Quantum Monte Carlo approach to the ground state eigenvalue problem of many-electron systems.

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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[3], dissociation energies of diatomic molecules[4], the uniform electron gas [5], and a first application to real solids[6].

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