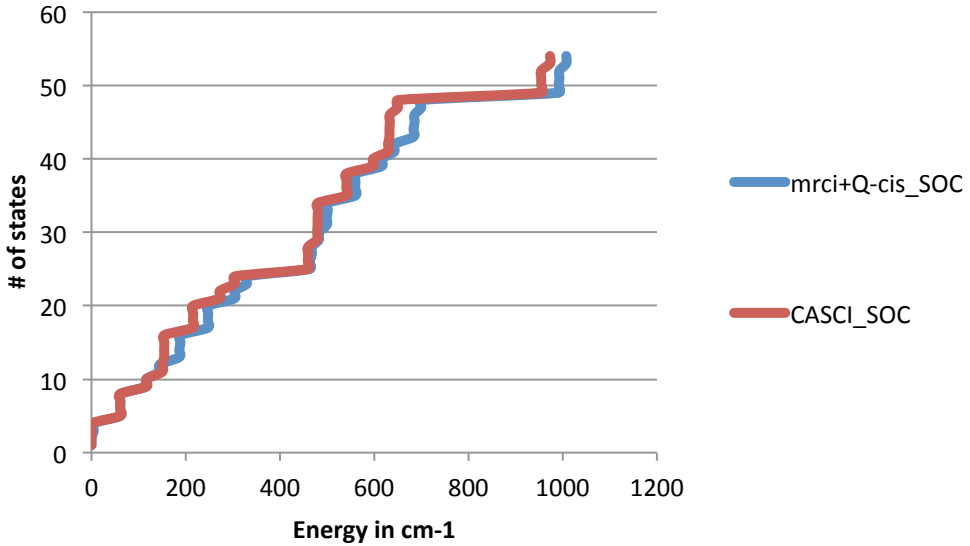
Dynamic correlation?

Cv:



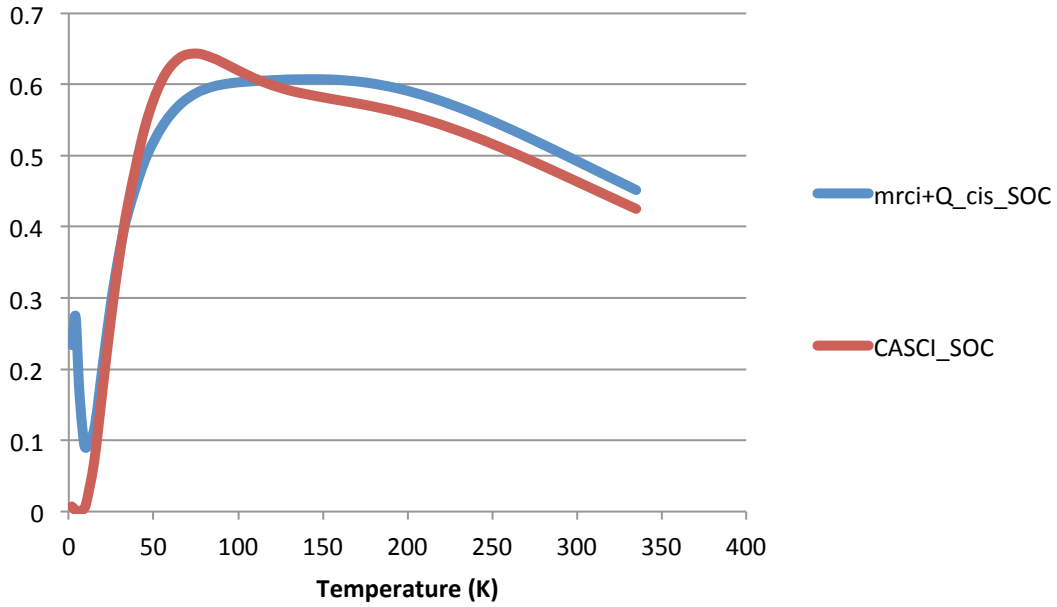
Stat-mech properties comparison of CASCI and MRCI+Q with SOC for ArFO

States E:



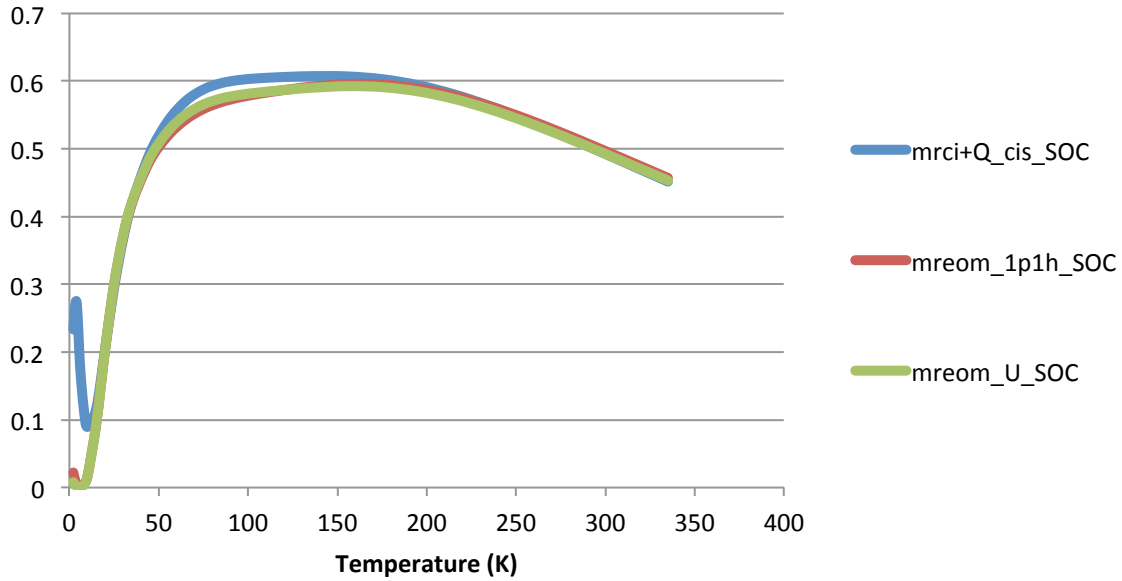
Dynamic correlation?

Cv:

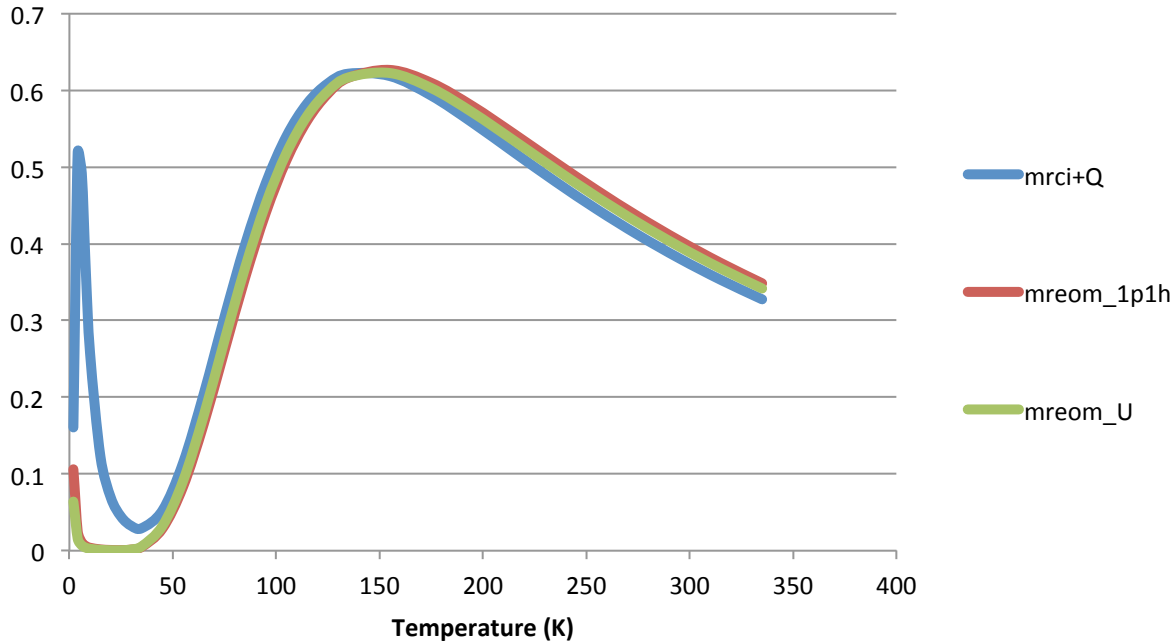


Stat-mech properties comparison (Molpro versus ORCA)

With SOC:

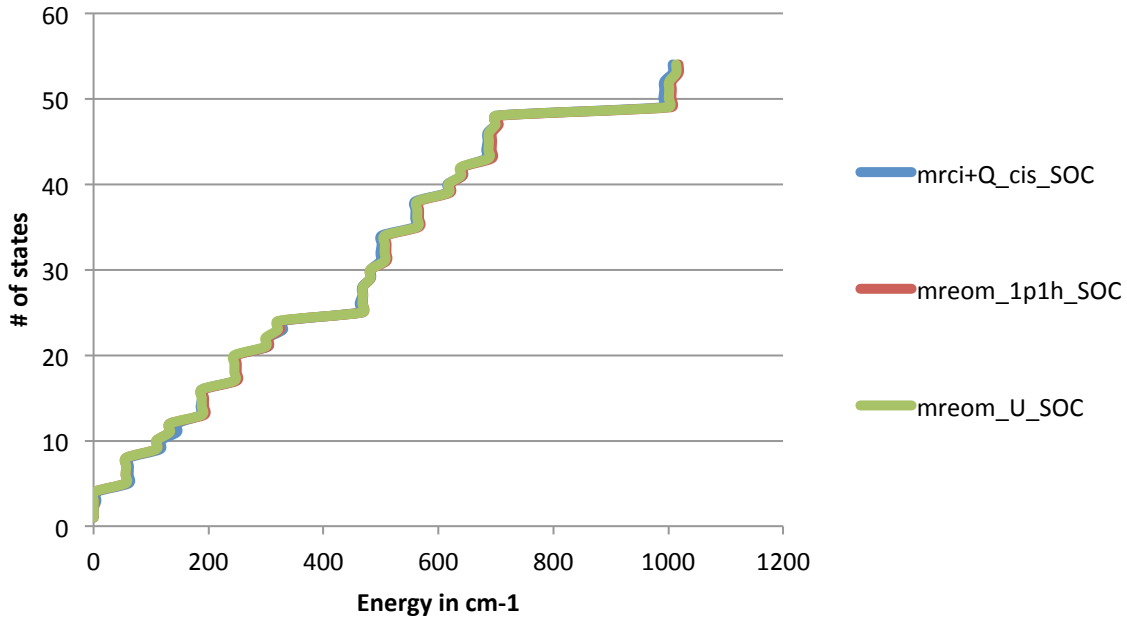


Without SOC:

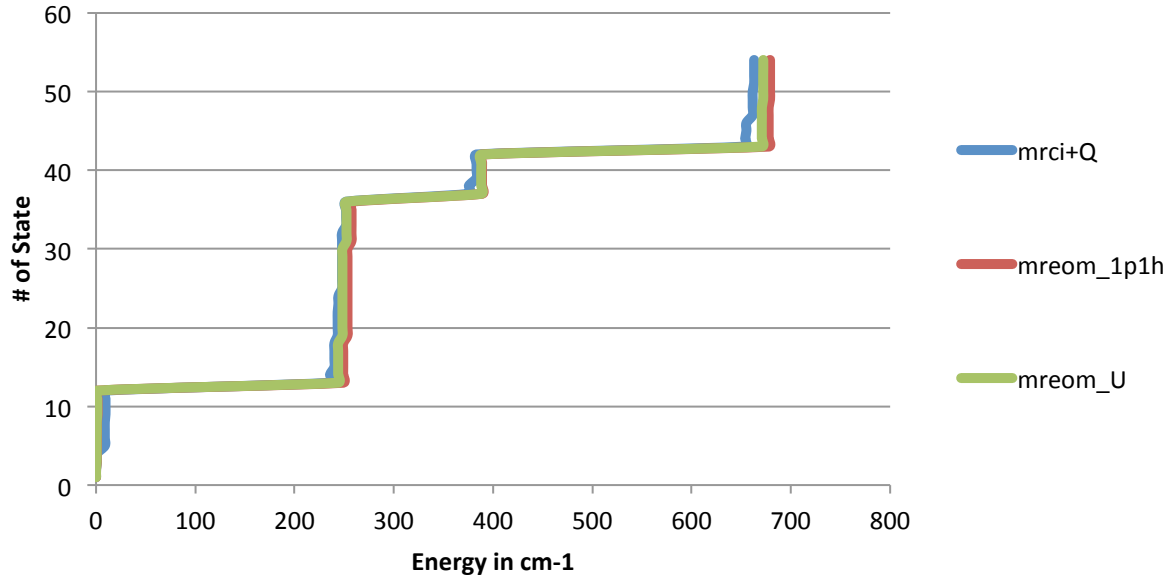


Stat-mech properties comparison (Molpro versus ORCA)

With SOC:



Without SOC:



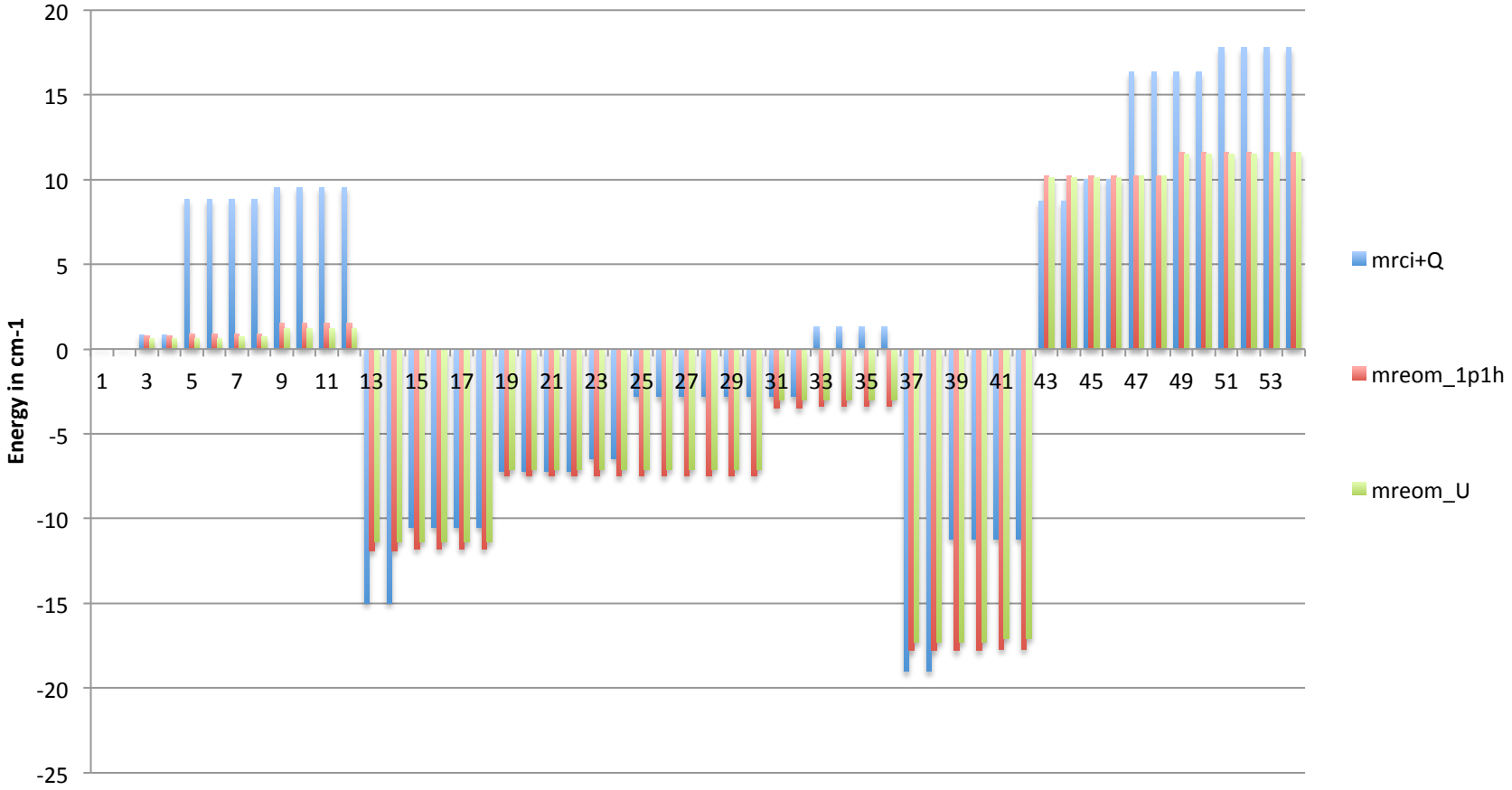
These methods look very similar if we look at energies plots or Cv plots.

What will happen if we look in more details at two-body energies:
Excitation energies of dimer (ArFO) − Sum of excitation energies monomers (ArF + ArO)

Investigate long distance behavior.

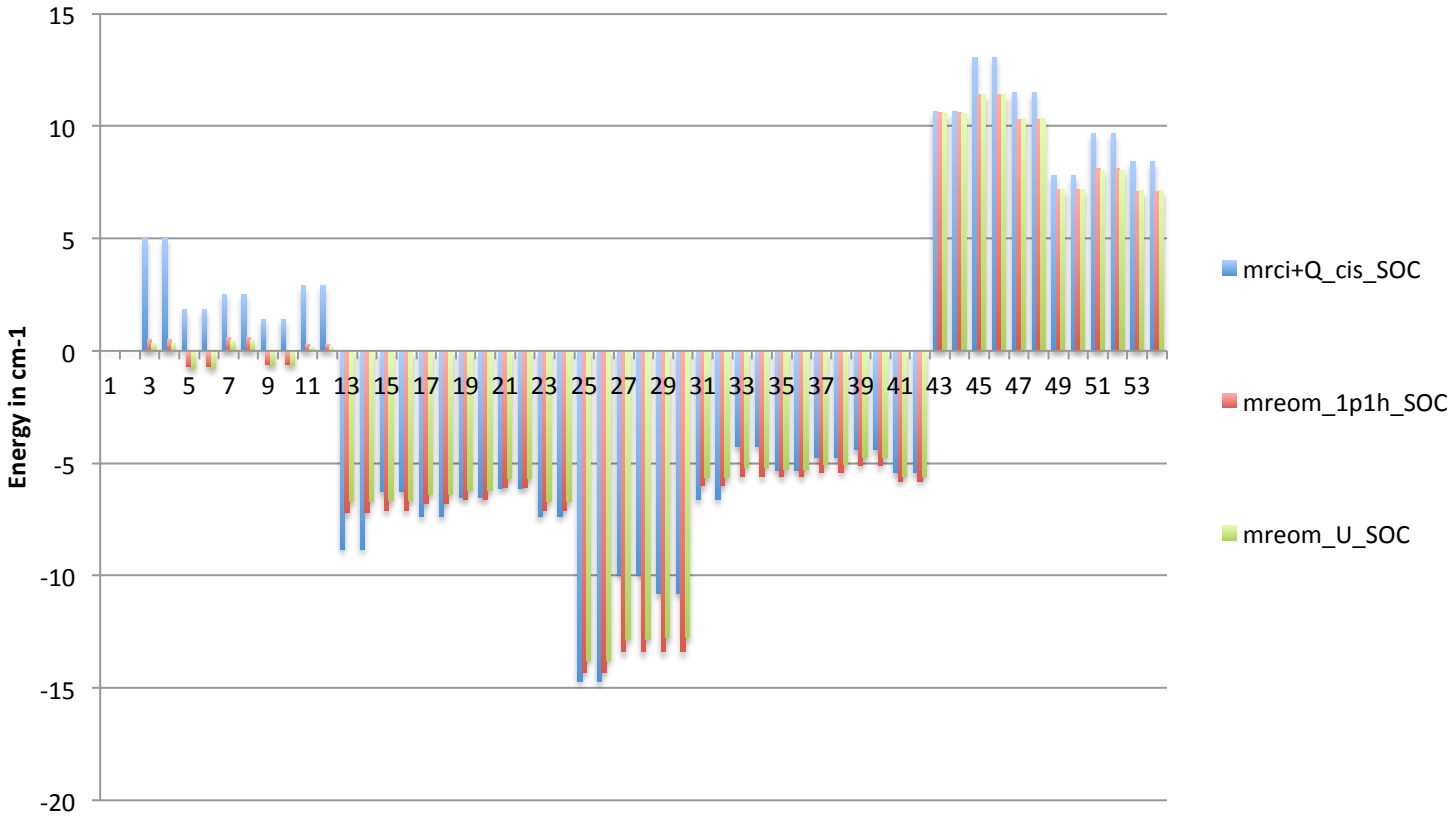
Two-body delta energies comparison (Molpro versus ORCA)

Without SOC:



Two-body delta energies comparison (Molpro versus ORCA)

With SOC:



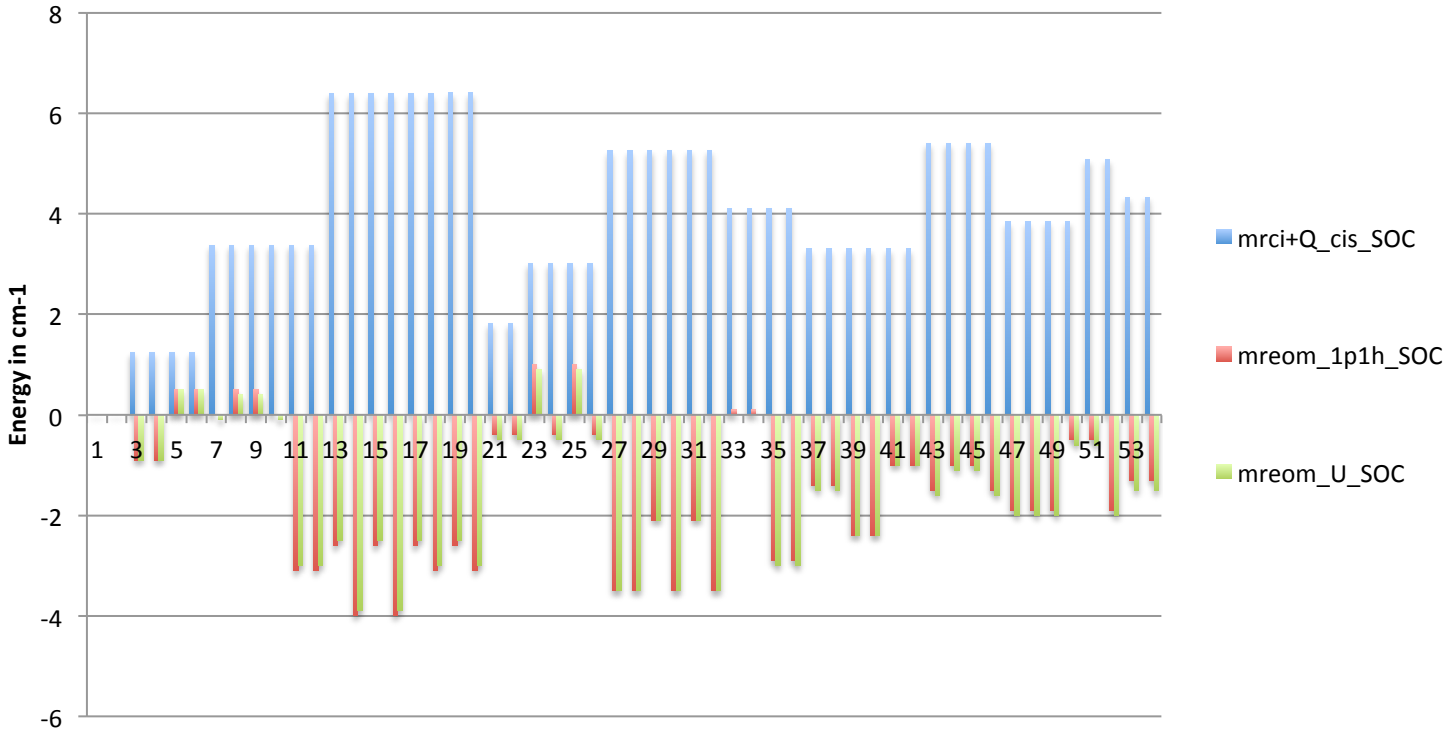
Question:

If we drag the bond length far apart, what will happen to our two-body energies plot?

Two-body delta energies comparison (Molpro versus ORCA)

Bond length = 10 Å

With SOC:



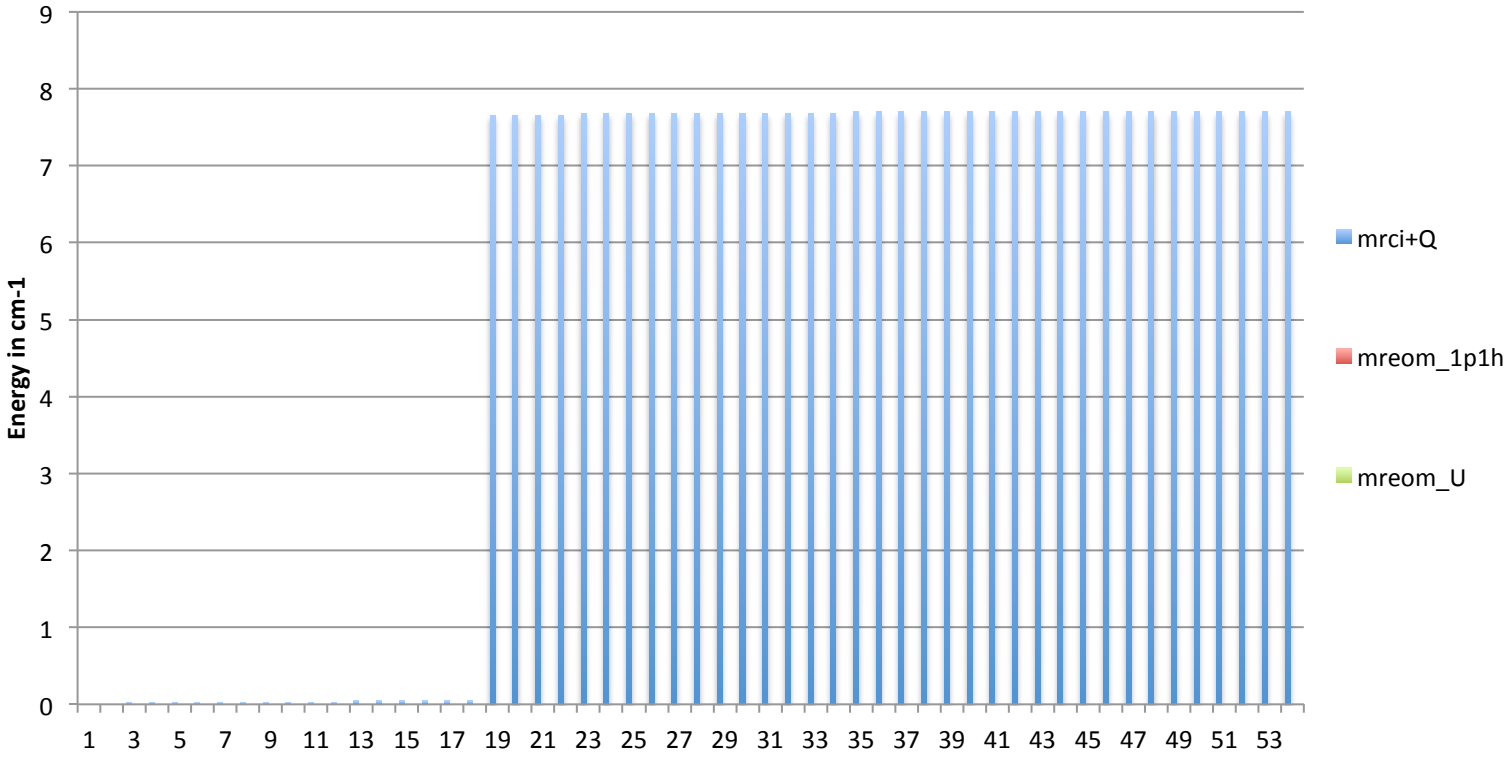
Two-body delta energies are not zero for all three methods.

Issue with SOC.

Two-body delta energies comparison (Molpro versus ORCA)

Bond length = 10 Å

Without SOC:



Two-body delta energies is not zero only for MRCI+Q.

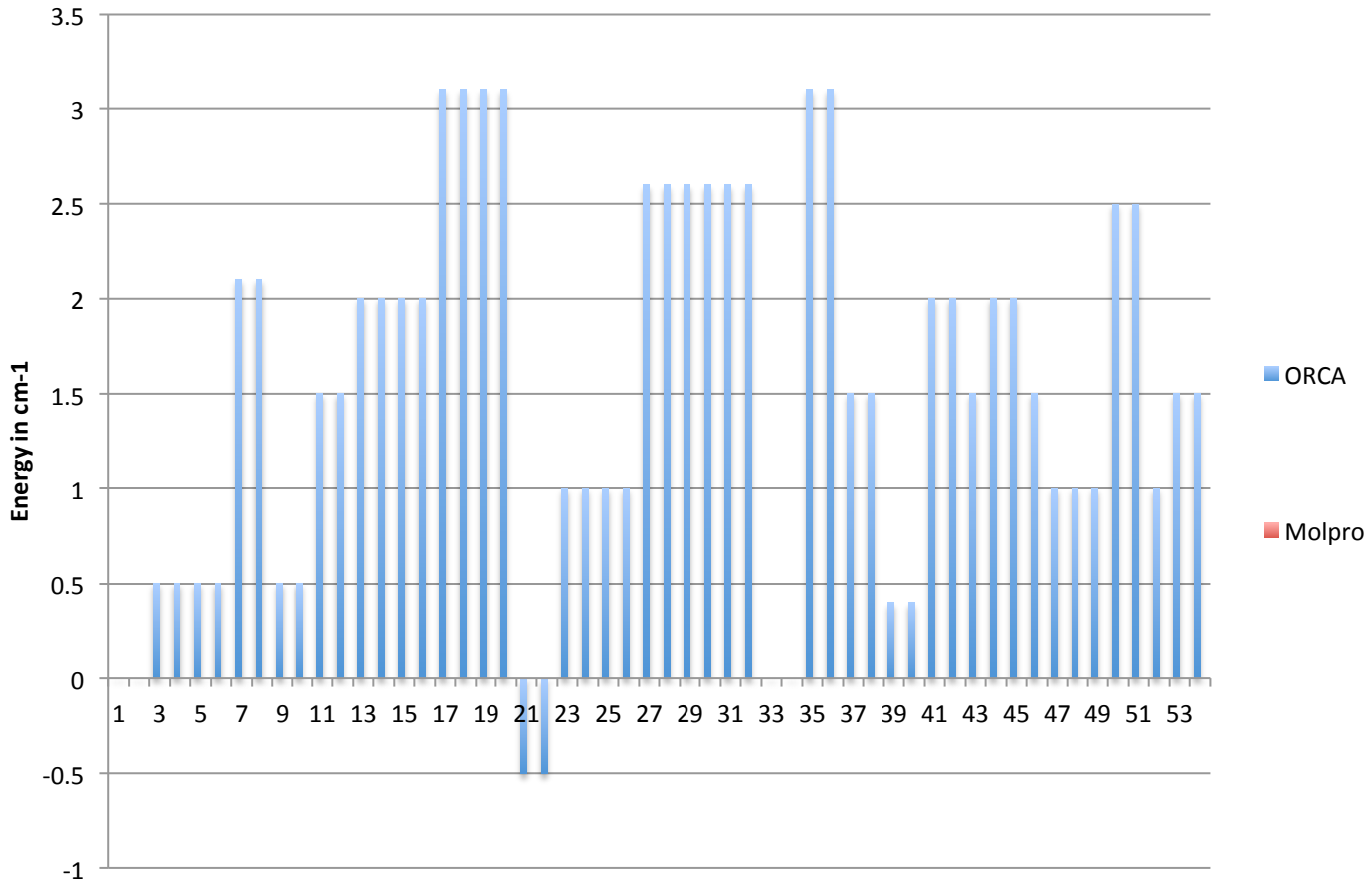
MREOM: size-consistent without SOC.

Question?

If we go back to CASCI level with spin-orbit coupling, what kind of behaviour can we observe?

Two-body delta energies comparison for CASCISOC (Molpro versus ORCA)

Bond length = 10 Å



Default CASCISOC calculation in ORCA is not size-consistent.

Spin-orbit Coupling methods in ORCA

SOMF(1X): Mean-field/effective potential.

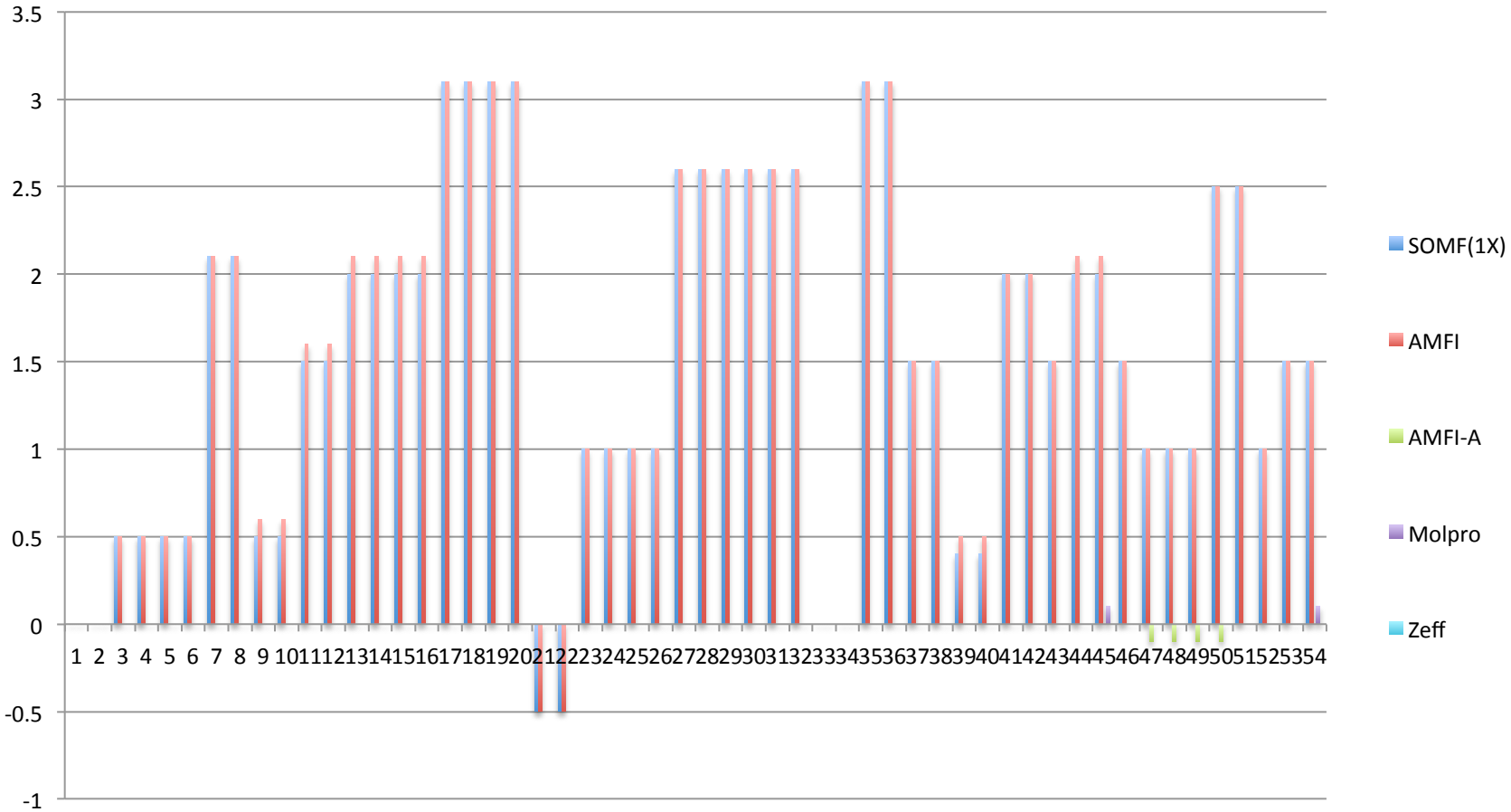
Zeff: Effective nuclear charge.

AMFI: mean-field with atomic densities generated on the fly.

AMFI-A: AMFI-like approach that uses pre-calculated atomic densities.

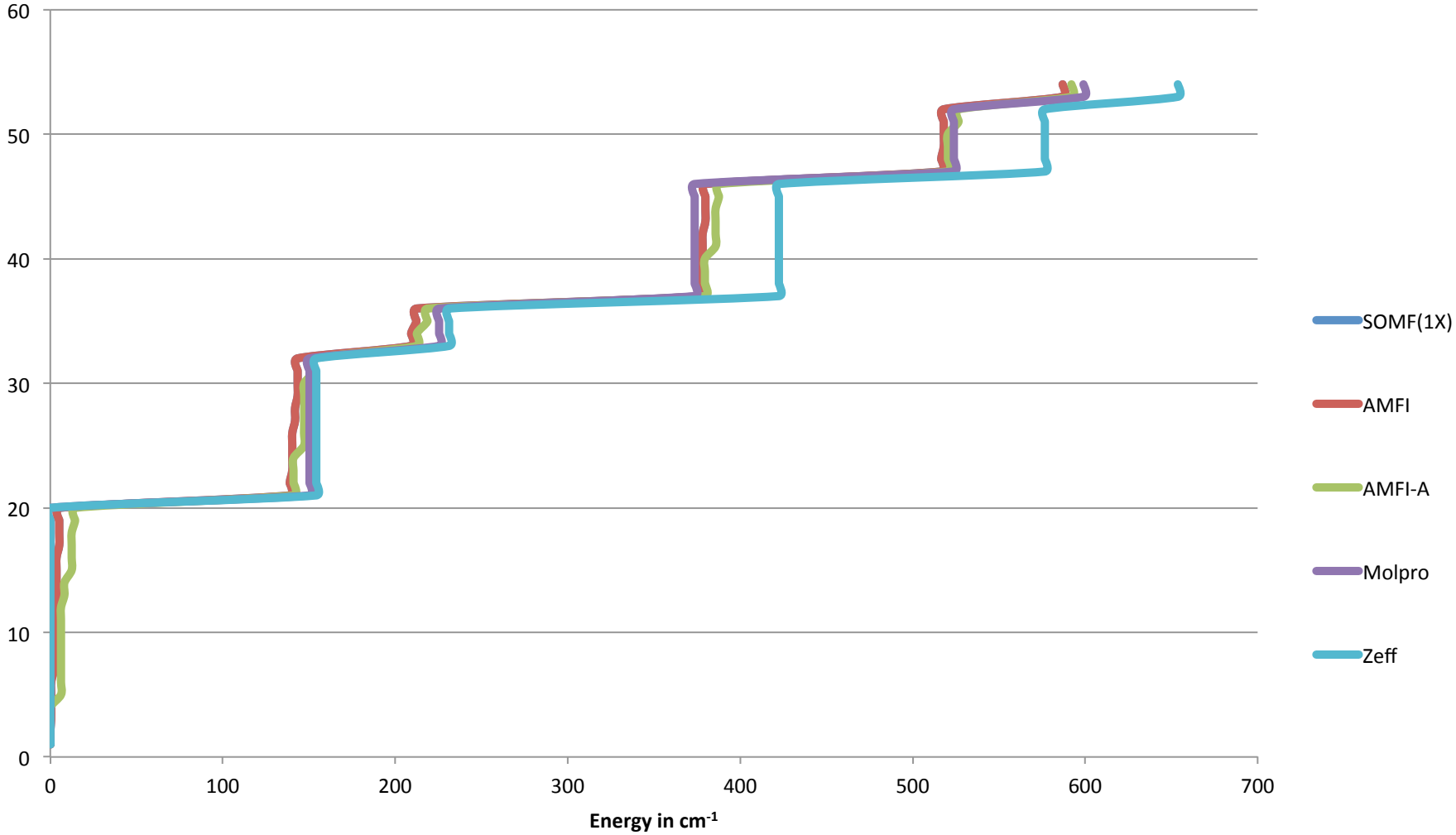
Two-body delta energies comparison in ORCA

Bond length = 10 Å



Molpro, Zeff, AMFI-A methods are size-consistent. Accuracy?

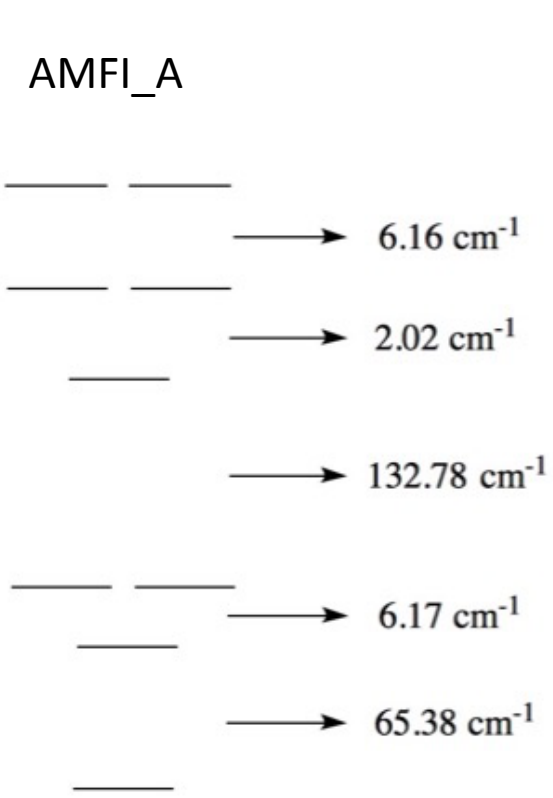
Energy comparison in ORCA

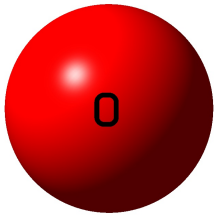


Zeff is not accurate compared to other methods.

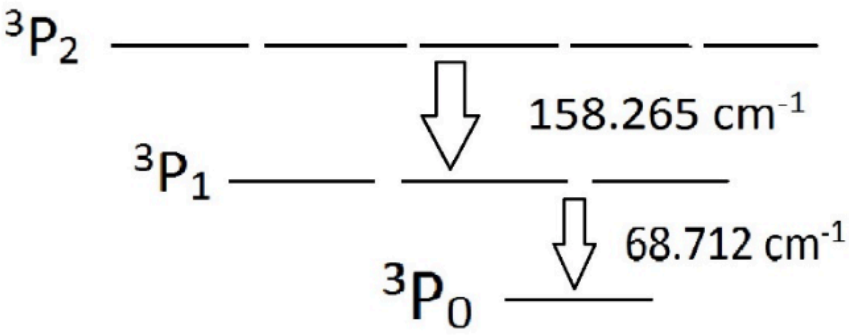
Low-lying states comparison for oxygen atom

AMFI_A





NIST



AMFI_A method is not accurate.

Conclusion & Future Work

- Compared with Cv plots, Energy plots in ORCA and Molpro package, MREOM methods and MRCI methods are quite reasonable and similar.
- MRCI methods is very expensive, and two-body delta energies are not good because they are size-inconsistent.
- Multireference methods with spin-orbit coupling in ORCA package have troubles.

Future work:

- Try to fix SOC issue in ORCA.
- Take a further look at magnetic trimer (eg. $ArOF_2$).
- Evaluate two-body and three-body delta energies at shorter and larger bond length.

References

1. Shamasundar, K. R., Knizia, G., & Werner, H. J. (2011). *A new internally contracted multi-reference configuration interaction method*. The Journal of chemical physics, *135*(5), 054101.
2. NIST Atomic Spectra Database. http://physics.nist.gov/PhysRefData/ASD/levels_form.html
3. Malmqvist, P.-H. & Roos, B. 0. *THE CASSCF STATE INTERACTION METHOD.* Chem. Phys. Lett. 155, (1989).
4. Malrieu, J. P., Caballol, R., Calzado, C. J., De Graaf, C., & Guihery, N. (2013). *Magnetic interactions in molecules and highly correlated materials: physical content, analytical derivation, and rigorous extraction of magnetic Hamiltonians*. *Chemical reviews*, *114*(1), 429-492.
5. Nooijen M, Demel O, Datta D, et al. Communication: *Multireference equation of motion coupled cluster: A transform and diagonalize approach to electronic structure[J]*. 2014.
6. Neese F. *Efficient and accurate approximations to the molecular spin-orbit coupling operator and their use in molecular g-tensor calculations[J]*. The Journal of chemical physics, 2005, 122(3): 034107.

Acknowledgement

I would like to express my deepest appreciation to my supervisor: *Marcel Nooijen* , and also many thanks to *Johnny Steffen*, *Patty Hu* for their support during this project.