Geometry Optimizations with Quantum Monte Carlo

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Computing excited states is highly demanding for electronic structure methods, which often struggle to ensure high accuracy. We will work in the alternative framework of quantum Monte Carlo methods which use stochastic algorithms to solve the Schrödinger equation, scale well with system size, and offer a balanced description of the ground and electronic excited states. In this work we are using the real-space methods variational (VMC) and diffusion Monte Carlo (DMC).
First, the analytical expression of the variational-drift approximation[1] for DMC has been implemented in CHAMP and its limitations and possibilities are explored. Second, a stochastic process with a stability property is utilized by subjecting two close trajectories to the same random noise which allows for the accurate calculation of forces with a low dependence on the trial wave function.[2] Finally, we will accelerate the computation of interatomic forces required to determine optimal structures and reaction pathways, by exploring existing and developing new improved estimators characterized by small fluctuations and reduced systematic error based on the zero-variance zero-bias principle[3] which allows to extend these properties to forces. The advantage are considerably shorter Monte Carlo simulations and equally accurate structures.

References

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