Towards Quantum Monte Carlo forces of heavier ions

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Computation of forces has been an essential challenge with continuum Quantum Monte Carlo methods for the past two decades. Reliable forces make for a central physical observable, but also an accurate and efficient means for relaxation of complicated atomic structures. The main challenges for QMC force estimators are their formally infinite variance and inclusion of explicit and implicit derivatives, the Pulay terms. Well-established techniques have been and are being developed to mitigate these problems. However, their nature and limitations have been largely unexplored, regarding heavier elements and the inevitable compromises of large-scale simulations.

Here we present how various systematic errors and statistical performances of QMC forces scale with the effective valence charge, Z_{eff} [1]. We use well-established, Pulay-corrected, zero-variance estimators for Variational and Diffusion Monte Carlo simulations [2], including a tail-regression estimator [3] to control the infinite variance problem. We compute QMC forces in selected dimers, including transition metal oxides, and discuss, e.g., consistency of the forces with experiments and the potential energy surface. Furthermore, we consider the intrinsic variances of the QMC forces and their scaling with Z_{eff}, enabling cost analysis and projections to larger applications.

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