LETTER TO THE EDITOR

Weakly bound triatomic He₂Li and He₂Na molecules

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Abstract. We study the existence of stable bound states of triatomic molecules containing two helium atoms and one alkali atom X (X = Li, Na) and examine the dependence of their binding energies on the mass of the constituent atoms. The three-body systems are solved within the adiabatic approximation in hyperspherical coordinates using the He–He and He–X pair van der Waals interactions that are available in the literature. The binding energies of these systems are shown to be of less than 1 K for some isotope combinations. For the lighter isotopes it is shown that no bound states exist. We found no evidence of the existence of halo states or Efimov states for these systems.

Within the last few years an accurate He–He potential has been determined [1–5] and it has been shown that the potential can support a very weakly bound state with a binding energy of about 1.3×10^{-3} K (0.11 μeV) [1, 2]. Experimentally the existence of He dimers has been confirmed in mass spectrometric measurements [6] and in diffraction experiments of low-temperature helium clusters through a transmission grating [7, 8]. The predicted binding energy of the helium dimer cannot be measured directly but the predicted size, which is related to the binding energy, has been determined experimentally by measuring the fraction of the helium dimer beam through nanoscale sieves [9]. The average size thus determined is $\langle r \rangle = 62 \pm 10$ Å which is to be compared with the theoretically calculated size of about 100 au. This unusually large size has prompted the claim of the He dimer as the largest diatomic molecule.

The helium dimer is predicted to have a bound state only when the dimer consists of two ^{4}He isotopes. No bound states exist for the ^{3}He^{4}He or ^{3}He$_2$ combinations. In the meanwhile, helium trimers have also attracted a great deal of attention since the 1970s [10] in connection with the peculiar Efimov states [11, 12] and recently in connection with the halo (Borromean) states [13–16]. A three-body system A₃ has been shown to have an infinite number of bound states (Efimov states) if there is a zero-energy two-body A₂ bound state [11]. Can one find examples of Efimov states in actual atomic and molecular systems? The binding energy of the ^{4}He₂ dimer is very small and thus the ^{4}He₃ trimer offers such a candidate. However, it is now known that the ^{4}He₃ trimer has two bound states only.

A halo state is a bound state in the three-body system A₃ when the two-body system A₂ has no bound states. While examples of halo states have been studied in models of nuclei [15, 16], the search for halo states in atomic and molecular systems so far has been unsuccessful. Such a search has been carried out recently by Esry *et al* [17] for the trimers

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of helium isotopes. Since ^{3}He^{4}He or ^{3}He$_2$ dimers do not have bound states, any bound states in ^{3}He$_2$^{4}He or ^{3}He$_3$ would qualify as halo states. However, the calculations of Esry *et al* show that there are no bound states for these two systems.

Besides the well studied helium dimers and helium trimers, there have been few examples of weakly bound diatomic or triatomic molecules that have binding energies of the order of 1 K or less. However, accurate van der Waals interaction potentials between He and alkali atoms are known to have very shallow wells. These potentials have been investigated experimentally since the 1970s by Dehmer and Wharton [18] from scattering experiments. For the alkali–helium systems the interatomic potentials have been obtained recently by Kleinekathöfer *et al* [19]. It turns out that the He–alkali potentials are weaker than the He–He potential, thus one may find weakly bound diatomic molecules HeX and triatomic molecules HeHeX (X = alkali) that will have comparable binding energies to helium dimers and helium trimers, respectively. Therefore one can also ask whether there are particular HeHeX triatomic molecules that would qualify as Efimov states or halo states.

A powerful theoretical approach for the study of weakly bound or any three-body systems is the hyperspherical approach. For the ground state of a three-body system, the binding energy can be accurately evaluated in the hyperspherical approach within the adiabatic approximation. This method was used by Esry *et al* [17] to examine the helium trimers. For the present systems, He–He–X, we chose 1 and 2 to represent helium atoms and 3 to represent X. If the two helium atoms are different, we use 1 to represent ^{3}He and 2 to represent ^{4}He. In the centre-of-mass frame, we use ρ_1 to be the vector from particle 1 to 2, and ρ_2 to be the vector from the centre of mass of 1 and 2 to 3. The mass-weighted hyperspherical coordinates are defined by

$$\mu R^2 = \mu_{1,2}\rho_1^2 + \mu_{12,3}\rho_2^2 \tag{1}$$

where $\mu_{1,2}$ is the reduced mass of m_1 and m_2 and $\mu_{12,3}$ is the reduced mass of $(m_1 + m_2)$ and m_3. The μ in equation (1) is arbitrary and we will choose $\mu = \mu_{1,2}$ in this work.

We consider states with zero total angular momentum, $J = 0$. Besides the hyperradius R, we use two other angles to describe the $J = 0$ states: the hyperangle ϕ and the angle θ, defined by

$$\tan \phi = \sqrt{\frac{\mu_{12,3}}{\mu_{1,2}}} \frac{\rho_2}{\rho_1} \tag{2}$$

and

$$\cos \theta = \frac{\rho_1 \cdot \rho_2}{\rho_1 \rho_2}. \tag{3}$$

Within the adiabatic approximation in hyperspherical coordinates the wavefunction is written as

$$\psi(R, \phi, \theta) = F_\nu(R)\, \Phi_\nu(R; \phi, \theta) \tag{4}$$

where the channel function $\Phi_\nu(R; \phi, \theta)$ satisfies

$$\left(\frac{\Lambda^2 - \frac{1}{4}}{2\mu R^2} + V \right) \Phi_\nu(R; \phi, \theta) = U_\nu(R)\, \Phi_\nu(R; \phi, \theta). \tag{5}$$

In the equation above, Λ is the grand angular momentum operator and V is the total interaction potential among the three particles. Within the adiabatic approximation, the binding energy for the nth state within channel ν is obtained by solving the hyperradial equation

$$\left(-\frac{1}{2\mu} \frac{d^2}{dR^2} + U_\nu(R) + W_{\nu\nu}(R) \right) F_{\nu n}(R) = E_{\nu n} F_{\nu n}(R). \tag{6}$$

The 'diagonal coupling term' in the equation above is defined by $W_{v,v} = -(1/2\mu)\langle\Phi_v(R)|\mathrm{d}^2/\mathrm{d}R^2|\Phi_v(R)\rangle$. The inclusion of this term gives an upper bound to the ground state energy [20]. In this paper we used essentially the same algorithms for the solution of the channel functions as in Esry *et al*. Thus the computational details are to be referred to that paper. Before presenting the results, it is appropriate to make some comments on the expected accuracy of the energy levels calculated within the adiabatic hyperspherical approximation. Using the same He–He potential, the binding energies of the two bound states of the helium trimer have been calculated using two methods. The adiabatic hyperspherical approximation gives -0.0981 K and -1.517 mK for the two states, while the Fadeev approach [21] gives -0.11 K and -1.6 mK, respectively. Using an improved dimer potential and the adiabatic hyperspherical approximation Esry *et al* obtained -0.106 K and -2.118 mK for the two states. Thus the results are more sensitive to the accuracy of the diatomic potential used than the errors from the adiabatic approximation. However, we expect that the two-body interaction potentials available for the present systems are accurate enough that the major conclusion of this paper will remain correct. In the future if spectroscopy can be performed on these molecules, then more accurate binding energies can be calculated using, for example, the hyperspherical close-coupling method which has been applied to Coulomb three-body systems [22–24].

In the present calculation we assume that the total interaction potential V is the sum of the pair interactions of the three particles. For helium trimers, this approximation is known to be valid to better than 1% according to some calculations [25]. We do not have the so-called three-body interaction information for the present systems and they will not be considered in this study.

In figure 1 we first show the He–He, He–Li and He–Na interaction potentials that are available in the literature [19]. Note that the He–Li and He–Na potentials are much shallower than the He–He potential, and that their minima occur at larger internuclear
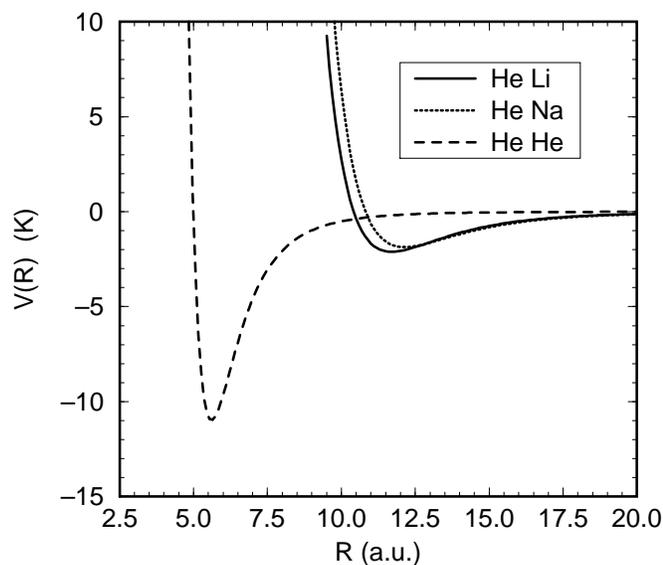
Figure 1. Interatomic potentials for He–He, He–Li and He–Na systems. Data from Kleinekathöfer *et al* [19].

Table 1. The theoretical binding energies of the ground states of some helium–alkali diatomic molecules and their average size. For each diatomic molecule, read the row and then the column to find out its binding energy and its size. The interatomic potentials were taken from [19] and the helium dimer results from [17]. The atomic masses for the isotopes are $m(^4\mathrm{He}) = 4.002\,603\,24$, $u = 7296.2994$ au; $m(^3\mathrm{He}) = 3.016\,029\,31$, $u = 5497.8852$ au; $m(^6\mathrm{Li}) = 6.015\,1214$, $u = 10\,964.896$ au; $m(^7\mathrm{Li}) = 7.016\,0030$, $u = 12\,789.391$ au; $m(^{23}\mathrm{Na}) = 22.989\,7677$, $u = 41\,907.783$ au (from 1996 *CRC Handbook of Chemistry and Physics* 77th edn, ed D R Lide (New York: Chemical Rubber Company).

		$^4\mathrm{He}$	$^3\mathrm{He}$	$^6\mathrm{Li}$	$^7\mathrm{Li}$	$^{23}\mathrm{Na}$
$^4\mathrm{He}$	E_b (mK)	1.31	—	0.12	2.16	28.98
	$\langle r \rangle$ (au)	97.88	—	287.46	77.31	29.12
$^3\mathrm{He}$	E_b (mK)	—	—	—	—	1.24
	$\langle r \rangle$ (au)	—	—	—	—	96.06

Table 2. The calculated ground state binding energies for the He–He–X triatomic molecules and their average size. To read the entries for each triatomic molecule, read the row symbol first, followed by the column symbol. A dash indicates that the system has no bound states. For $^3\mathrm{He}^4\mathrm{He}^6\mathrm{Li}$, see text.

		$^4\mathrm{He}$	$^3\mathrm{He}$	$^6\mathrm{Li}$	$^7\mathrm{Li}$	$^{23}\mathrm{Na}$
$^4\mathrm{He}_2$	E_b (mK)	106.0	10.2	31.4	45.7	103.1
	$\langle \rho \rangle$ (au)	31.8	67.6	50.2	46.6	35.0
$^3\mathrm{He}^4\mathrm{He}$	E_b (mK)	10.2	—	?	2.2	18.3
	$\langle \rho \rangle$ (au)	67.6	—	—	135.6	56.6
$^3\mathrm{He}_2$	E_b (mK)	—	—	—	—	5.7
	$\langle \rho \rangle$ (au)	—	—	—	—	101.6

separations. Using these potentials we solved the two-body radial equation numerically for the binding energies of the various isotope combinations and the results are shown in table 1. From the eigenfunctions we also calculated their average size $\langle r \rangle$. Since the binding energy depends sensitively on the reduced mass, we also list the atomic mass for each isotope used in the calculation. Note that $^4\mathrm{He}^7\mathrm{Li}$ has a larger binding energy than $^4\mathrm{He}_2$ even though the He–He potential is deeper than the He–Li potential. However, the binding energy of $^4\mathrm{He}^6\mathrm{Li}$ (0.12 mK) is smaller than that for $^4\mathrm{He}_2$ (1.32 mK). The average distance between the two helium atoms in $^4\mathrm{He}_2$ is calculated to be 97.8 au, which is smaller than the value of 287.5 au for $^4\mathrm{He}^6\mathrm{Li}$. This example precludes $^4\mathrm{He}_2$ from being labelled as the largest diatomic molecule. Note that the large size is a reflection of the much smaller binding energy for the latter system, or vice versa. When $^4\mathrm{He}$ is replaced by $^3\mathrm{He}$, we found that only $^3\mathrm{He}^{23}\mathrm{Na}$ possesses a bound state. The other mass combinations do not form stable diatomic molecules. The results for the diatomic HeX molecules are summarized in table 1 together with the results for the helium dimer.

   With the two-body potentials given as shown in figure 1, we then solved the three-body problems using the hyperspherical approach as outlined above. By choosing different mass combinations, we obtained the hyperspherical potential curves in the adiabatic approximation and then solved the hyperradial equation to calculate the ground state binding energy for each system. The results are summarized in table 2 where we also include the results from Esry *et al* for the helium trimers. We also calculated the 'size' of each three-body system. This size parameter $\langle \rho \rangle$ is defined to be the square root of the expectation value of $(\rho_1^2 + \rho_2^2)$

where ρ_1 is the distance between the two helium atoms and ρ_2 is the distance from the centre of mass of the two helium atoms to the third particle.

The results in table 2 show that the binding energies of the He–He–X triatomic molecules depend sensitively on the mass of each of the particles in the system. For ^{4}He$_2$X the three-body bound states do exist for X = ^{6}Li, ^{7}Li and ^{23}Na. For ^{4}He^{3}HeX, bound states exist for X = ^{7}Li and ^{23}Na. The situation for X = ^{6}Li is less certain. Using the potential curve we have calculated we cannot find a bound state for this system, but the potential well is attractive enough that a bound state may be found if the parameters in the calculations are changed in some favourable way. For ^{3}He^{3}HeX the only system that can have a bound state is for X = ^{23}Na. The binding energies listed in this table all refer to the ground state of each of the systems. For the ^{4}He$_3$ trimer, it is known to have an excited state [17]. We have searched for an excited state for ^{4}He^{4}He^{23}Na but none was found. All the other systems studied do not have excited states either.

We have also tabulated the average size $\langle \rho \rangle$ for each system in table 2. Since direct measurement of the binding energies of weakly bound molecular systems is not likely in the foreseeable future, an indirect piece of evidence for their existence is to measure their size. This method has been employed for the study of He$_2$ dimers and He$_3$ trimers [9]. It appears that the same method can be used to study the molecules examined here since they are of comparable dimensions.

The remaining part of this paper gives more details about the calculations. In figure 2 we show the lowest potential curves for the three systems, ^{4}He^{4}He^{7}Li, ^{4}He^{3}He^{7}Li and ^{3}He^{3}He^{7}Li. The interaction potentials between each pair of particles used in the calculations
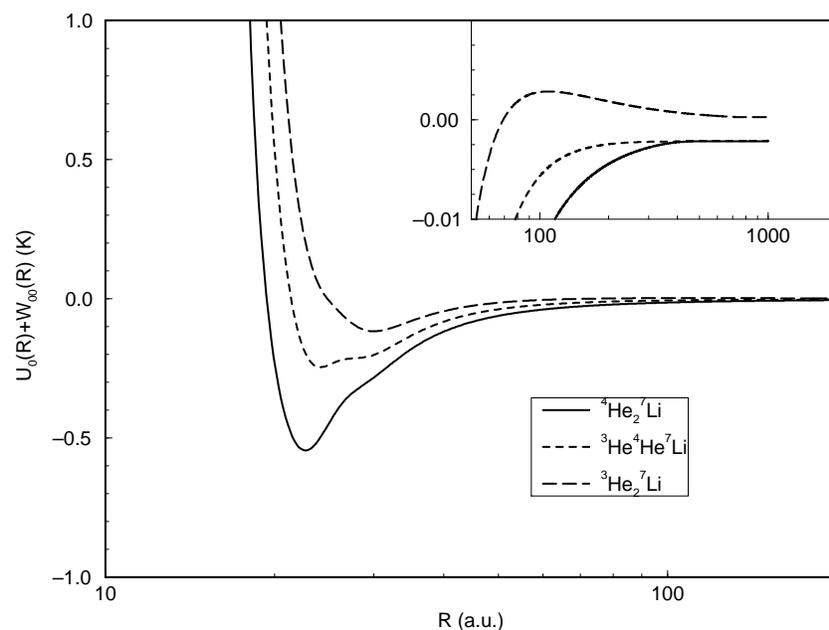
Figure 2. The lowest hyperspherical potential curves for each of the triatomic systems, ^{4}He^{4}He^{7}Li, ^{4}He^{3}He^{7}Li and ^{3}He^{3}He^{7}Li. The inset gives the asymptotic limit where the two lower curves converge to the ground state of ^{4}He^{7}Li. Note that there is no bound state for ^{3}He^{7}Li nor for ^{3}He$_2$ such that the uppermost potential curve approaches the three-particle dissociation limit at large hyperradius.
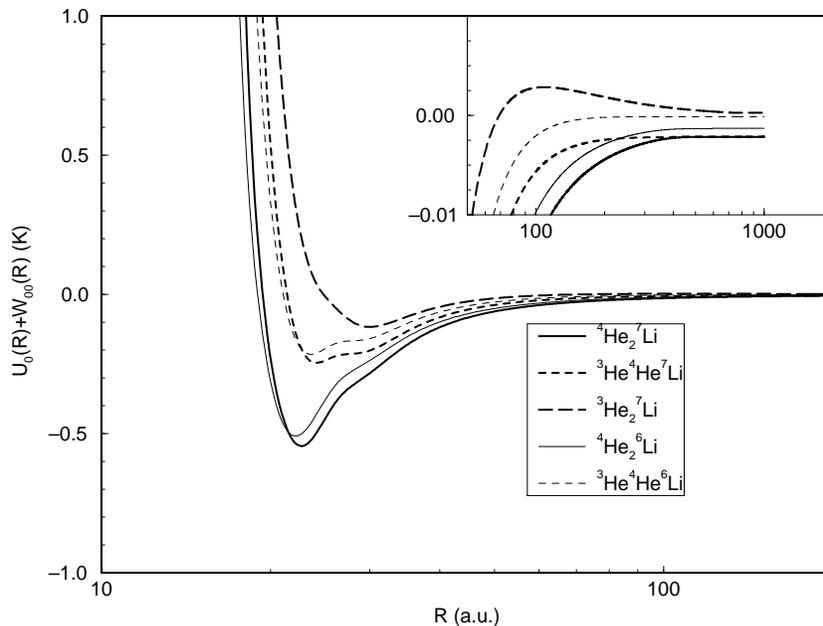
Figure 3. Comparison of the lowest potential curves for each of the triatomic systems shown. The replacement of ^{7}Li by ^{6}Li tends to make the corresponding potential curves less attractive near the potential minimum. The inset gives the asymptotic limits of the potential curves corresponding to the different energies for the diatomic molecules. The first three limits, counting from the bottom, correspond to the energies of ^{4}He^{7}Li, ^{4}He$_2$, and ^{4}He^{6}Li, respectively. The uppermost curve corresponds to the three-body dissociation limit.

are identical, thus the differences in the hyperspherical potential curves are due to the different masses in each system. Clearly the potential curve for ^{4}He^{4}He^{7}Li is the lowest. Each potential curve shows a slight kink near the minimum which is due to the non-negligible diagonal coupling term $W_{\nu,\nu}$. In the large-R limit (see the inset) each potential curve approaches the dissociation limit. For ^{4}He^{4}He^{7}Li and ^{4}He^{3}He^{7}Li, this limit is the ground state of ^{4}He^{7}Li, which has a binding energy of -2.16 mK according to table 1. For ^{3}He^{3}He^{7}Li, both ^{3}He^{3}He and ^{3}He^{7}Li have no bound states so the asymptotic limit consists of three free particles and the potential curve approaches zero at large R. If there were bound states for ^{3}He^{3}He^{7}Li, then they would be examples of halo states. However, the potential curve in figure 2 for ^{3}He^{3}He^{7}Li does not support any bound states.

In figure 3 we show the potential curves for ^{4}He^{4}He^{6}Li and ^{4}He^{3}He^{6}Li, and compare them with the three curves in figure 2. The substitution of ^{7}Li by the lighter ^{6}Li isotope gives a shallower potential well and the curve is also shifted toward smaller hyperradius. The latter is the result of our definition of the mass-weighted hyperradius. The binding energy for He–He–^{6}Li is smaller than that for He–He–^{7}Li. This is first reflected in the shallower hyperspherical potential curve for the former, but also in the asymptotic limit as shown in the inset. For ^{4}He^{4}He^{6}Li, the two-body break-up limit is ^{4}He$_2 + ^6$Li since ^{4}He$_2$ has a binding energy of -1.31 mK while ^{4}He^{6}Li has a binding energy of -0.12 mK. The four different asymptotic limits in the inset thus correspond to ^{4}He^{7}Li $+ ^4$He, ^{4}He$_2 + ^6$Li, ^{4}He^{6}Li $+ ^3$He and the three-body breakup, respectively, if counted from below. In figure 4 we show the calculated adiabatic hyperspherical potential curves for ^{4}He^{4}He^{23}Na, ^{4}He^{3}He^{23}Na and
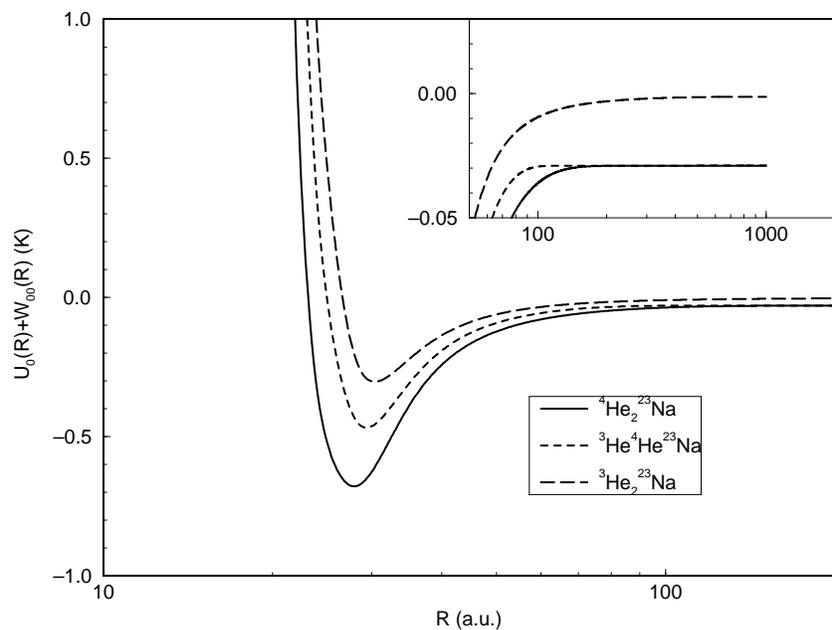
Figure 4. The lowest hyperspherical potential curve for each of the triatomic systems, ^{4}He^{4}He^{23}Na, ^{4}He^{3}He^{23}Na and ^{3}He^{3}He^{23}Na. The inset gives the asymptotic limit where the two lower curves converge to the ^{4}He^{23}Na ground state and the uppermost curve converges to the ^{3}He^{23}Na ground state.
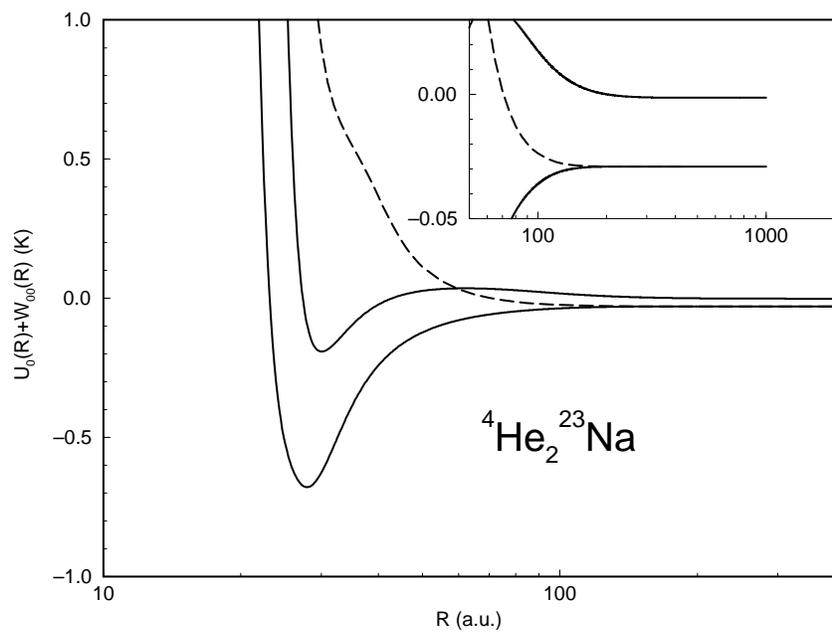
Figure 5. The lowest three hyperspherical potential curves for the $J = 0$ states of the ^{4}He^{4}He^{23}Na system. The two full curves are for symmetric (gerade) states where the wavefunction is symmetric under the exchange of the two helium atoms. The broken curve is for antisymmetric (ungerade) states.

^{3}He^{3}He^{23}Na. Although the inter-atomic potential between He–Na is slightly weaker than that for He–Li (see figure 1), the heavier mass of ^{23}Na results in the existence of bound states for all three of these systems. The ^{3}He^{3}He^{23}Na molecule deserves special mention since it is the first system with a bound state containing two ^{3}He isotopes. However, this is not an example of halo states since a bound state does exist between ^{3}He and ^{23}Na. The two asymptotic limits in the inset approach the ^{4}He^{23}Na (the lower one) and the ^{3}He^{23}Na (the upper one) diatomic bound states, respectively.

In figure 5 we show the three lowest $J = 0$ potential curves for the ^{4}He^{4}He^{23}Na molecule. The broken curve, which is mostly repulsive, corresponds to an 'anti-bonding' state where the spatial wavefunction is antisymmetric under the exchange of the two ^{4}He atoms. This antisymmetric curve does not support any bound states. The second full curve which dissociates to ^{4}He$_2$ + ^{23}Na in the asymptotic limit has an attractive potential well, but this well is not deep and broad enough to support a bound state. If such a bound state exists, it can decay to the lowest channel through the coupling between the two channels and will be observed as a resonance experimentally. In the three-body systems examined in this paper we found no such resonances since the second potential curve is, in general, too shallow.

In summary, we have studied the existence of bound states for the HeHeX (X = Li and Na) molecules. The interatomic potentials between He and Li and between He and Na are very weak, and resemble the potential between two He atoms. These weak diatomic potentials prompt us to look for weakly bound HeHeX triatomic systems which are expected to be very similar to the helium trimers that have been the focus of several novel experiments recently. We performed hyperspherical calculations on a number of different isotope combinations for the HeHeX molecules and obtained the binding energies and their typical sizes. We found that the binding energies are very sensitive to the isotope combinations and the binding energies are of the order of less than 1 K. The size of each of these systems is comparable to the helium trimer and it will be of interest to see the experimental techniques used for helium dimers and trimers extended to the weakly bound triatomic molecules reported here. The hyperspherical approach used in the present paper can be applied to any other triatomic molecules if the two-body diatomic potentials are known (the method can incorporate the three-body potential as well). There are other weak interatomic van der Waals potentials between rare gas atoms and between helium and heavier alkali atoms. One can perceive a class of such weakly bound diatomic and triatomic molecules where the binding energies are of the order of 1 K or less and the size of these molecules is of the order of 30 au or more. A systematic experimental search for these exotic molecules and future possible spectroscopy measurements would stimulate further theoretical development. High-precision data from such measurements would test the accuracy of the interatomic potential to the degree of accuracy as those achieved by photoassociation spectroscopy in cold atom collisions [26, 27]. Similarly the high-precision spectroscopy data for these weakly bound triatomic molecules would offer the possibility of studying the role of three-body forces in these systems.

References

[1] Janzen A R and Aziz R A 1995 *J. Chem. Phys.* **103** 9626
[2] Janzen A R and Aziz R A 1997 *J. Chem. Phys.* **107** 914

[3] Anderson J B, Traynor C A and Boghasian B M 1993 *J. Chem. Phys.* **99** 345
[4] Liu B and McLean A D 1989 *J. Chem. Phys.* **91** 2348
[5] Aziz R A and Slaman M J 1991 *J. Chem. Phys.* **94** 8047
[6] Luo F, McBane G C, Kim G, Giese C F and Gentry W R 1993 *J. Chem. Phys.* **98** 3564
[7] Schöllkopf W and Toennies J P 1996 *J. Chem. Phys.* **104** 1155
[8] Schöllkopf W and Toennies J P 1994 *Science* **266** 1345
[9] Luo F, Giese C F and Gentry W R *J. Chem. Phys.* 1996 **104** 1151
[10] Lim T K, Duffy S K and Lambert W K 1977 *Phys. Rev. Lett.* **38** 341
[11] Efimov V 1970 *Phys. Lett.* B **33** 563
[12] Macek J 1986 *Z. Phys.* D **3** 31
[13] Richard J M and Fleck S 1994 *Phys. Rev. Lett.* **73** 1464
[14] Goy J, Richard J M and Fleck S 1995 *Phys. Rev.* A **52** 3511
[15] Zhukov M V, Danilin B V, Federov D V, Bang J M, Thompson I S and Vaagen J S 1993 *Phys. Rep.* **231** 151
[16] Federov D V, Jensen A S and Riisager K 1994 *Phys. Rev. Lett.* **73** 2817
[17] Esry B D, Lin C D and Greene C H 1996 *Phys. Rev.* A **54** 394
[18] Dehmer P and Wharton L 1972 *J. Chem. Phys.* **57** 4821
[19] Kleinekathöfer U, Tang K T, Toennies J P and Yiu C L 1996 *Chem. Phys. Lett.* **249** 257
[20] Sucre M G, Goychman F and Lefebvre R 1970 *Phys. Rev.* A **2** 1738
[21] Cornelius T and Glöckle W 1986 *J. Chem. Phys.* **85** 3906
[22] Tang J Z, Watanabe S and Matsuzawa M 1992 *Phys. Rev.* A **46** 2437
[23] Tang J Z and Shimamura I 1995 *Phys. Rev.* A **51** R1738
[24] Zhou Yan and Lin C D 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** 4907
[25] Roeggen I and Almlöf J 1995 *J. Chem. Phys.* **102** 7095
[26] Wang H, Li J, Wang X T, Williams C J, Gould P L and Stwalley W C 1997 *Phys. Rev.* A **55** R1569
[27] Kharchenko P, Babb J F and Dalgarno A 1997 *Phys. Rev.* A **55** 3566