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Many-electron correlated exponential wavefunctions. A quantum Monte Carlo application to H_2 and He_2^+

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Abstract

We propose to expand the solution of the Schrödinger equation for an atomic or molecular system as a linear combination of many-electron explicitly correlated exponentials. A series of trial wavefunctions has been optimized, minimizing the variance of the local energy for H_2 and He_2^+ in their ground state at the equilibrium distance, and their variational energy has been computed using the variational Monte Carlo method. The He_2^+ wavefunctions have been used in a series of fixed node diffusion Monte Carlo simulations, showing that, using a small number of terms, one can obtain a good estimate of the exact energy.

1. Introduction

One of the central problems of quantum chemistry is the accurate description of electron correlation, through the development of methods that go beyond the simple Hartree–Fock picture. The most common way to include correlation into a wavefunction is to use a configuration interaction (CI) expansion: unfortunately this method has been found to be slowly convergent to the exact value. An alternative approach is the explicit inclusion of the interelectronic coordinates into an approximate wavefunction; this is an old method to build accurate solutions of the Schrödinger equation. Hylleraas [1] and James and Coolidge [2] showed how to obtain very good results for two electron systems by including in the wavefunction the interelectronic distance r_{12}. However, it is not easy to generalize these methods for systems with more than two electrons since the resulting integrals are difficult to evaluate. In 1960 Boys [3] and Singer [4] suggested using explicitly correlated Gaussian functions as this choice leads to tractable integrals in closed form [5]. More recently various researchers have shown that these explicitly correlated Gaussian functions can give accurate results on a variety of two [6], three [7] and four [8] electron systems, provided careful optimization of the nonlinear parameters is performed. Unfortunately this type of function poorly reproduces the cusp conditions [9], i.e. the behaviour of the wavefunction when two particles collide, and this has the unpleasant effect of slowing down the convergence. As a result, a large number of functions is needed to reach high accuracy, increasing the number of nonlinear parameters, and making their optimization a demanding task.

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