

# Optimization of VQMC trial wave functions using the Newton's method

Mosè Casalegno and Massimo Mella

*Dipartimento di Chimica Fisica e Elettrochimica, Universita' degli studi di Milano, Milano, Italy*

Xi Lin

*Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139*

Andrew M. Rappe

*Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323*

The quantum Monte Carlo method has been shown to be a powerful and flexible tool in analyzing the electronic states of atoms and molecules. The choice of the trial wave function represents a crucial issue for both variational quantum Monte Carlo (VQMC) and diffusion quantum Monte Carlo (DQMC) calculations, since it affects both the efficiency and the accuracy of the simulations. In order to obtain a high-quality wave function, an efficient and reliable optimization algorithm is needed. In recent years, fixed sample based algorithms have been widely used for variance minimization. Despite the impressive variational estimates achieved, variance-optimized wave functions lead to less accurate energies with respect to their energy-optimized counterparts. We show that the expectation value of the energy can be efficiently minimized by computing its first- and second-order derivatives and updating the set of variational parameters according to the Newton's method.

We present the results obtained by applying this technique to several atomic and molecular systems. For the first row-elements, ground state energies have been calculated and compared with those obtained by the variance minimization approach. We also extend the same approach to the diatomic molecules  $H_2$ ,  $LiH$  and  $Li_2$ . We optimize Jastrow correlation factors as well as Slater determinant parameters, in order to further lower the VQMC energy and improve the nodal surfaces. For each of these systems, we report ground state energies and other relevant properties. Finally, we discuss the ground state energies obtained by optimizing different basis sets and CPU timing estimates.