Variational principles in quantum Monte Carlo: the troubled story of variance minimization

Alice Cuzzocrea [a], Anthony Scemama[b], Saverio Moroni[c], Wim J. Briels[a] and Claudia Filippi [a]

[a] *MESA+ Institute for Nanotechnology, University of Twente,The Netherland*
[b] *Université Paul Sabatier Toulouse III, CNRS, UPS, France*
[c] *CNR-IOM DEMOCRITOS, Istituto Officina dei Materiali, and SISSA, Italy*

We investigate the use of different variational principles in quantum Monte Carlo, namely energy and variance minimization, prompted by the interest in the robust and accurate estimate of electronic excited states. We first focus on the computation of excitation energies in energy minimization and show how for cyanine dyes molecules of various size, with an appropriate choice of the wave function, we readily reach chemical accuracy with the best available references. For this systems, in which ground and excited states have different symmetry, we use energy minimization in a state-specific fashion. However, in Ref.[1], very positive results are also reported for state-average energy minimization in the case of states of the same symmetry. On the other hand, for variance minimization, where the use of suitable functionals is expected to target specific states regardless of their symmetry, we encounter severe problems: as the variance converges, the energy drifts away from that of the selected state. This unexpected behavior is sometimes observed even when the target state is the ground state, and generally prevents the robust estimate of total and excitation energies. We analyze this problem using a very simple wave function and infer that the optimization finds little or no barrier to escape from a local minimum or local plateau, eventually converging to the unique lowest-variance state instead of the target state. In conclusion, even if the loss of the state of interest can be delayed and possibly avoided by reducing the statistical error of the gradient, for the full optimization of realistic wave functions, variance minimization with current functionals appears to be an impractical route.

[1] A. Cuzzocrea, A. Scemama, W. J. Briels, S. Moroni, and C. Filippi, Journal of Chemical Theory and Computation 16, 4203 (2020).