

# Alternative Single Reference Coupled-cluster approaches for multi-reference problems: pCCD+TCCSD for Excited States

Rodney Bartlett<sup>1</sup>, Moneesha Ravi<sup>1</sup>, Ajith Perera<sup>1</sup>, Young Choon Park<sup>1</sup>

<sup>1</sup> Quantum Theory Project, University of Florida, Gainesville, FL USA

I17

## To Joe Paldus: A mentor to all of us

In the competition between single reference CC/EOM-CC and multi-reference methods, SR-CC/EOM usually provides better results at far less effort. The reason is that CC/EOM gets to the full CI very quickly, and the full CI does not suffer from any MR aspect. The argument for MR methods is that choosing 'active' orbitals to define a MR starting point should be superior, since it offers a better zeroth-order starting point that is worth all the additional MR overhead required. But is that true? The objective of predictive quantum chemistry is a basis set converged full CI, but when one introduces a selection of 'active' orbitals that necessitates a MR description, the calculation must also converge for the particular active orbital choice. And there will be different choices for different states or situations. Contrast this with the fact that CCSD is virtually insensitive to orbital choice, rapidly approaching the invariance of the full CI. But SR-CC can also readily use UHF, Brueckner, Natural, KS, ROHF, QRHF, orbital optimized, and our COT orbital choices as easily as HF ones, if orbital choice offers anything important to a calculation.

What about 'strong correlation'. I think that strong correlation should mean that there is no subset of 'active' orbitals that can describe the situation. requiring that all be included: an obvious impossibility. In between this strong correlation limit and real-world problems lie cases where a couple of active orbitals would be a natural choice in a MR-CC method like GVB -PP for single bond breaking. We presented TD-CCSD some years ago as the simplest state universal, Hilbert space method for open-shell singlets and GVB examples. But even this simple method retains its two determinant reference form, making adding things like EOM on top of it different than in the normal SR case.

When SR-CC fails, it is usually because the single reference determinant prohibits correct separation, commonly like RHF references for closed shell molecules separating into open shell fragments. UHF fixes the incorrect separation, but likely by breaking symmetry. Some would say a better solution for this would be a GVB reference that can retain spin symmetry. But what is useful is a *single reference form* of the GVB solution that can be improved by adding higher orders of CC theory. This is where the pair coupled-cluster doubles method becomes useful. John Cullen recognized that if one modified a CCD program to only retain the pair double excitations like T2 ( $A\alpha, A\beta; I\alpha, I\beta$ ) (only  $N_{\text{occ}}N_{\text{virt}}$  in number) followed with an orbital optimization, then one would essentially have a GVB wavefunction in CC form. As GVB PP can correctly break a single bond, it manifests non-dynamic correlation. Consequently, adding dynamic correlation via higher-order CC to

such a fixed starting point offers a more quantitative description. We call this 'tailoring', where the essential dynamic correlation is described by additional terms in the CC like the rest of the T2's plus singles. This method is termed pCCD+TCCSD. Any such 'tailored' CC wavefunction can be used almost exactly like its untailored counterpart, to treat excited states with EOM, analytical gradients, density matrices, properties, etc.

In this talk we will discuss pCCD +TCCSD for excited states, looking at singly excited, doubly excited, and singlet-triplet separations for multi-reference biradical problems, and as a function of selected orbital choices, as pCCD is not orbitally invariant to even occ-occ or virt-virt rotations. pCCD+TCCSD benefits from tailoring with pCCD, though the other examples do not. We will show that only the last has important MR effects, enabling tailoring with pCCD to pay dividends, particularly with GVB orbitals.

- [1] M. Ravi, Y. C. Park, A. Perera, R. J. Bartlett, J. Chem. Phys., **156** (2022), 201102.
- [2] V. Rishi, M. Ravi, A. Perera, R. J. Bartlett, J. Phys. Chem. A, **127** (2023), 828-834.
- [3] M. Ravi, A. Perera, Y.C. Park, R. J. Bartlett, J. Chem. Phys., submitted.