

# Auxiliary-field quantum Monte Carlo with a Gaussian basis—Applications to atoms and molecules

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We extend the recently introduced phaseless auxiliary-field quantum Monte Carlo (AF QMC) approach<sup>1</sup> to any single-particle basis, and apply it to molecular systems with Gaussian basis sets<sup>2</sup>. The AF QMC method obtains the many-body ground state by a stochastic average of independent-particle solutions in fluctuating external fields. The well-known sign/phase problem is controlled using the phaseless method by constraining the paths in the auxiliary-field space with a trial wave function from mean-field theory. Results on first-row and post-d systems will be presented. For equilibrium properties, the AF QMC total energies show typical systematic errors of no more than a few milli-Hartrees compared to exact results, which is roughly comparable to the accuracy of CCSD(T), coupled-cluster with single and double excitations plus an approximate treatment of triple excitations. For stretched bonds in H<sub>2</sub>O and N<sub>2</sub>, our method exhibits better overall accuracy and more uniform behavior than CCSD(T) in mapping the potential energy surface.

[1] S. Zhang and H. Krakauer, Phys. Rev. Lett. **90**, 136 401 (2003).

[2] W. A. Al-Saidi, S. Zhang, and H. Krakauer, J. Chem. Phys. **124**, 224101 (2006)

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