Few-Body Systems 34, 131–135 (2004)
DOI 10.1007/s00601-004-0022-x

Few-Body Systems
Printed in Austria

Stability of $^3He_2{}^4He_M$ and $^3He_3{}^4He_M$ $L = 0, 1$ Clusters*

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Received October 17, 2003; accepted November 4, 2003
Published online May 24, 2004;

Abstract. We have studied the stability of mixed ^{3}He/^{4}He clusters in $L = 0$ and $L = 1$ states by the diffusion Monte Carlo method, employing the Tang-Toennies-Yiu (TTY) He-He potential. The clusters $^3He^4He_M$ ($L = 0$, $S = \frac{1}{2}$) and $^3He_2{}^4He_M$ ($L = 0$, $S = 0$) are stable for $M > 1$, while to bind two ^{3}He in a triplet state the minimum number of ^{4}He is four. Considering clusters with three ^{3}He, $^3He_3{}^4He_4$ is the smallest stable system in the $L = 1$ state, while $^3He_3{}^4He_8$ is the smallest stable system in the $L = 0$ state.

1 Introduction

In recent years a growing number of experimentalists and theoreticians have studied helium clusters and droplets, both pure and doped with an impurity. The combination of the extremely weak interaction between helium atoms and the small atomic masses makes helium clusters very weakly bound and by far the most intriguing van der Waals clusters with high quantum features. Initial investigations were devoted to pure ^{4}He clusters and droplets [1, 2]. More recently, however, a growing number of studies have focused on pure ^{3}He clusters and droplets [3, 4] and also on mixed clusters [5, 6]. The helium-helium interaction potential does not distinguish between the two isotopic species, the fermion ^{3}He and the boson ^{4}He, and this allows one to study effects entirely due to the zero-point motion of the species and to the different obeying statistics. The most interesting feature of these clusters is with no doubt the possibility to attain a superfluid state with a relatively small number of ^{4}He atoms [7]. The superfluidity and the low temperature of

* Article based on the presentation by D. Bressanini at the Third Workshop on the Dynamics and Structure of Critically Stable Quantum Few-Body Systems, Trento, Italy, September 2003

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helium clusters can be fruitfully exploited to perform high-resolution spectroscopy on impurities and to study molecular reaction dynamics of chemical reactions.

2 Stability of Pure and Mixed Clusters

In the past decade, quantum Monte Carlo (QMC) methods have been invaluable in providing a clear picture of helium clusters, both pure and doped with an impurity. Here we use QMC methods to investigate the stability of $^3He_N{}^4He_M$ clusters. For the technical details, we refer to the literature [8].

It is known that all ^{4}He clusters, starting from the dimer, are bound. On the other hand the minimum number of ^{4}He atoms necessary to form a stable cluster is not yet known. In an early investigation, Pandharipande et al. [9] found that eight ^{3}He atoms would form a bound state if they were bosons, despite the lighter mass, and eight ^{4}He atoms would be bound even if they were fermions, but eight ^{3}He fermions do not form a bound state. Their variational Monte Carlo (VMC) calculations indicated that systems with more than $N = 40$ ^{3}He are bound, while $N = 20$ atoms are unable to ensure the binding. Recently this bound has been greatly improved by Guardiola and Navarro [3] who established at $N = 35$ a stricter upper bound to the minimum number of ^{3}He atoms needed to form a stable cluster. This cluster might be seen as the largest Borromean system [10] since all 2-, 3-, and $(N-1)$-body subsystems are unbound.

On the experimental side, Schöllkopf and Toennies [11] introduced the diffraction techniques from a transmission grating to study small clusters, that allowed the detection of the helium dimer [11, 12] and trimer [13, 14]. However, the current experiments are not yet able to investigate the problem of the critical size of ^{3}He clusters as they cannot be built adding ^{3}He atoms one by one starting from the dimer.

Much less is known on the mixed $^3He_N{}^4He_M$ clusters. The stability of the clusters $^3He^4He_M$ for $M > 1$ was predicted by Bressanini et al. [15] by diffusion Monte Carlo (DMC) simulations and later shown experimentally [16]. As to the stability of a cluster containing two ^{3}He in a singlet state, the system $^3He_2{}^4He$ is unstable, while the trimer $^3He^4He_2$ is very weakly bound with a total energy an order of magnitude smaller than the pure trimer $^4He_3$. Nevertheless it is possible to add a second ^{3}He atom and form the stable species $^3He_2{}^4He_2$ with the odd feature of having five out of six unbound pairs. That prediction has been recently verified experimentally [16]. Adding more ^{4}He atoms to this cluster further increases its stability [17]. A first attempt to study mixed clusters with three or more ^{3}He has been recently published by Guardiola and Navarro [18, 19]. They computed, using VMC, the minimum number of ^{3}He atoms that can bind to a given number of ^{4}He atoms. Bressanini and Morosi [17], studying the $^3He_3{}^4He_M$ cluster with the constraint $L = 0$, found that $M = 9$ was the minimum number of bosons able to bind the cluster. Guardiola and Navarro [20] have recently reinvestigated at DMC level the minimum number of ^{3}He atoms that can form stable mixed clusters with up to eight ^{4}He.

The stability of pure ^3He_N and mixed $^3He_N{}^4He_M$ clusters is a delicate balance between the fermionic nature of the ^{3}He, requiring an antisymmetric wave function, the weakly attractive He-He potential, and the kinetic energy effects due to the

lighter mass of the fermionic isotope. The simulation of the ground state of $^3He^4He_M$ and $^3He_2{}^4He_M$ poses no particular problems to DMC [7]: The wave function is positive everywhere, even when there are two fermionic atoms forming a singlet state. This is sufficient to ensure that the DMC method is able to compute the exact energy, within the statistical error. However, the addition of further ^{3}He atoms introduces a node in the ground-state wave function. The same happens to excited states of systems with less than three ^{3}He. In these cases, the DMC energy is exact only if the nodal surface is exact, otherwise DMC simulations give an upper bound to the exact energy. Past experience with electronic systems nevertheless suggests that using approximate nodes from approximate trial wave functions can lead to very good energies.

In this paper we continue our exploration of the stability diagram of mixed clusters, studying states with different total angular momentum and spin symmetry. We approximate the wave function of the cluster $^3He_N{}^4He_M$ with the product form

$$\Psi_{\mathrm{T}}(\boldsymbol{R}) = L(\boldsymbol{R})\,\phi_{\mathrm{BB}}(\boldsymbol{R})\,\phi_{\mathrm{BF}}(\boldsymbol{R})\,\phi_{\mathrm{FF}}(\boldsymbol{R}), \tag{1}$$

where the subscripts B and F indicate Boson and Fermion, respectively. When there is only a single fermionic atom, ϕ_{FF} is missing. Each many-body wave function ϕ is written as product of the two-body functions [21]

$$f(r) = \exp\left(-\frac{p_5}{r^5} - \frac{p_2}{r^2} - p_0 \ln r - p_1 r\right). \tag{2}$$

This two-body function has been widely used in helium clusters simulations by QMC methods [2, 21, 22] and has proved to give accurate results. The parameters of the pair functions for ^{4}He-^{4}He are all the same, implying that the corresponding ϕ_{BB} is symmetric, and the same is true for ϕ_{BF} and ϕ_{FF}. The function $L(\boldsymbol{R})$, usually a polynomial of the coordinates of the atoms, is used to impose the desired total angular momentum and spin symmetry, that is it has the task to introduce a nodal surface into the trial wave function. Such a trial function, when used in a DMC simulation within the fixed-node approximation, gives an upper bound to the exact energy. The accuracy of the results depends on the quality of the nodes of the trial wave function. For few-electron atomic and molecular systems the computed energies are very accurate and we expect this to be true also for small clusters.

The simulations have been performed using the DMC method [8], with 5000 walkers and a time step of 50 hartree^{-1}. The trial wave functions have been optimized minimizing the absolute deviation of the local energy [23], a procedure that we found numerically more robust than the usually adopted variance minimization [24]. The energies for the systems $^3He_N{}^4He_M$ are reported in Table 1. For $N = 0$, 1, and 2, the only error present is the time-step bias, which we checked to be of the same order of magnitude of the statistical uncertainty, and so the extrapolation to zero time step should not modify the conclusions of this work. For $N = 3$ an additional error, due to the approximate nodal surface of the trial wave function, is present, so our results are an upper bound of the exact energies. However, as discussed above, we expect these energies to be very close to the exact values.

As mentioned previously, the ground state of $^3He_2{}^4He_M$ has $L = 0$ and $S = 0$. In superfluid liquid ^{3}He, helium atoms form Cooper pairs exhibiting spin-triplet p-wave pairing. So it is interesting to investigate this kind of pairing in mixed

Table 1. Energies, in cm^{-1}, of $^3He_N{}^4He_M$ clusters in various (L, S) states with angular momentum $L = 0, 1$ and spin S

M	$N=0$	$N=1$	$N=2$		$N=3$	
			$(0,0)$	$(1,1)$	$\left(0,\frac{1}{2}\right)$	$\left(1,\frac{1}{2}\right)$
2	−0.00089(1)	−0.00984(5)	−0.0693(6)	–	–	–
3	−0.08784(7)	−0.2062(2)	−0.3986(5)	–	–	–
4	−0.3881(3)	−0.6332(5)	−0.9473(4)	−0.6472(3)	–	−1.0173(7)
5	−0.9031(6)	−1.2638(7)	−1.687(1)	−1.3680(8)	–	−1.849(1)
6	−1.6078(4)	−2.0709(4)	−2.597(1)	−2.269(1)	–	−2.844(1)
7	−2.4799(8)	−3.034(1)	−3.640(1)	−3.324(1)	–	−3.981(2)
8	−3.499(1)	−4.138(2)	−4.819(1)	−4.511(1)	−4.828(3)	−5.242(1)
9	−4.641(1)	−5.361(2)	−6.112(2)	−5.812(1)	−6.176(2)	−6.607(1)
10	−5.915(2)	−6.690(3)	−7.511(2)	−7.216(1)	−7.653(3)	−8.076(1)
17	−17.234(2)	−18.347(2)	−19.47(2)	−19.253(5)	−20.045(4)	−20.389(7)

helium clusters. If we consider the simple qualitative model where fermionic atoms move in an effective potential generated by the ^{4}He cluster, and make the further assumption that the energy levels follow approximately those of a three-dimensional harmonic oscillator, then it is easy to see that the first excited state of $^3He_2{}^4He_M$, if it exists, will have $L = 1$ and $S = 1$. In order to check this prediction, we fixed the spin-state symmetry of our trial wave function by using $L(\boldsymbol{R}) = \boldsymbol{x}_2 - \boldsymbol{x}_1$, where 1 and 2 refer to the ^{3}He atoms. Results for increasing M are shown in Table 1. From our calculations, a cluster of four ^{4}He is sufficient to support an excited state of the two ^{3}He in an $L = 1$ and $S = 1$ state. Note that $^3He_2{}^4He_4$ $(L = 1, S = 1)$ obviously has higher energy than the ground state $^3He_2{}^4He_4$ $(L = 0, S = 0)$, but it has a slightly lower energy than the $^3He^4He_4$ ground state, so it is stable against the loss of a helium atom.

Guardiola and Navarro [18] found, using VMC, that four ^{4}He are sufficient to bind three ^{3}He in an $L = 1$ state. This result is not surprising in the light of our findings about the stability of the $^3He_2{}^4He_4$ $(L = 1, S = 1)$, which in the three-dimensional harmonic oscillator model corresponds to the configuration $1s\,1p$. In fact the addition of a third ^{3}He of opposite spin would simply doubly occupy the $1s$ level, with a further increase of the binding energy. However, the VMC results were not fully converged, and the possibility that a lower number of ^{4}He atoms would be sufficient to bind three ^{3}He was left open. Here we study the $^3He_3{}^4He_M$ $\left(L = 1, S = \frac{1}{2}\right)$ at the DMC level, in order to definitively resolve the matter. As shown in Table 1, indeed, the smallest stable cluster is $^3He_3{}^4He_4$, a result that might be inferred from recent experimental data [16]. For $^3He_3{}^4He_M$ clusters we recomputed the $L = 0$ states with a smaller time step than in our previous work [17], in order to reduce the time step bias. This time we were able to form a stable cluster with $L = 0$ with eight ^{4}He atoms, a result that we attribute to the reduced time step bias and to a better optimized trial wave function. The differences of the energies of the states of the clusters including two fermions are fairly constant, and the same is true for clusters including three fermions, even if the variations are slightly larger. These results suggest that the simple 3D harmonic oscillator model gives

the correct description, at least for the lowest states. The $L = 0$ states, corresponding to a $1s^2\,2s$ configuration, are higher in energy than $L = 1$ states with $1s^2\,1p$ configuration, as expected from the model.

Acknowledgement. This work was supported by Italian MIUR Grant No. MM03265212.

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