

The Role of High-Order Electron Correlation Effects in a Model System for Non-valence Correlation-bound Anions

Shiv Upadhyay(1), Amanda Dumi(1), James Shee(2),
Kenneth D. Jordan(1)

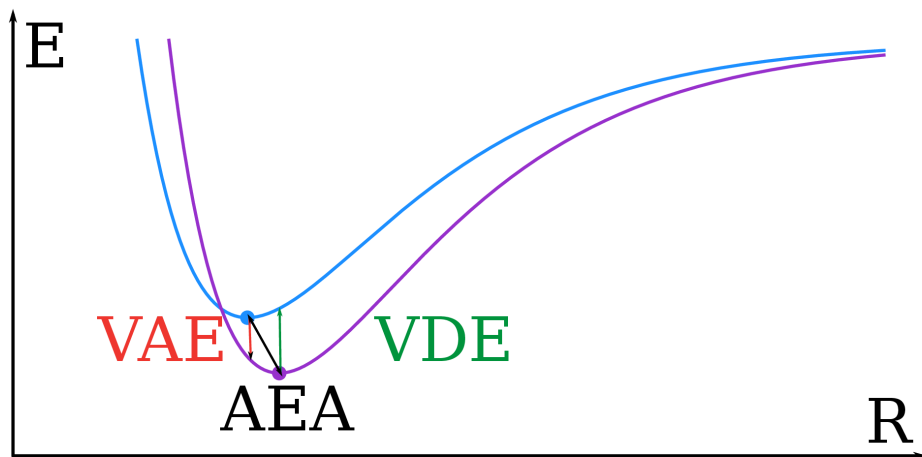
(1)Department of Chemistry, University of Pittsburgh, Pittsburgh,
Pennsylvania 15260,USA

(2)Department of Chemistry, University of California Berkeley,
Berkeley, California,94720, USA

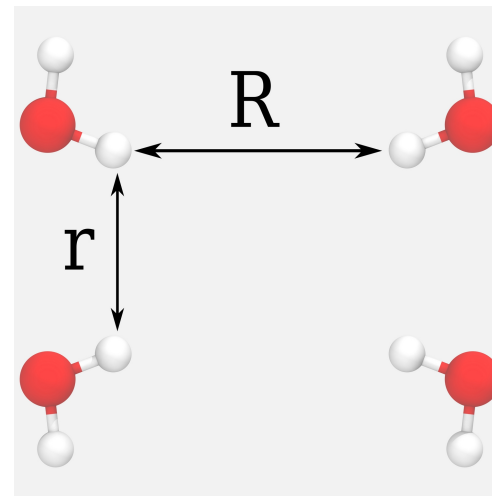
$\langle P|Q|I \rangle$



Nonvalence anions



(Fig 1.) A cartoon illustrating the binding energy of a fictitious anion system. It is important to note that the adiabatic binding energy becomes equal to the vertical attachment or detachment energy in the limit that the geometry change approaches zero.



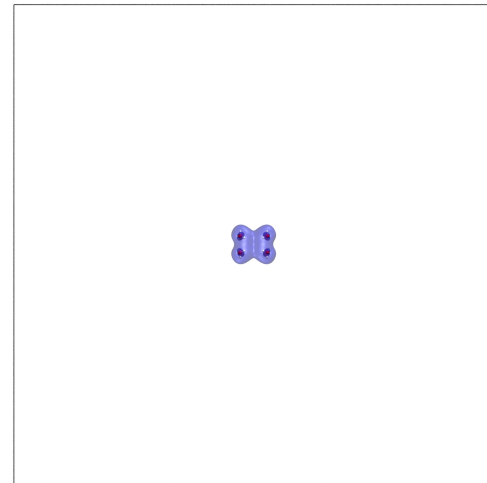
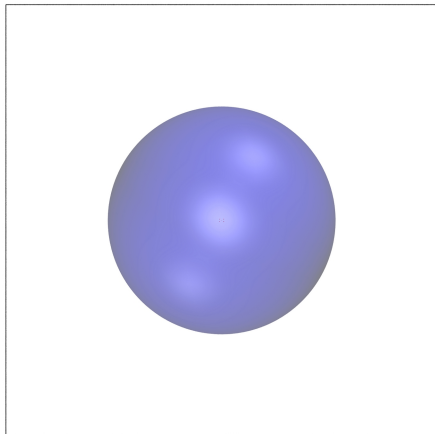
(Fig 2.) The $(H_2O)_4$ system used which can bind an excess electron in a diffuse (i.e. not valence) orbital, hence the term nonvalence anions.

Quantum Monte Carlo

$$\Psi(R', \tau') = \int_R G(R \rightarrow R', \Delta\tau) \Psi(R, \tau) \quad (1)$$

Embarassingly parallel, can be made extremely accurate due to controllable systematic error introduced by trial wave function

(Fig 2) Trial wavefunctions for the $(\text{H}_2\text{O})_4$ system calculated with Hartree-Fock, B3LYP, and EOM-CCSD respectively



Conclusion:

Method	EBE / meV
EOM-CCSD(T)(a)*	195.8
DMC	183 +/- 10
AFQMC	194 +/- 10

Key Point:

Quantum Monte Carlo of two flavors:
diffusion Monte Carlo (DMC)
and auxiliary field Monte Carlo (AFQMC)
can recover from an unphysical trial wave function!

DOI: 10.1063/5.0030942

