Calculations of the binding energies of weakly bound He–He–H, He–He–H⁻ and He–H–H molecules

Yong Li and C D Lin

Department of Physics, Kansas State University, Manhattan, KS 66506-2601, USA

Abstract. We searched for the existence of weakly bound He–He–H, He–He–H⁻ and He–H–H molecules where the binding energies are expected to be of the order of degrees Kelvin. By employing the best empirical interaction between each pair of particles, we solved the Schrödinger equation for the triatomic systems using hyperspherical coordinates in the adiabatic approximation. We found no bound states for ^{4}He–^{4}He–^{1}H, three bound states for ^{4}He–^{4}He–^{1}H⁻ and one bound state for ^{4}He–^{1}H–^{1}H. Bound states for other isotope combinations are also examined.

1. Introduction

The search for weakly bound simple molecular species is a fascinating subject. The stability of these systems depends sensitively on the interaction potentials and the masses of the particles. Quantum symmetry is also known to play an essential role [1] in determining the stability of the system and the binding energies. Simple well known rules for the binding of molecules which are valid for the more tightly bound systems cannot be applied to draw conclusions for the weakly bound molecular systems. For example, He_2 dimers and He_3 trimers have been predicted [2–8] and have also been confirmed experimentally [9–12], yet their existence cannot be anticipated based on the conventional theory of chemical bonding.

For a system consisting of three identical particles, A_3, there are two peculiar situations that have been well investigated theoretically in nuclear physics. One is that of the so-called halo states (or the Borromean states) which are defined for the bound states of a three-body system A_3 when its two-body system A_2 does not have any bound states [13, 14]. Another is that of the Efimov states [15, 16] where the three-body system supports an infinite number of bound states when the two-body system supports only one bound state with zero binding energy. No known examples of halo states or Efimov states for three identical particles have been found in atomic and molecular systems, although the second bound state of the helium trimer appears to have properties similar to those of an Efimov state [2, 17, 18].

When the three particles are not all identical, there are new possibilities for the existence of three-body bound states. In particular, weakly bound triatomic molecules beyond ^{4}He$_3$ and ^{4}He^{4}He^{3}He [2] have been investigated for other systems such as He–He-Li and He–He–Na molecules [19]. These molecules have binding energies of the order of less than 1 K and the binding energies depend sensitively on the isotopes. In this paper we present the results of our search for the He–He–H, He–He–H⁻ and He–H–H triatomic molecules or anions. Since H and He are the most abundant species in the universe, these molecules may play a role in the chemistry of the interstellar molecular cloud. These molecules can

exist only in a cold environment and thus are not expected to exist under normal laboratory conditions. With the advent of laser cooling and other cooling methods for atoms and molecules [20–22], it may be possible to make observations of these species in the near future.

2. Theoretical methods

We solved the Schrödinger equation for three interacting atoms using the adiabatic hyperspherical method [2, 23]. We consider only the most favourable conditions for the lowest states, namely $J = 0$. Starting with the Schrödinger equation in the centre-of-mass frame and defining the Jacobi coordinates $\vec{\rho}_1$, the vector from particle 1 to particle 2, and $\vec{\rho}_2$, the vector from the centre of mass of the first pair to particle 3, we then transforming to mass-weighted hyperspherical coordinates [23],

$$\mu R^2 = \mu_1 \rho_1^2 + \mu_2 \rho_2^2 \qquad \tan \phi = \sqrt{\frac{\mu_2}{\mu_1}} \frac{\rho_2}{\rho_1}$$

and

$$\cos \theta = \frac{\boldsymbol{\rho}_1 \cdot \boldsymbol{\rho}_2}{\rho_1 \rho_2}.$$

In this expression, μ is an arbitrary scaling factor which we chose to be the reduced mass of the pair of identical particles. Since we consider states with $J = 0$ only, the Schrödinger equation then involves only the three internal coordinates R, ϕ, and θ (in atomic units) [2, 23],

$$\left(-\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\Lambda^2 - \frac{1}{4}}{2\mu R^2} + V(R, \phi, \theta) \right) \psi = E \psi. \tag{1}$$

Here Λ^2 is the 'grand angular momentum' operator [23]. Note also that the wavefunction $\psi(R, \phi, \theta)$ is rescaled from the 'true wavefunction' by a factor of $R^{5/2} \sin \phi \cos \phi$ in order to eliminate first derivatives from the kinetic energy operator. In the adiabatic approach, we treat R initially as a fixed parameter and solve the remaining eigenvalue equation

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

The full solution to the Schrödinger equation is found in the adiabatic approximation by writing

$$\psi(R, \phi, \theta) = \sum_\nu F_\nu(R) \, \Phi_\nu(R; \phi, \theta).$$

If the coupling terms between different channels are neglected, then we obtain the hyperradial equation in the adiabatic approximation

$$\left(-\frac{1}{2\mu} \frac{d^2}{dR^2} + U_\nu(R) + W_{\nu\nu}(R) \right) F_{\nu n}(R) = E_{\nu n} F_{\nu n}(R) \tag{3}$$

where

$$W_{\nu\nu}(R) = -\frac{1}{2\mu} \left\langle \Phi_\nu(R) \left| \frac{d^2}{dR^2} \right| \Phi_\nu(R) \right\rangle.$$

It can be shown [24] that the ground state energy obtained by solving equation (3) is an upper bound to the true ground state energy.
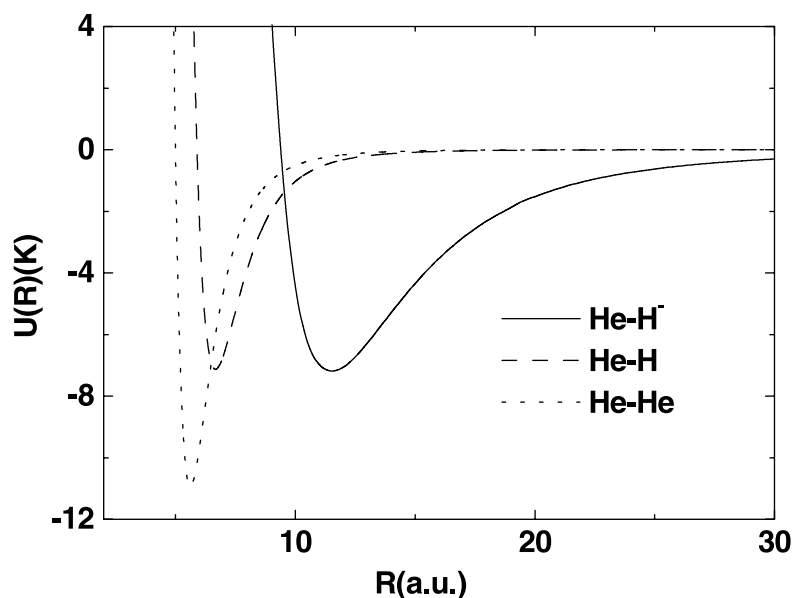
Figure 1. Pair interaction potentials for He–He, He–H and He–H⁻ 'two-body' systems.

To calculate the binding energies of He–He–H and He–H–H molecules, we consider each molecule as consisting of three atoms, and the elementary interactions are two-body interactions between each pair. In other words, we do not consider any possible 'three-body' forces. The latter is expected to be small and in the case of the He–He–He system it has been shown to contribute to less than 1% to the ground state energy [25, 26]. For the He–He pair interaction, we used the one from Aziz and Slaman [27]. Other newer potentials have been proposed recently [29, 30], but they do not differ much from the one employed here. For the He–H pair interaction, we used the potential proposed by Meyer and Frommhold [28]. These potentials are considered to be among the best available and they were obtained from quantum chemistry calculations and fitted and adjusted so that the low-energy atom–atom scattering data are reproduced. For the He–He–H⁻ anion, we treat H⁻ as an elementary constituent. The interaction potential between He–H⁻ has been calculated recently [31] by us. In figure 1 we show the pairwise interaction potentials for He–H, He–He and He–H⁻ which serve as the input data for the present calculations. Note that the potential wells are expressed in Kelvin.

3. Results and discussion

3.1. The He–He–H system

The hyperspherical potential curves for six isotope combinations for the He–He–H system are presented in figure 2. Note that only the ^{4}He–^{4}He dimer has a bound state with a binding energy at -1.4 mK and all the other two-body combinations have no bound states. Thus each of the lowest potential curves for the ^{4}He–^{4}He–^{n}H ($n = 1$–3) system converges to the ^{4}He–^{4}He limit in the asymptotic region. For each of the ^{4}He–^{3}He–^{n}H ($n = 1$–3) system the dissociation limit is the three-body breakup threshold. Thus if the latter have bound states they would correspond to the halo states. From the calculated potential
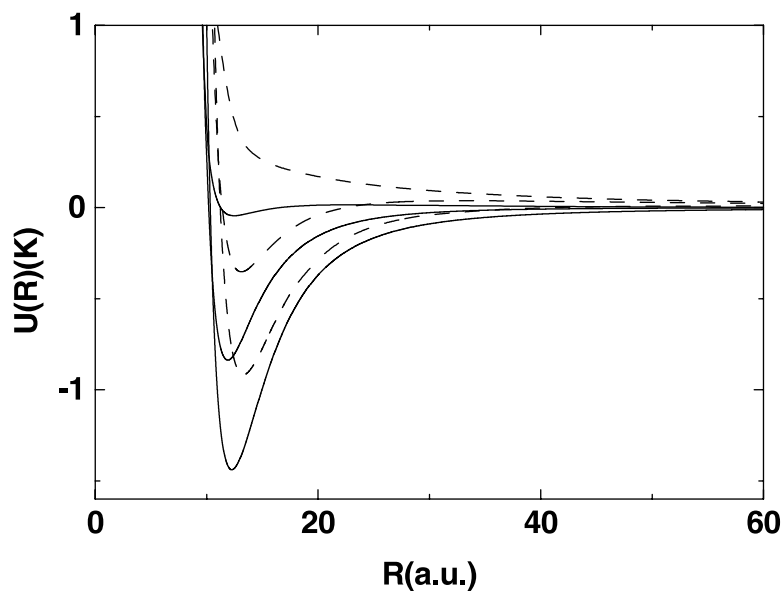
Figure 2. The lowest adiabatic hyperspherical potential curves for the $^4\text{He}^4\text{He}^n\text{H}$ ($n = 1, 2, 3$) (full curves) and $^4\text{He}^3\text{He}^n\text{H}$ ($n = 1, 2, 3$) (broken curves) triatomic systems. In each group, the system with the higher total mass has the lower potential. Only $^4\text{He}^4\text{He}^3\text{H}$ was found to support one bound state.

curves shown in figure 2 we did not find any bound states for the $^4\text{He}-^3\text{He}-^n\text{H}$ ($n = 1$–3) molecules, thus we still have no examples of halo states in molecular systems. Among the combinations $^4\text{He}-^4\text{He}-^n\text{H}$ ($n = 1$–3), only $^4\text{He}-^4\text{He}-^3\text{H}$ has a potential well attractive enough to support a bound state and the binding energy was found to be -6.8 mK. This is one of the weakest bound molecules that we have found. In comparison, the $^4\text{He}_3$ trimer has a binding energy of 106 mK, and $^4\text{He}_2-^3\text{He}$ has a binding energy of 10.2 mK [2], where all the binding energies are measured from the ground state of the lowest bound pair. The present example illustrates the sensitive dependence of the binding energies with respect to the masses in the molecular system. Note that the pair interaction potentials used in all six isotope combinations are all identical, but the hyperspherical potential curves, unlike the potential curves calculated in the Born–Oppenheimer approximation, are mass dependent.

3.2. The He–H–H system

We next consider the HeH_2 molecular system, which is modelled as a three-body system. The He–H pair interaction is shown in figure 1 and the H–H interaction is given by the Born–Oppenheimer potential of the ground state of H_2 [32]. The ground vibrational level of H_2 has a binding energy of -4.4774 eV. In figure 3 we show the calculated hyperspherical potential curves for the two systems, $^4\text{He}-^1\text{H}-^1\text{H}$ and $^3\text{He}-^1\text{H}-^1\text{H}$. The two curves are very similar except that the former system stretches out further. From the potential curves we calculated the bound states supported by each curve. We found that each curve can support only one bound state, the energies are at -68.2 mK for the former, and at -10.35 mK for the latter. These results are to be compared with the results of -42.9 and -2.3 mK reported by Balakrishnan
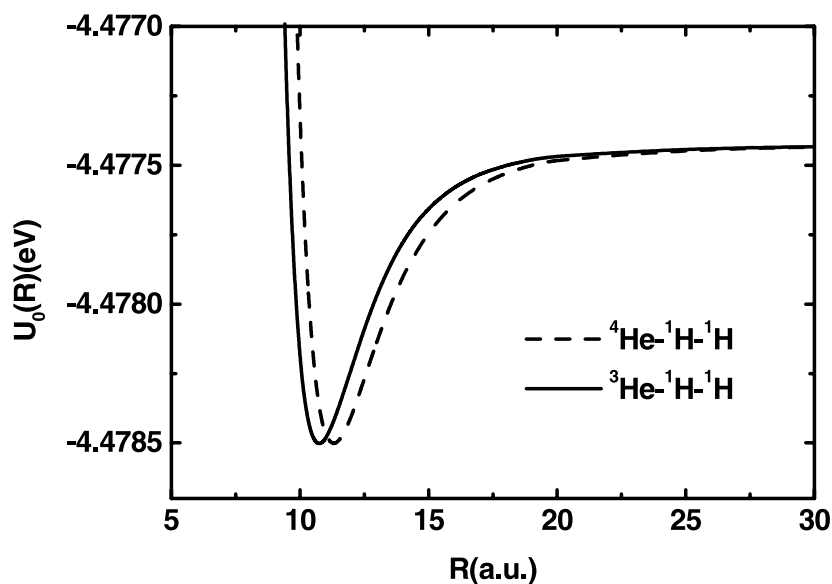
Figure 3. The lowest adiabatic hyperspherical potential curves for the ^{4}He^{1}H^{1}H and ^{3}He^{1}H^{1}H systems. Each was found to support one and only one bound state.

et al [33], respectively. While the numerical values depend on the potentials adopted and the method used in the calculation, the conclusion for the existence of one bound state for each system is clearly established.

3.3. The He–He–H⁻ system

The He–He–H system, as shown in the first subsection, has no bound state except for the less abundant molecule ^{4}He–^{4}He–^{3}H. We next look for bound states in the anion He–He–H⁻. The He–H⁻ pair interaction is governed by the long-range $1/r^4$ induced dipole potential and thus He–He–H⁻ may be capable of forming a diffuse triatomic molecular ion. By treating ^{4}He–^{4}He–^{1}H⁻ as a three-body system, we solved the hyperspherical potential curves. In figure 4 the two lowest curves are shown. According to the model potential we have used, the lowest curve converges to the ground state of the He–H⁻ system at -1.37 K and the second curve converges to the first rotational excited state ($J = 1$) of the He–H⁻ system at -0.566 K [31]. In figure 4 we show the two lowest curves since the lowest one displays some unusual structure where it exhibits a kink at R near 25 au. The origin of this kink was traced to a change of the geometry of the ^{4}He–^{4}He–^{1}H⁻ molecule. At smaller hyper-radius the potential energy is smaller for the geometry (He–He) + H⁻, i.e. the two helium atoms form a pair with H⁻ at a larger distance away. This geometry is favoured since at small interatomic distances, the helium pair has a deeper potential well (see figure 1). At larger hyper-radius where the interatomic distances are larger, the He–H⁻ interaction is stronger than the He–He interaction such that H⁻ favours to pair with one of the helium atoms. The ground state energy calculated from the lowest curve is -1.71 K. It can support two more bound states (at -0.78 and -0.0053 K) within the single-channel approximation but for these two higher states the channel coupling with the upper curve must be considered. We did not pursue this issue since our goal is to search for the ground state. Our conclusion is that there is at least one bound state for the ^{4}He^{4}He^{1}H⁻ system.

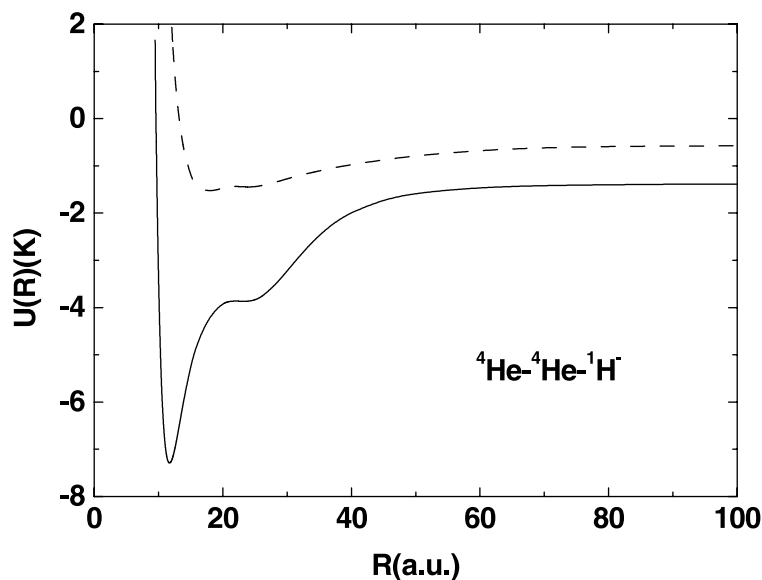**Figure 4.** The two lowest hyperspherical potential curves for the ^{4}He^{4}He^{1}H$^-$ system. The kink in the lowest curve is due to the change in the shape of the system as the hyper-radius is varied.

4. Summary

In summary we have used the hyperspherical adiabatic approximation to search for the existence of some weakly bound triatomic molecules and anions consisting of light atoms of H and He. These molecules have binding energies of the order of 1 K or less and can only exist in a very cold environment. Our calculations are based on the empirical diatomic pair interaction potentials that we considered the best available for each pair. While it is difficult to speculate on the accuracy of the present results, the existence of the predicted stable bound systems should be quite reliable. Improvement of the calculated energies can be expected if there are better potential surfaces available in the future. It is our goal to perform these calculations to provide some guidance for the experimentalists in their search for such weakly bound molecules or anions.

Acknowledgment

References

[1] Bao C G, Yang X Z and Lin C D 1997 *Phys. Rev.* A **55** 4168
[2] Esry B D, Lin C D and Greene C H 1996 *Phys. Rev.* A **54** 394
[3] Cornelius T and Glöckle W 1986 *J. Chem. Phys.* **85** 3906
[4] Huber S 1985 *Phys. Rev.* A **31** 3981
[5] Lim T K 1986 *Phys. Rev.* A **34** 4424
[6] Anderson J B, Traynor C A and Boghasian B M 1993 *J. Chem. Phys.* **99** 345
[7] Uang Y H and Stwalley W C 1982 *J. Chem. Phys.* **76** 5069
[8] Liu B and McLean A D 1989 *J. Chem. Phys.* **91** 2348

   [9] Schöllkopf W and Toennies J P 1994 *Science* **266** 1345

  [10] Schöllkopf W and Toennies J P 1996 *J. Chem. Phys.* **104** 1155

  [11] Luo F, McBane G C, Kim G, Giese C F and Gentry W R 1993 *J. Chem. Phys.* **98** 3564

  [12] Luo F, Giese C F and Gentry W R 1996 *J. Chem. Phys.* **104** 1151

  [13] Richard J M and Fleck S 1994 *Phys. Rev. Lett.* **73** 1464

  [14] Federov D V, Jensen A S and Riisager K 1994 *Phys. Rev. Lett.* **73** 2817

  [15] Efimov V 1970 *Phys. Lett.* B **33** 563

  [16] Macek J 1986 *Z. Phys.* D **3** 31

  [17] Gonzalez-Lezana T, Rubayo-Soneira J, Miret-Artes S, Gianturco F A, Delgado-Barrio G and Villarreal P 1999 *Phys. Rev. Lett.* **82** 1648

  [18] Nielsen E, Fedorov D V and Jensen A S 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 4085

  [19] Jianmin Yuan and Lin C D 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** L637

  [20] Friedrich B, deCarvalho R, Kim J, Patterson D, Weinstein J A and Doyle J M 1998 *J. Chem. Soc., Faraday Trans.* **94** 1783

  [21] Weinstein J D *et al* 1998 *Nature* **395** 148

  [22] Doyle J M, Friedrick B, Kim J and Patterson D 1995 *Phys. Rev.* A **52** R2525

  [23] Lin C D 1995 *Phys. Rep.* **257** 1

  [24] Starace A and Webster G L 1979 *Phys. Rev.* A **19** 1629

  [25] Parish C A and Dykstra C E 1994 *J. Chem. Phys.* **101** 7618

  [26] Roeggen I and Almlof J 1995 *J. Chem. Phys.* **102** 7095

  [27] Aziz R A and Slaman M J 1991 *J. Chem. Phys.* **94** 8047

  [28] Meyer W and Frommhold L 1994 *Theor. Chin. Acta* **88** 201

  [29] Kleinekathofer U, Tang K T, Toennies J P and Yiu C L 1996 *Chem. Phys. Lett.* **249** 257

  [30] Kleinekathofer U, Tang K T, Toennies J P and Yiu C L 1997 *J. Chem. Phys.* **107** 9502

  [31] Li Yong and Lin C D 1999 *Phys. Rev.* A **60** 2009

  [32] Kolos W and Wolniewicz L 1965 *J. Chem. Phys.* **43** 2429

  [33] Balakrishnan N, Forrey R C and Dalgarno A 1998 *Phys. Rev. Lett.* **80** 3224