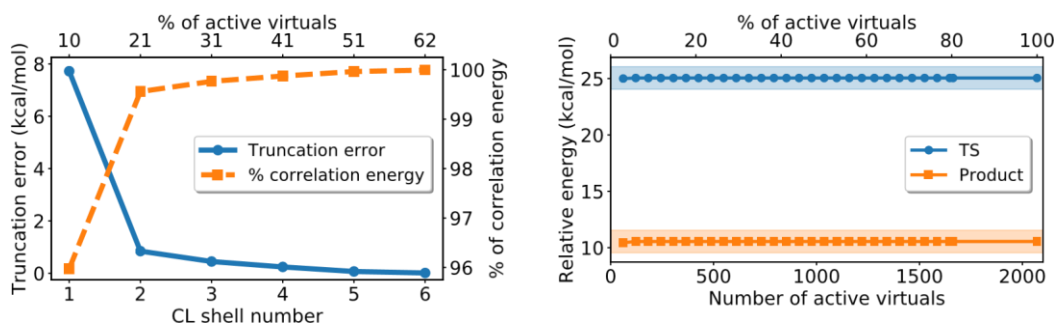


# Compact and optimal representation of embedded wave functions via concentric localization

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Despite well-known and exact theoretical frameworks, reliable quantum chemistry is often reserved to relatively small systems due to the computational burden that follows from increasing the system size. Wave function-in-density functional theory (WF-in-DFT) embedding has experienced great success in working around this limitation, whereby a local chemical domain is treated with some costly WF theory and embedded in a DFT potential from an environment comprised of the remainder of the molecular system. In particular, projection-based embedding[1] makes such a distinction in terms of the occupied orbital space, whereas the bottleneck in WF methods originates from the number of virtual orbitals. In other words, the expected advantages of embedding a WF that correlates fewer electrons can be easily overshadowed by the large number of virtual orbitals in the entire molecular system. This shortcoming is successfully overcome with our newly developed concentric localization (CL) scheme.[2] Projection of the virtual space onto the embedded subsystem provides a small, yet well-defined set of CL orbitals that can be used to start spanning the virtual space via recursive singular value decomposition of the Fock matrix. At each step, the CL orbitals are found spatially more distant from the embedded subsystem and provide consistently lower correlation energy recovery constituting a series that rapidly converges to the total embedded correlation energy, signaling a natural truncation and defining the embedded wave function's own choice of virtual space. Quantitative correlation energy recovery is achieved with two CL orbital shells, number which is found to be largely insensitive to the environment and atomic rearrangements resulting from the exploration of potential energy surfaces. As an illustration of the aptness of the CL approach, a remarkable 90% reduction of the virtual space is observed in the Menshutkin reaction inside a carbon nanotube, with deviations far below chemical accuracy.



Convergence of CL shells in 8-pentadecanone (left) and the energies of the TS (transition state) and Product relative to the Reactant in the Menshutkin reaction of  $\text{NH}_3$  and  $\text{CH}_3\text{Cl}$  inside a carbon nanotube (right). The shaded areas represent the chemical accuracy range around the reference energies.

## References

- [1] F. R. Manby, M. Stella, J. D. Goodpaster, and T. F. Miller. *J. Chem. Theory Comput.*, 8:2564, 2012.
- [2] D. Claudino and N. J. Mayhall. *J. Chem. Theory Comput.*, 15:6085, 2019.