Point to be made: Embedding VB-like ideas in MO-based MB theories

UGA-SS-MRCC (known in the literature as Mk-MRCC) Ansatz is

$$\Psi = \sum_{\mu} \{\exp(T_{\mu})\} \Phi_{\mu} C_{\mu}$$

where the normal order is defined with respect to a common closed shell vacuum, namely the core. The UGA-SSMRPT (MkMRPT) is the perturbative approximant to the UGA-SSMRCC

Using fragment optimized orbitals, even approximate ones, and using singles and doubles, we can compactify the wf.

Alternative view: Starting with orbitals which are adapted to fragment point group symmetry, avoiding spurious symmetry breaking.

Role of nonorthogonal valence orbitals to compactify the wavefunction and to ameliorate symmetry breaking: embedding VB ideas

Reflections on the VB-inspired MO-based MR Formalisms

Use of fragment localized orbitals for the supermolecule at medium-to-short distances. These sets are non-orthogonal in the two fragments, reminiscent of a VB description, but they are not optimized.

In order to use orthogonal orbitals for computational simplicity, we will Lowdin-orthogonalize them, and enforce GBT in disguise to improve the orbitals to localized CASSCF quality.

In order to avoid very many cluster operators, we use Thouless parametrization to simulate a compact set of mu-dependent nonorthogonal orbitals.

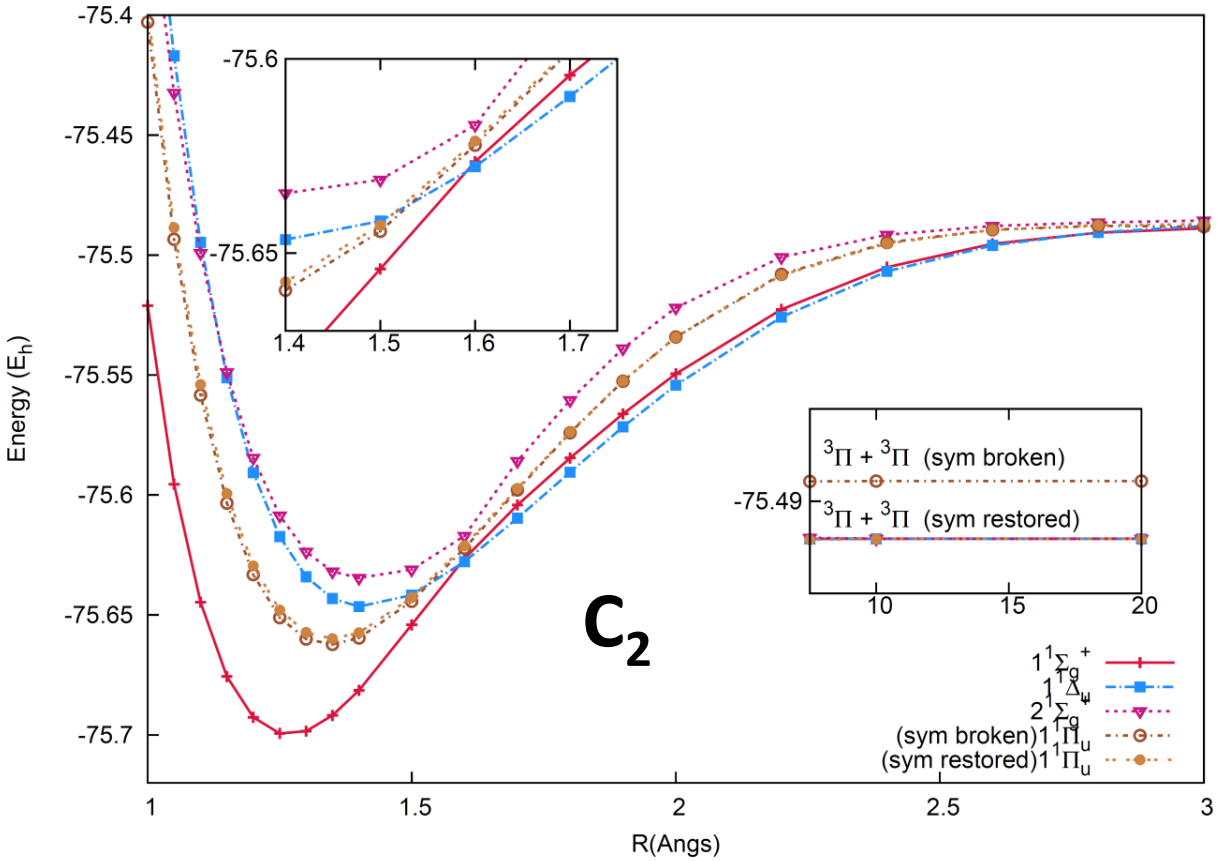
The Ansatz

$$\Psi = \sum_{\mu} \{\exp(T_{\mu})\} \Phi_{\mu} C_{\mu}$$

has enough flexibility to simulate non-orthogonality with orthogonal orbitals, and to relax them, depending on the CSF Φ_{μ} they are in. This is in the spirit of the breathing orbital description in the VB approach.

RCAMOS,
at IACS

RESULTS of UGA-SSMRPT2



PES of C_2 computed with CAS(8,8)/cc-pVDZ basis using UGA-SSMRPT2. The region of multiple curve crossing is focused in the inset.

	C Atom ^3P ^3P	C_2 molecule $X^1\Sigma_g^+, B^1\Delta_g, B'^1\Sigma_g^+, A^1\Pi_u$ $^3P + ^3P$
symmetry broken wave-function		
CASSCF	-37.7010866	-75.4021733
SCE		⋆
UGA-SSMRPT2	-37.7446730	-75.4893461
SCE		⋆
symmetry restored wave-function		
CASSCF	-37.6997393	-75.3994785
SCE		⋆
UGA-SSMRPT2	-37.7456144	-75.4912289
SCE		⋆

C_2 Molecule: Size-consistency check with cc-pVDZ basis set. Localized orbitals are used for UGASSMRPT2 computations.

⋆Below the convergence threshold (μE_h).