Stability of $^3He_2{}^4He_N$ and $^3He_3{}^4He_N$ $L = 0$ Clusters

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We have studied the stability of mixed $^3He/^4He$ clusters in $L = 0$ states by the diffusion Monte Carlo method, employing the Tang-Toennies-Yiu He-He potential. The clusters $^3He^4He_N$ and $^3He_2{}^4He_N$ are stable for $N > 1$. The lighter atoms tend to move to the surface of the cluster. The minimum number of ^4He atoms able to bind three ^3He atoms in a $L = 0$ state is nine. Two of three fermionic helium atoms stay on the surface, while the third one penetrates into the cluster.

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In recent years weakly bound helium clusters and droplets have attracted the attention of a growing number of experimentalists and theoreticians. 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 highly quantum features. The helium-helium interaction potential does not distinguish between the two isotopic species, the fermion ^3He and the boson ^4He, 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 ^4He atoms [1]. The superfluidity and the low temperature of helium clusters can be fruitfully exploited to perform high-resolution spectroscopy on impurities and to study the chemical reaction dynamics of species absorbed into the clusters.

Initial investigations were devoted to pure ^4He clusters and droplets [2]. More recently, however, a growing number of studies have focused on pure ^3He clusters and droplets [3–6]. While all ^4He clusters, starting from the dimer, are bound, it is not yet known what is the minimum number of ^3He atoms necessary to form a stable cluster. In an early investigation, Pandharipande *et al.* [7] found that eight ^3He atoms would form a bound state if they were bosons, despite the lighter mass, and eight ^4He atoms would be bound even if they were fermions, but eight ^3He fermions do not form a bound state. Their variational Monte Carlo (VMC) calculations indicated that systems with more than 40 ^3He are bound, while 20 atoms are unable to ensure the binding. Recently this bound has been greatly improved by Guardiola and Navarro [3] who established at 35 a stricter upper bound to the minimum number of ^3He atoms needed to form a stable cluster. On the experimental side, Schöllkopf and Toennies [8] introduced the diffraction techniques from a transmission grating to study small clusters that allowed the detection of the helium dimer [8,9] and trimer [10,11]; however, the current experiments are not yet able to investigate the problem of the critical size of ^3He clusters. The information on the mixed $^3He/^4He$ systems is even poorer. The stability of the clusters $^3He^4He_N$ for $N > 1$ was predicted by Bressanini *et al.* [12] and later shown experimentally [13]. In the same paper, Bressanini *et al.* examined the stability of a cluster containing two ^3He. They showed that 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 ^3He atom and form the stable species $^3He_2{}^4He_2$ with the odd feature of having five out of six unbound pairs.

The stability of pure ^3He_M and mixed $^3He_M{}^4He_N$ clusters is a delicate balance between the fermionic nature of the ^3He that introduces nodes in the ground state wave function, the weakly attractive He-He potential, and the kinetic energy effects due to the lighter mass of the fermionic isotope. A first attempt to study mixed clusters with more than three ^3He has been recently published by Guardiola and Navarro [14]. They studied small mixed $^3He/^4He$ clusters keeping fixed the number of bosonic atoms to 2, 3, 4, and 8, and increasing the number of ^3He to investigate the stability of the clusters. They found that a single ^4He cannot bind less than 20 ^3He, two ^4He can bind 18 or more ^3He, three ^4He form a metastable cluster with 3,4,5,9 ^3He, while the only unbound cluster with four ^4He is the one with nine ^3He. These interesting results, however, are preliminary and need to be confirmed, due to the incomplete convergence of their calculations. The exploration of the stability diagram of $^3He_M{}^4He_N$ is just at the beginning and very complicated, due to the fact that for each cluster it is not even known what are the preferred spin multiplicity and angular momentum.

The simulation of the ground state of $^3He^4He_N$ and $^3He_2{}^4He_N$ poses no particular problems to diffusion Monte Carlo (DMC) [15]: 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. The addition of further ^3He atoms, however, introduces a node in the ground state wave function. 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 preliminary work, we explore the stability diagram in a different way than Guardiola and Navarro [14]: they kept fixed the number of bosons and increased the number of fermions, while we ask ourselves what is the minimum number of ^{4}He atoms able to bind three ^{3}He atoms fixing the angular momentum to $L = 0$ and the spin momentum to $S = 1/2$. The constraint $L = 0$ allows us to write the trial wave function as a function of the interparticle distances only and to avoid the problem of the center of mass separation. If a cluster is bound, more stable states with higher L can stress only its stability. Furthermore, we use the Tang-Toennies-Yiu (TTY) potential [16] instead of the HFD-B(HE) potential [17], as in better agreement with the most accurate calculated values [18].

We approximate the wave function of the cluster $^3\mathrm{He}_M{}^4\mathrm{He}_N$ with the product form

$$\Psi_T(\mathbf{R}) = \phi_{BB}\phi_{BF}\phi_{FF}. \quad (1)$$

The subscripts B and F stand for 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 a product of the two-body functions [19]

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

This two-body wave function has been widely used in helium clusters simulations by quantum Monte Carlo methods [2,19,20] and has proved to give accurate results. ϕ_{FF} includes an antisymmetrizer operator chosen to generate a pure doublet state. While 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}), the ^{3}He-^{3}He pair functions are all different, in order to have a non-null antisymmetrized product. The explicit action of the antisymmetrizer on the product of these pair functions generates the node. 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. To our knowledge, there have been no systematic studies on the quality of the nodes of the trial wave functions for fermionic clusters.

$\Psi_T(\mathbf{R})$ has a pure space-spin symmetry, and represents a doublet state with $L = 0$ angular momentum. States with higher angular momentum and different spin multiplicity will be the subject of a future exploration of the stability diagram.

TABLE I. Energies (cm^{-1}) of the clusters $^3\mathrm{He}_N{}^4\mathrm{He}_M$ in $L = 0$ states.

M	$N = 0$	$N = 1$	$N = 2$	$N = 3$
8	−3.493(1)	−4.133(1)	−4.813(1)	Unbound
9	−4.633(1)	−5.352(5)	−6.102(1)	−6.168(3)
10	−5.897(2)	−6.675(2)	−7.500(2)	−7.644(3)
12	−8.743(2)	−9.632(1)	−10.553(2)	−10.833(2)
14	−11.932(3)	−12.915(5)	−13.925(5)	−14.339(5)
17	−17.233(6)	−18.329(3)	−19.483(3)	−20.036(6)

The simulations have been performed using the diffusion Monte Carlo [15] method, with 5000 walkers and a time step of 100 hartree^{-1}. The trial wave functions have been optimized minimizing the absolute deviation of the local energy [21], a procedure we found numerically more robust than the usually adopted variance minimization [22]. In Table I we report the energies for the systems $^3\mathrm{He}_N{}^4\mathrm{He}_M$ for $N = 0$, 1, 2, 3, and M up to 17. For $N = 0$, 1, and 2, the only error present is the time step bias, which we checked is of the same order of magnitude of the statistical uncertainty, and so it 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.

Our simulations confirm that the systems $^3\mathrm{He}{}^4\mathrm{He}_N$ for $N > 1$ are stable [12]. The stability is not spoiled by the addition of a second ^{3}He atom. As to the $^3\mathrm{He}_2{}^4\mathrm{He}_N$ structure, in Fig. 1 we report the radial distribution functions of ^{4}He and ^{3}He with respect to the center of mass of the system. The plot is for $N = 10$, but the features of the plot are the same for all the explored values of N.

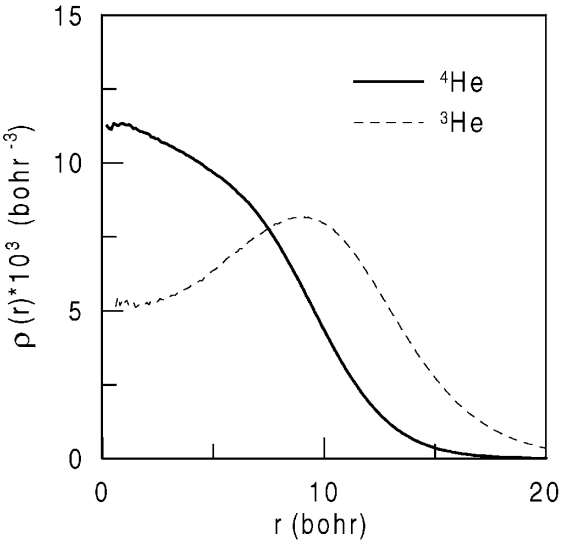

FIG. 1. Radial distribution functions of ^{3}He and ^{4}He in $^3\mathrm{He}_2{}^4\mathrm{He}_{10}$ with respect to the center of mass.

The lighter ^{3}He atoms tend to stay on the surface of the cluster, although they are free to penetrate into the cluster core. The addition of the third ^{3}He destabilizes the system, and we found that nine bosonic atoms are necessary to bind three fermionic atoms in a $L = 0$ state. We have not been able to perform a stable simulation with eight or less bosons. In these cases, the simulations ended with a fermionic atom leaving the cluster. This result is supported also by the observation that the energy gap between $^3He_2{}^4He_N$ and $^3He_3{}^4He_N$ progressively decreases upon reducing N and is nearly zero for $N = 9$. As to the structure of these clusters, we present in Fig. 2 the radial distribution functions with respect to the center of mass for $^3He_3{}^4He_{10}$. Given our choice to simulate a doublet state, we assigned, as usual in DMC simulations, spin labels to the fermionic atoms. We plot separately the two distributions of the two α ^{3}He to gain more insight; however, only the average of the two has physical meaning. Figure 2 reveals that the third fermionic impurity is pushed inside the cluster, while the other two stay on the surface and move farther out with respect to the situation in $^3He_2{}^4He_{10}$.

This is rather unexpected, in the light of the results of the systems with one or two ^{3}He. This outcome, however, can be rationalized by looking at the nodal structure of the system: it is not difficult to see that ϕ_{FF} is zero whenever the two α-spin ^{3}He are at the same distance from the β-spin ^{3}He. For this reason, the three ^{3}He atoms are not free to move on the surface of the ^{4}He cluster, and one of the two α-spin ^{3}He is pushed inside the boson cluster, in order to stay away from the nodal surface.

Although closely related, the interesting study recently published by Guardiola and Navarro [14] cannot be directly compared with ours since they used the HFD-B(HE) potential [17] instead of the slightly less binding TTY one [16] we employed. A comparison of the binding properties of these two potentials was performed by Lewerenz [20]. Furthermore, Guardiola and Navarro fixed the angular momentum to the one predicted by the harmonic oscillator shell model. They studied small mixed ^{3}He/^{4}He clusters keeping fixed the number of bosonic atoms to 2, 3, 4, and 8, and increased the number of ^{3}He to investigate the stability of the cluster. They found that the cluster $^3He_3{}^4He_4$ with $L = 1$ is stable, having a lower energy than $^3He_2{}^4He_4$. We note, however, that their calculations are not converged. This can be evidenced by comparing the literature numbers on $^4He_4$ and $^4He_8$: in a previous paper Guardiola, Portesi, and Navarro [23] obtained lower energies than in the most recent one (see Table II), while Lewerenz [20], with the same potential and using DMC, obtained even lower estimates of the exact energies.

A similar case happens for the $^4He_8$ system. Since the difference between the exact DMC result and VMC for the pure ^{4}He cluster is of the same order of magnitude of the difference between the $^3He_2{}^4He_N$ and $^3He_3{}^4He_N$ systems, a more thorough investigation is needed before a definitive conclusion can be reached.

In order to further check the convergence of their calculations, we simulated the $^3He_2{}^4He_4$ and $^3He_2{}^4He_8$ clusters by the diffusion Monte Carlo method and the HFD-B(HE) potential. The ground state wave function of these systems is positive everywhere, so the DMC method is able to give a statistically exact ground state energy. For $^3He_2{}^4He_4$ we obtain $-0.978(1)$ cm^{-1}, an energy lower than Guardiola and Navarro, but even lower than their value for $^3He_3{}^4He_4$, so it is no longer possible to conclude that this system is stable, since its energy is above the exact $^3He_2{}^4He_4$. We reach the same conclusions for $^3He_2{}^4He_8$, with an exact energy of $-4.918(1)$ cm^{-1}, below both the energy they obtained for $^3He_2{}^4He_8$ and $^3He_3{}^4He_8$. The conclusion is that it is certainly possible that $^3He_3{}^4He_4$ and $^3He_3{}^4He_8$, with $L = 1$, are stable species, but more calculations are necessary to

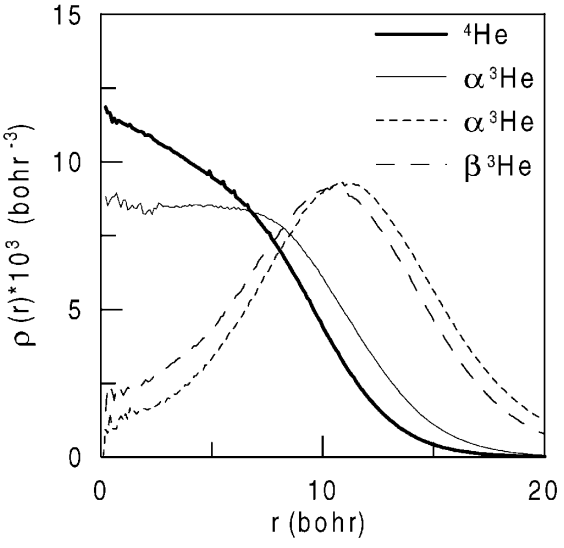

FIG. 2. Radial distribution functions of ^{3}He and ^{4}He in $^3He_3{}^4He_{10}$ with respect to the center of mass. For the two α spin ^{3}He distributions see the text.

TABLE II. Comparison with previous results. Energies in cm^{-1}.

^{3}He	^{4}He	VMC [14]	VMC [23]	DMC
0	4	$-0.371(1)$	$-0.388(4)$	$-0.4012(5)$ [20]
1	4	$-0.614(1)$		
2	4	$-0.925(1)$		$-0.978(1)$[a]
3	4	$-0.956(2)$		
0	8	$-3.351(4)$	$-3.496(7)$	$-3.568(2)$ [20]
1	8	$-3.927(5)$		
2	8	$-4.542(6)$		$-4.918(1)$[a]
3	8	$-4.879(9)$		

[a]Present work.

substantiate this statement. In order to resolve the matter, we are in the process, as a natural following of the present work, to apply DMC to $L = 1$ states of mixed ^{3}He/^{4}He clusters.

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