# Proposal of a Multi-State Multi-Reference Coupled Cluster Method

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# Search of a multi-state MRCC formalism

Recall: State Specific MRCC exist
Face the multiple parentage problem: How to define the amplitudes of excitations sending from the N references $|I>$ to the same excited determinant $|r>$?

Not enough equations→have to add conditions:

-"Equal parentage" of Debashis Mukherjee

- Scale amplitudes on the values of the matrix elements $<I|H|r>$
( JPM, Meller, Caballol, JCP, 104,4068 (1996)) physically based on perturbation theory, lack of implementation)

Instead of solving set of non linear equations, guess amplitudes from (MR)SDCI ,coefficients, than calculate the effect of the Triples and Quadruples as a dressing of the CI matrix and iterate

The MS-MR-SDCC would be simple if one looked for the same number M of roots as the number of references

Model space $P_0 = \sum_{I=1,M} |I\rangle\langle I|$ $\xrightarrow{\Omega}$ Target space $P = \sum_{m=1,M} |\Psi_m\rangle\langle\Psi_m|$

Jeziorski-Monkhorst wave operator $P = \Omega P_0 = \sum_I \Omega_I |I\rangle\langle I|$

1) Perform an MR-SDCI→M eigenstates $\left|\Psi'_m\right\rangle = \sum_I C_I^m |I\rangle + \sum_{r\notin S_0} C_r^m |r\rangle$

2)Define state-independent reference-dependant amplitudes giving the coefficients of the outer-space determinants from those of the main MS

$$C_r^m = \sum_I d_{rI} C_I^m, m = 1, M$$

i.e.

$$d_{rI} = \sum_{m=1,M} C_r^m C_{mI}^{-1}$$

(invertible matrix of the coefficients in the main model space)

$$P_{MRSD} = \sum_m \left|\Psi'_m\right\rangle\left\langle\Psi'_m\right| = \sum_I S_I |I\rangle\langle I|$$

$$S_I = \sum_r d_{rI} T^+_{I\to r}$$

3) Exponentialize Ω $$P_{MRCC} = \Omega P_0 = \sum_I \exp S_I \left| I \right\rangle \left\langle I \right|$$

Dress the MRSDCI matrix under the effect of the triples and quadruples, the coefficients of which come from $S^2$, to convergence, as for single reference

But in the real life we always need more references than states !

# A paradigmatic problem

- The lowest states of ethylene, or of typical magnetic systems

2 e- in 2 orbitals. localized a and b (eventually from CASSCF) → 4 VB determinants

2 neutral VB $\left|core.a\bar{b}\right| = \left|a\bar{b}\right|$ and $\left|core.b\bar{a}\right| = \left|b\bar{a}\right|$

2 ionic VB $\left|core.a\bar{a}\right| = \left|a\bar{a}\right|$ and $\left|core.b\bar{b}\right| = \left|b\bar{b}\right|$

4 eigenstates, 2 neutral $\Psi_g^1 = \lambda(\left|a\bar{b}\right| + \left|b\bar{a}\right|) + \mu(\left|a\bar{a}\right| + \left|b\bar{b}\right|), \lambda > \mu > 0$

$$\Psi_u^3 = (\left|a\bar{b}\right| - \left|b\bar{a}\right|) / \sqrt{2}$$

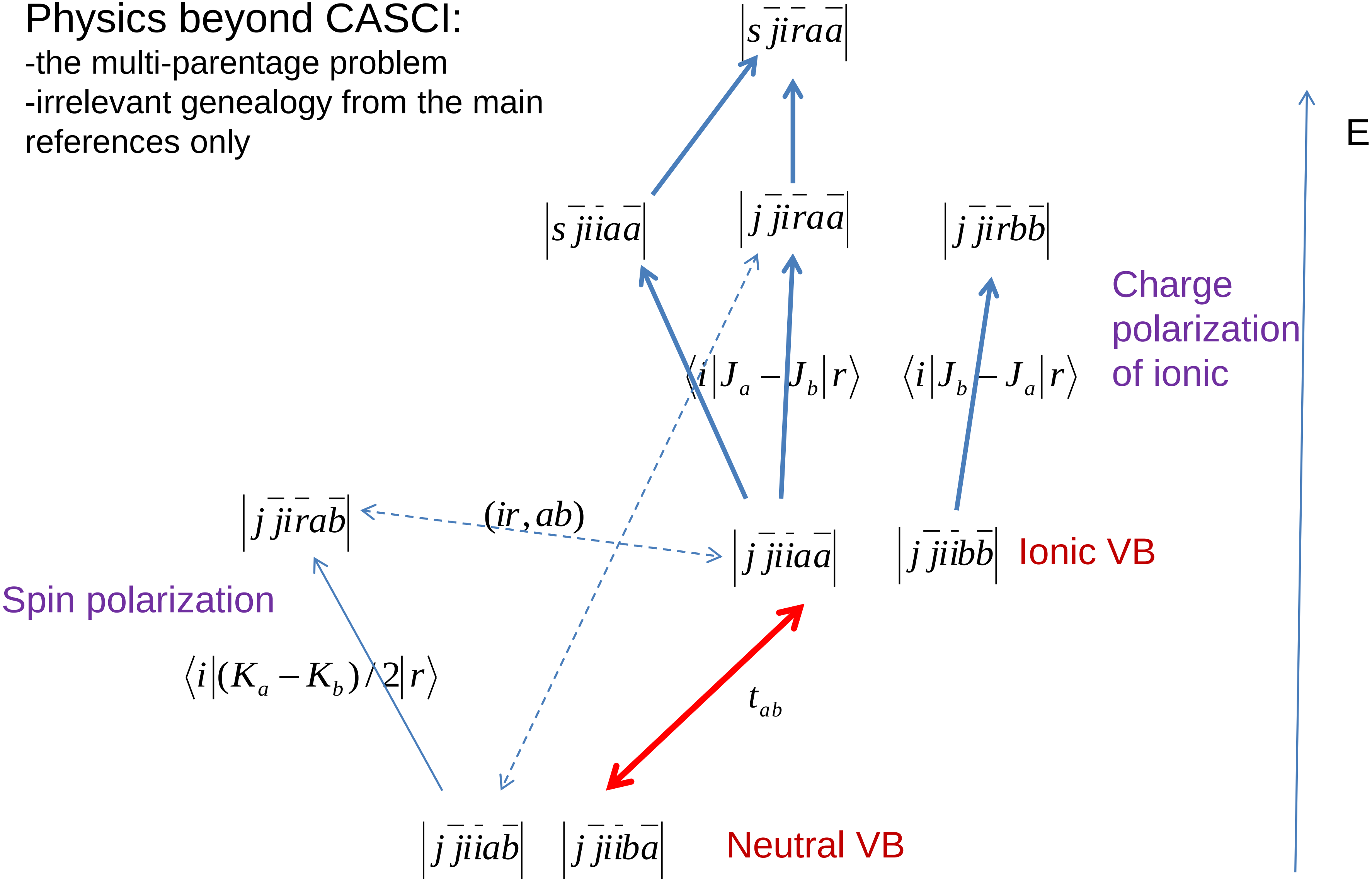
2 ionic $^{*}\Psi_g^1 = -\mu(\left|a\bar{b}\right| + \left|a\bar{b}\right|) + \lambda(\left|a\bar{a}\right| + \left|b\bar{b}\right|)$

$$\Psi_u^1 = (\left|a\bar{a}\right| - \left|b\bar{b}\right|) / \sqrt{2}$$

# Physics beyond CASCI:

-the multi-parentage problem

-irrelevant genealogy from the main references only



The 2 lowest states are essentially neutral, but the singlet has crucial ionic VB components → 4 references

The eigenstates which have large components on the ionic VB components are not the 3$^{rd}$ and 4$^{th}$ eigenstates and may eventually be embedded in the continuum → impossible correspondence between iso-dimensional model space and target space

Need to go the intermediate effective Hamiltonian formalism: more references (N) than desired states (M<N)
(JPM, Durand, Daudey J. Phys. A, 18, 209 (1985))

Clear illustration of the multi-parentage problem,
The monoexcitations on ionic VB components are doubly excited from the neutral VB components but their weight comes from the ionic VB components, therefore these components must be generators.

Distinguish, for a CAS model space,

-a main model space: the M references, |I>, having the largest coefficients in the M desired eigenstates

-an intermediate model space: the other determinants, |i>, of the CAS

-the Singles and Doubles, |r>,on the top of the CAS,

-the Triples and Quadruples, |α>, which will be generated from an exponential wave operator acting on the CAS

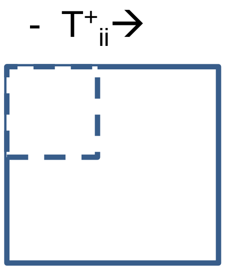
1) from the CASCI vectors define amplitudes of excitations $T^{+}_{I->i}$ from the main I to the intermediate i

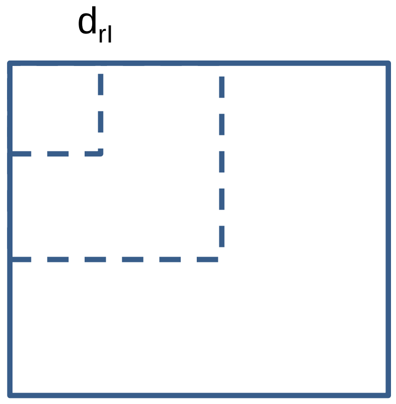
$$P_0 H P_0 \left|\Psi''_m\right\rangle = E''_m \left|\Psi''_m\right\rangle$$

$$\left|\Psi''_m\right\rangle = \sum_I C''^{m}_{I}\left|I\right\rangle + \sum_i C''^{m}_{i}\left|i\right\rangle$$

$$t'_{I->i} = \sum_{m=1,M} C''^{m}_{i} C''^{-1}_{mI}$$

$$\left|\Psi''_m\right\rangle = \sum_I (1+\sum_r t'_{I->i} T^{+}_{I->i})\left|I\right\rangle C''^{m}_{I}$$




2) Perform the full MRSDCI

For each r, from the M coefficients $C^{m}_{r}$ define state-independent amplitudes

$$d_{rI} = \sum_{m=1,M} C^{m}_{r} C^{-1}_{mI}$$

But one wants a wave operator from the whole model space, since many |*r* > do not interact with the main references |*I*>, are children of intermediate determinants. One would like to define the amplitudes of excitations from |*i* > to |*r*>

$$T^{+}_{i\rightarrow r}$$

One may write $d_{rI} = t_{I->r} + \sum_i t^I_{i->r} t_{I->i}$

.

And impose a proportionality of the amplitudes $t^I_{i->r}$ to *<i|H|r>*.

$$t^I_{i->r} = \lambda_{I,r} H_{ir}$$

Actually from QDPT on main model space, 1st + partial 2nd-order

$$d_{rI} = \frac{\langle r|H|I\rangle}{H_{II} - H_{rr}} + \frac{\sum_i \langle r|H|i\rangle\langle i|H|I\rangle}{(H_{II} - H_{rr})(H_{II} - H_{ii})} -> \frac{\langle r|H|I\rangle + \sum_i \langle r|H|i\rangle t_{I->i}}{H_{II} - H_{rr}}$$

This suggests to write

$$d_{rI} = \lambda_{I,r}(H_{Ir} + \sum_i H_{ir} t_{I->i})$$

which fixes $\lambda_{I,r}$, hence all $t_{I->r}$ $t^I_{i->r}$

One may write a wave operator from the main model space

$$P_{CASSDCI} = (1 + \sum_I S_I |I\rangle\langle I|)$$

$$S_I = S_{ID} + S_{I\,\mathrm{int}} + S^I_{\mathrm{int}D}$$

with

$$S_{ID} = \sum_{r \in SD} t_{Ir} T^+_{Ir}$$

$$S_{I\,\mathrm{int}} = \sum_i t_{Ii} T^+_{Ii}$$

$$S_{\mathrm{int}D} = \sum_{r \in SD} \sum_i t^I_{ir} T^+_{ir}$$

- exponentialize the $\Omega_I$'s in a MR-Generalized CC formalism (Noijen)

# Simpler solution

One wants to define a wave operator from the entire model space

$$(1+S)P_0 = P_O + \sum_{r,I} t_{I->r} T^{+}_{I->r} \left| I \right\rangle \left\langle I \right| + \sum_{r,i} t_{i->r} T^{+}_{i->r} \left| i \right\rangle \left\langle i \right|$$

For that one needs to define amplitudes of the $T^{+}_{i \to r}$ operators independent from the main model space determinants.

Define for each |*r* > a unique parameter $\lambda_r$ ( effective energy denominator)

$$d_{rI}(\lambda_r) = \lambda_r (H_{Ir} + \sum_i H_{ir} t_{I->i})$$

and optimize it such that $\sum_I \left| d_{Ir}(\lambda_r) - d_{Ir} \right|$ minimum/ $\lambda_r$

Best fit of the CASDCI vectors with main-reference independent amplitudes of the excitations from the intermediate to the Singles and Doubles

The Multi State MRCC will exploit the definition of S from the CAS-SDCI vectors

$$(1+S)P_0 = P_O + \sum_{r,I} t_{I->r} T^{+}_{I->r} \left|I\right\rangle\left\langle I\right| + \sum_{r,i} t_{i->r} T^{+}_{i->r} \left|i\right\rangle\left\langle i\right|$$

All determinants of the model space are formally treated on equal foot, now forget the differences between main and intermediate determinants

$$S = \sum_{k=I,i} S_k$$

Exponentialize the wave operator

$$\Omega' P_0 = \sum_{k \in S_0} \exp S_k \left|k\right\rangle\left\langle k\right|$$

In practice it consists in calculating the coefficients of the triples and quadruples, |α>, from $(1/2)S^2 P_0$

$$d_{\alpha k} = \sum_{<r,s> T^{+}_{k\to r} T^{+}_{k\to r} \left|k\right\rangle = \left|\alpha\right\rangle} t_{k\to r} t_{k\to r}$$

since $$C^m_\alpha = \sum_k d_{\alpha k} C^m_k = \sum_k (C^m_k \sum_{<r,s> T^{+}_{k\to r} T^{+}_{k\to r} \left|k\right\rangle = \left|\alpha\right\rangle} t_{k\to r} t_{k\to r})$$

- Dress the CAS SDCI matrix under the effect of the Triples and Quadruples, according to the column (between references and SD) dressing

$$\Delta_{rk} = \sum_{\alpha} H_{r\alpha} d_{\alpha k}$$

-its diagonalization leads to new values of the coefficients $C_k^m$ and $C_r^m$

- Hence to new values of the amplitudes $t_{k \to r}$ of the double excitations

- And iterate till convergence

Allows to treat several states of the same symmetry
Only double excitation operators
Un-contracted formalism

Not very simple but feasible and general !

See JPM, Mol. Phys., Special issue in honor of W. Kutzelnigg

Sorry for the complexity

Thanks for your tolerance

Remember QDPT/ full model space

$$\frac{\langle I|V|r\rangle\langle r|V|J\rangle}{\Delta E_{Jr}}+\frac{\langle I|V|s\rangle\langle s|V|r\rangle\langle r|V|J\rangle}{\Delta E_{Js}\Delta E_{Jr}}+\ldots->\langle I|\Delta|J\rangle$$

1) Perform MR CISD without the intermediate references

$$(1-P_i)H(1-P_i)|\Psi'_m\rangle = E'_m|\Psi'_m\rangle$$

$$|\Psi'_m\rangle = \sum_I C'^m_I|I\rangle + \sum_{r\notin S_0} C'^m_r|r\rangle$$

Enables to define amplitudes of the operators $T^+_{I->r}$ sending from I to r

$$t'_{I->r} = d'_{rI} = \sum_{m=1,M} C'^m_r C'^{-1}_{mI}$$

$$|\Psi'_m\rangle = \sum_I (1+\sum_r t'_{I->r}T^+_{I->r})|I\rangle C'^m_I$$