

Optimal single-particle orbitals from energy fluctuations in correlated wavefunctions

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ABSTRACT

A quantum Monte Carlo method [J. Chem. Phys. **112**, 3523-31 (2000)] of determining Jastrow-Slater wavefunctions for which the energy is stationary with respect to variations in the single-particle orbitals is presented. A (non-local) potential is determined by a least-squares fitting of fluctuations in the energy with a linear combination of one-body operators. This potential is used in a self-consistent scheme for the orbitals in the determinant whose self-consistent solution ensures that the energy of the correlated many-body wavefunction is stationary with respect to variations in those orbitals. The method is feasible for atoms, molecules, and solids.