Title of talk: Quantum Monte Carlo approach to the Full CI problem: recent progress.

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Abstract: The ground-state eigenvalue problem posed by the electronic Schrödinger equation can be cast as a stochastic process involving an annihilating population of positive and negative walkers that inhabit Slater determinant space [1]. The population of walkers evolve according to a simple set of rules (akin to a "game of life"), which are derived from the underlying imaginary-time Schrödinger equation, such that the long-time distribution of the walkers matches the exact ground-state eigenvector. We show that this algorithm has a remarkable emergence characteristic, akin to symmetry-breaking phase transitions in classical statistical mechanical systems.

The use of Slater determinants obviates the usual Fermion sign problem of diffusion Monte Carlo (namely the collapse onto Bosonic wavefunctions), but instead introduces a different sign problem associated the fact that the off-diagonal Hamiltonian matrix elements are both positive and negative. This sign problem however can be solved through a combination of walker annihilation and a "survival of the fittest" criterion [2] (the latter greatly reducing the dependence of the algorithm on walker annihilation).
The method provides a way to compute exact electronic energies within a specified N-electron basis set. We will give examples of the algorithm at work in real systems in sizeable basis sets, ranging from atomic ionization potentials and electron affinities, to dissociation energies of diatomic molecules. We discuss the scaling of the algorithm with the number of electrons and orbitals[3].

Finally, we will present some recent work on the calculation of (i) reduced density matrices, which potentially open the route to property calcualtions, and (ii) biased (or Importance) sampling to accelerate convergence of initiator and stochastic error.

[1] G.H. Booth, A.J.W. Thom and Ali Alavi, J. Chem. Phys., 131 , 054106, (2009). [2] Deidre Cleland, G.H. Booth, and Ali Alavi, J. Chem. Phys., 132 , 041103, (2010). [3] Deidre Cleland, George Booth, and Ali Alavi, J. Chem.
Phys., 134 , 024112, (2011)