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Stability of few-body systems and Quantum Monte Carlo methods

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Abstract. Quantum Monte Carlo methods are well suited to study the stability of few-body systems. Their capabilities are illustrated by studying the critical stability of the Hydrogen molecular ion whose nuclei and electron interact through the Yukawa potential, and the stability of small Helium clusters.

1 Introduction

Mean field methods allow to investigate the stability of strongly bound systems at qualitative and even semi quantitative level. For weakly bound systems an accurate description of the particle correlation is crucial, usually by a Configuration Interaction expansion. A basis set of single particle functions allows an easy calculation of integrals, but unfortunately the convergence to the exact value is very slow. The explicit inclusion of the interparticle distances gave almost exact results for two electron systems [1] [2]. However these methods cannot be extended to systems with more than two electrons since the resulting integrals are extremely difficult or impossible to evaluate analytically and one has to turn to numerical methods.

In this paper we show that the various stochastic methods, developed in the last few decades, for their accuracy and flexibility are well suited to study the stability of few-body systems with arbitrary potential.

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2 Quantum Monte Carlo methods

2.1 Variational Monte Carlo

The variational Monte Carlo (VMC) method [3] can easily compute expectation values of any kind of trial wave function, since it requires only the evaluation of the wave function, its gradient, and its Laplacian. Since Monte Carlo methods are well described in the literature [3], we only summarize the main points and equations. If we define the local energy as

$$E_l(\boldsymbol{R}) = H\Psi_T(\boldsymbol{R})/\Psi_T(\boldsymbol{R}) \ , \tag{1}$$

we can compute the mean energy according to the variational principle as

$$\langle H \rangle = \frac{\int \Psi_T^2(\boldsymbol{R}) E_l(\boldsymbol{R})\, \mathrm{d}\boldsymbol{R}}{\int \Psi_T^2 \,\mathrm{d}\boldsymbol{R}} \approx \frac{1}{N}\sum_{i=1}^{N} E_l(\boldsymbol{R}_i) \ . \tag{2}$$

The N sampled configurations must be distributed according to $f = \Psi_T^2$ and this distribution can be obtained by using the original Metropolis algorithm [4] or by simulating the Fokker–Planck differential equation [3]

$$-\frac{\partial f(\boldsymbol{R},\tau)}{\partial \tau} = -\sum_i D_i \nabla_i^2 f(\boldsymbol{R},\tau) + \sum_i D_i \nabla_i \cdot f(\boldsymbol{R},\tau)\boldsymbol{F}_i(\boldsymbol{R}) \ , \tag{3}$$

where $\boldsymbol{F}_i(\boldsymbol{R}) = \nabla_i \ln[\Psi_T(\boldsymbol{R})^2]$ is called the quantum force and $D_i = 1/(2m_i)$ is the diffusion coefficient for a given particle. The simulation is realized using the Langevin equation

$$\boldsymbol{r}_i' = \boldsymbol{r}_i + D_i \tau \boldsymbol{F}_i(\boldsymbol{R}) + \boldsymbol{\chi} \ , \tag{4}$$

where $\boldsymbol{\chi}$ is a three-dimensional Gaussian random variable with zero mean and τ/m_i variance. This equation is used to select an attempted displacement for each particle, which is accepted with probability

$$P(\boldsymbol{R} \to \boldsymbol{R}') = \min\left[1, \frac{T(\boldsymbol{R}' \to \boldsymbol{R},\tau)\Psi_T(\boldsymbol{R}')^2}{T(\boldsymbol{R} \to \boldsymbol{R}',\tau)\Psi_T(\boldsymbol{R})^2}\right] \ , \tag{5}$$

where $T(\boldsymbol{R} \to \boldsymbol{R}',\tau)$ is the transition matrix for the particle to move from $\boldsymbol{R}$ to $\boldsymbol{R}'$. The transition matrix corresponding to the Langevin equation is

$$T(\boldsymbol{R} \to \boldsymbol{R}',\tau) = \prod_i \frac{1}{(4D_i\tau)^{3/2}} \exp\left(-\frac{[\boldsymbol{R}_i' - \boldsymbol{R}_i - D_i\tau\boldsymbol{F}_i(\boldsymbol{R})]^2}{4D_i\tau}\right) \ . \tag{6}$$

The optimization of the trial wave function by minimization of the variance of the local energy has been described by Umrigar et al. [5] and by Bressanini and Reynolds [6]. The mean energy value is an upper bound to the exact value and the quality of the result depends critically on the trial wave function.

2.2 Diffusion Monte Carlo

Exact results in principle can be obtained projecting out the exact ground-state of the time-independent Schrödinger equation, $\Phi_0(\boldsymbol{R})$, from any initial distribution $\Psi_T(\boldsymbol{R},0)$, not orthogonal to $\Phi_0(\boldsymbol{R})$, using the diffusion Monte Carlo (DMC) method. The time dependent Schrödinger equation in imaginary time

$$-\partial\Psi(\boldsymbol{R},\tau)/\partial\tau = (-D\nabla^2 + V)\Psi(\boldsymbol{R},\tau) \ , \tag{7}$$

may be viewed as a classical diffusion equation, along with a birth/death process that mimics a reaction exhibiting first-order kinetics. This interpretation requires the wave function, rather than its square, to be considered a probability density. While this presents no difficulties in the symmetric (boson) ground state, excited-state wave functions (including the fermion ground-state wave function) change sign as nodes are crossed and the classical analogy breaks down. Usually DMC simulations employ the technique of importance sampling [3]: a trial wave function $\Psi_T(\boldsymbol{R})$ is used to bias the random walk so as to sample a different probability distribution $f(\boldsymbol{R},\tau) = \Psi_T(\boldsymbol{R})\Psi(\boldsymbol{R},\tau)$, and the time-dependent Schrödinger equation (TDSE) in imaginary time takes the form

$$\frac{\partial f(\boldsymbol{R},\tau)}{\partial\tau} = \sum_i D_i\nabla_i^2 f(\boldsymbol{R},\tau) - \sum_i D_i\nabla_i \cdot f(\boldsymbol{R},\tau)\boldsymbol{F}_i(\boldsymbol{R}) - [E_R - E_l(\boldsymbol{R})]f(\boldsymbol{R},\tau) \ , \tag{8}$$

where the only difference with the Fokker–Planck equation, used in VMC, is the additional term $[E_R - E_l(\boldsymbol{R})]f(\boldsymbol{R},\tau)$.

For the diffusion analogy to hold in this case, it is necessary that $f(\boldsymbol{R},\tau)$ rather than $\Psi(\boldsymbol{R},\tau)$ remain positive definite. One way to project out the fermion ground state (or any other excited state) is to employ the fixed-node approximation, in which the nodes of $\Psi_T(\boldsymbol{R})$ are imposed as a boundary condition upon the evolving solution $\Psi(\boldsymbol{R},\tau)$. This boundary condition ensures that $f(\boldsymbol{R},\tau)$ is positive definite since $\Psi_T(\boldsymbol{R})$ and $\Psi(\boldsymbol{R},\tau)$ have the same sign for all $\boldsymbol{R}$. If the nodes of $\Psi_T(\boldsymbol{R})$ coincide with those of the exact wave function $\Phi_0(\boldsymbol{R})$, the fixed-node DMC energy will be exactly E_0 (i.e., there would be no inaccuracy).

The formal solution of the TDSE in imaginary time, written using the eigenfunctions Φ_i of the Hamiltonian, i.e.,

$$f(\boldsymbol{R},\tau) = \sum_i \Psi_T(\boldsymbol{R})\Phi_i(\boldsymbol{R}) \exp\left[-(E_i - E_R)\tau\right] \ , \tag{9}$$

shows that the only long time surviving contribution is due to the ground state. This can be used to estimate the energy by means of the mixed estimator

$$E = \frac{\int f(\boldsymbol{R},\infty)E_l(\boldsymbol{R})\,\mathrm{d}\boldsymbol{R}}{\int f(\boldsymbol{R},\infty)\,\mathrm{d}\boldsymbol{R}} \tag{10}$$

The trial wave function is used to guide the walk of the configurations in the space, to reduce the fluctuations of the population simulating the birth-death process described by the term $[E_R - E_l(\boldsymbol{R})]f(\boldsymbol{R},\tau)$ and to compute the energy value by means of the mixed estimator.

These methods were successfully used to compute the stability region of the system $(M^+m^+M^-m^-)$ as a function of the ratio M/m in three dimensions [7] and of the system $(M^+M^+m^-m^-)$ in two dimensions [8].

In the following we present two more examples of few-body systems whose stability prediction requires high quality results and we show that the stochastic methods meet this requirement.

3 Stability of H_2^+ with Yukawa potential

Screened potentials are widespread in many different areas of physics and chemistry, to approximate many-body interactions. One of the most important is the statically screened Coulomb potential, or Yukawa potential $Z\exp(-\lambda r)/r$, where $Z = q_1 q_2$, q_1 and q_2 being the charges of the interacting particles. This potential is quite often used to describe the shielding effects between charges due to thermal ionization in plasmas [9]. It is applied also in solid-state physics, mainly to describe electronic properties in metals [10].

Here we report the results of non-adiabatic diffusion Monte Carlo (DMC) calculations on the ground states of H and H_2^+, upon variation of the screening parameter λ. In particular we are interested in calculating the range of stability upon variation of λ from the unscreened case $\lambda = 0$ to large λ values, to evaluate the critical parameter λ_c beyond which a system is unbound.

The energies calculated by means of DMC simulations for various values of λ are shown in Table 1. The energy of H_2^+ is always below the energy of the H atom, and the H_2^+ critical parameter is greater than the one for H, since for $\lambda = 1.2$ H_2^+ is bound, while H is not. An estimate of the critical parameter for H_2^+ can be obtained by fitting the available data with a second degree polynomial, obtaining $\lambda_c(H_2^+) \approx 1.35$.

Table 1. Non-adiabatic ground-state energy of H_2^+, and H energy, in hartree

λ	$E(H_2^+)$	$E(H)$	λ	$E(H_2^+)$	$E(H)$
0.0	−0.597059(9)	−0.499727	1.25	−0.007104(37)	unbound
0.1	−0.503330(10)	−0.406789	1.27	−0.005358(48)	unbound
0.7	−0.135561(13)	−0.071678	1.29	−0.003779(30)	unbound
1.2	−0.012278(15)	unbound	1.305	−0.002745(47)	unbound
1.21	−0.011028(28)	unbound	1.32	−0.001706(43)	unbound
1.23	−0.009026(34)	unbound			

For $\lambda < \lambda_c(H)$ the hydrogen like atoms are stable, H plus H^+ give the relevant threshold, and this means that H_2^+ is stable against the dissociation:

$$H_2^+ \to H + H^+ \ . \tag{11}$$

For $\lambda_c(H) < \lambda < \lambda_c(H_2^+)$, the system is stable against the dissociation:

$$H_2^+ \to 2H^+ + e^- \ , \tag{12}$$

because in this range of values the hydrogen-like atom is not bound. A few interesting conclusions can be drawn from our results: since H_2^+ is stable even when H is not, H_2^+ can be considered as a prototype for a new class of Borromean systems [11], a three-body system with two of the two-body potentials attractive and one repulsive (an exploration of the stability domain of this class of systems could be an interesting development of this work). Moreover, if one compares the value of –0.000000103 hartree for the energy of the hydrogen-like system with $\lambda = 1.19$ as computed by Vrscay [12], with the energy value –0.012278(15) hartree of H_2^+ with $\lambda = 1.2$ shown in Table 1, it strikes that the total energy lowers by a factor of 10^5 when a proton is added to the hydrogen-like atom. Although it is hard to properly assess the different contributions to this effect that come from each part of the Hamiltonian operator, it appears strictly dependent on the simultaneous action of the two attractive contributions due to the interaction of the nuclei with the electron, since it is present also in Born–Oppenheimer calculations. It remains to be understood how much of this effect is due to the symmetry of the Hamiltonian itself, i.e., same mass for the positive particles and same screening constant λ in the potential, and how much the ground state energy might change upon variation of these physical parameters.

4 Stability of small mixed $^4\mathrm{He}_N{}^3\mathrm{He}_M$ clusters

In the past decade, QMC methods have been invaluable in providing a clear picture of highly quantum clusters of Hydrogen and Helium, both pure and doped with an impurity. Here we investigate the stability of $^4\mathrm{He}_N{}^3\mathrm{He}_M$ clusters. For the technical details, we refer to the literature [13, 14, 15]. The results are reported in Table 2.

Table 2. Energies, in cm^{-1}, of various $^4\mathrm{He}_N{}^3\mathrm{He}_M$.

N	$^4\mathrm{He}_N$	$^4\mathrm{He}_N{}^3\mathrm{He}$	$^4\mathrm{He}_N{}^3\mathrm{He}_2$	$^4\mathrm{He}_N{}^3\mathrm{He}_3$
1		unbound	unbound	unbound
2	–0.00089(1)	–0.00984(5)	–0.071(1)	unbound
3	–0.08784(7)	–0.2062(1)	–0.3973(8)	unbound
4	–0.3886(1)	–0.6326(2)	–0.9468(3)	?
5	–0.9015(3)	–1.2626(4)	–1.529(2)	?

All the $^4\mathrm{He}_N$ clusters are bound, for any N. As to the mixed $^3\mathrm{He}$ and $^4\mathrm{He}$ clusters, we did not find any sign of existence of the hypothetical dimers $^4\mathrm{He}^3\mathrm{He}$ and $^3\mathrm{He}^3\mathrm{He}$, and there is a general consensus that they should be unbound. In general, the substitution of a single $^4\mathrm{He}$ atom in a pure cluster with a $^3\mathrm{He}$ atom leads to an energetic destabilization. In fact the trimer $^4\mathrm{He}_2{}^3\mathrm{He}$ is a stable entity, but its energy is one order of magnitude smaller than the pure $^4\mathrm{He}_3$. For $^4\mathrm{He}^3\mathrm{He}_2$ DMC simulations show all the constituent particles to go away from each other and the system is unbound (although the possibility of borromean binding could not be excluded a-priori). Even if the trimer $^4\mathrm{He}_2{}^3\mathrm{He}$ is very weakly bound, it is possible to add a second $^3\mathrm{He}$ atom and form the stable species $^4\mathrm{He}_2{}^3\mathrm{He}_2$. The clusters $^4He_N{}^3He_2$ are as easy to simulate as the systems including only bosons, because the space part of the ground state wave function is positive, since for two fermions in a singlet state the antisymmetry of the wave function is guaranteed by the spin function. We were able to optimize a trial wave function for $^4He_2{}^3He_2$ with a VMC energy of -0.0595(1) cm^{-1} and a DMC energy of –0.071(1) cm^{-1}. This tetramer has the odd feature of having five out of six unbound pairs. Our simulations show that starting from $^4He_2{}^3He_2$ all the clusters with two fermionic Helium atoms in their singlet state are stable species.

The addition of a third ^3He introduces a node in the ground state wave function that destabilizes the system with respect to its bosonic counterpart. It is not known, at present, what is the minimum number of ^4He atoms able to bind three ^3He atoms. Our preliminary results show that $^4He_3{}^3He_3$ is not bound. $^3He_{35}$ is bound [16], although it is still not yet proved whether this is the smallest stable ^3He cluster. This means that $^4He_{32}{}^3He_3$ is surely bound, and sets an upper bound to the critical value N for which $^4He_N{}^3He_3$ is critically stable.

5 Conclusions

The quantum Monte Carlo methods are well suited to study the critical stability of small few-body systems owing to their very high accuracy. Their flexibility makes easy the study of a large variety of systems. Using these methods we investigated the stability of the H_2^+ molecule with the Yukawa Coulomb screened potential, and the stability of small $^4He_N{}^3He_M$ clusters.

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