Trial wave-functions for Quantum Monte Carlo with numerically stable analytical gradients over exponential type orbitals.

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Abstract

Trial wave-functions used in Quantum Monte Carlo calculations are demonstrated to require the correct nuclear cusp and exponential decay. They also should possess the correct nodal structure of the molecular orbitals for the ground state system. These conditions are seen to be catered for by Sturmian basis functions.

The trial wave-function can advantageously include electron correlation, which is frequently implemented *a posteriori* using a Jastrow factor in the internuclear variable. The possibility of Sturmian geminal basis functions in this variable is briefly mentioned.

Graphic examples of electron density and its gradient will be shown including the chlorine atom and the water molecule in ETO basis sets readily available (Thakkar, ADF) and more extended examples. These are contrasted with results in a gaussian basis.

Keywords: Analytical Coulomb potential, Coulomb Sturmians, explicit correlation.