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# Models for Low-Temperature Helium Dimers and Trimers

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**ABSTRACT:** We have shown that a simple model based on pairwise deltafunction potentials can, with an appropriate choice of parameters, represent the general behavior of ultra-low temperature helium dimers and trimers, including all possible isotopomers. The species  $^4\text{He}_2$ ,  $^4\text{He}_3$ , and  $^4\text{He}_2^3\text{He}$  are stable, with binding energies of approximately 1.3, 100, and 10 mK, respectively. An Efimov state for  $^4\text{He}_2^3\text{He}$  is also predicted, bound by 2.4 mK. The remaining dimers and trimers,  $^4\text{He}^3\text{He}$ ,  $^3\text{He}_2$ ,  $^4\text{He}^3\text{He}_2$ , and  $^3\text{He}_3$ , are evidently unstable. © 2002 Wiley Periodicals, Inc. *Int J Quantum Chem* 90: 419–423, 2002

**Key words:** helium dimer; helium trimer; deltafunction potential; Efimov state

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## Introduction

The stability of small clusters of helium atoms, with binding energies in the millikelvin range, has been confirmed in recent years using highly refined experimental techniques including mass spectroscopy and diffraction by nanoscale sieves [1–5]. Concurrent theoretical work has determined a highly accurate He–He interatomic potential [6–8] and confirmed the stability of certain helium dimers and trimers. A highly accurate quantum Monte Carlo computation by Anderson et al. [9] predicted the stability of the  $^4\text{He}_2$  dimer. The computed minimum of the potential well is at 5.61 b (2.97 Å), with a well depth corresponding to  $\epsilon/k = 10.970$  K. This potential can support only a single bound state with  $v = 0$ ,  $J = 0$  and a remarkably minute binding energy of 1.310 mK. Such weak bonding allows the

average internuclear separation to expand to 98.1 b (51.9 Å). No bound states exist for the isotopomers  $^4\text{He}^3\text{He}$  or  $^3\text{He}_2$ .

The helium trimer has been the subject of many computational studies [10–22]. Among the more recent of these, Nielsen et al. [20] used Faddeev methods [23, 24] to obtain binding energies of 125.2 and 2.269 mK, respectively, for the ground and excited states of  $^4\text{He}_3$  and a binding energy of 13.06 mK for the ground state of  $^4\text{He}_2^3\text{He}$ . Also using Faddeev methods, Roudnev and Yukovlev [21] obtained binding energies of 117.1 and 1.665 mK, respectively, for the ground and excited states of  $^4\text{He}_3$ . In both studies the energy of the  $^4\text{He}_3$  excited state lies slightly below that of the  $^4\text{He}_2$  ground state. The results of Blume et al. [22] obtained using hyperspherical coordinates for  $^4\text{He}_3$  agree to within 1% with those of Nielsen et al. The various studies are in agreement that the isotopomers  $^4\text{He}^3\text{He}_2$  and  $^3\text{He}_3$  are unbound, as are the dimers  $^4\text{He}^3\text{He}$  and  $^3\text{He}_2$ .

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## Deltafunction Models

The purpose of this article is to present a highly idealized model which reproduces the essential features of helium dimers and trimers without the need for elaborate computations. The fact that the  $^4\text{He}$  dimer supports but a single bound state is highly suggestive of a deltafunction potential, which has the same property. Moreover a deltafunction can be very weakly bonding, allowing for highly delocalized wave functions. Indeed Jee et al. [17] have employed fitted spherical delta-shell potentials in their study of  $^4\text{He}_3$ , obtaining a binding energy of 183 mK, about 50% higher than the accepted value of around 120 mK. Their value, like ours given below, is very much dependent on the choice of parameters in the potential.

In an earlier contribution to this journal [25], the authors proposed a ‘‘Dirac bubble potential’’ in which the interatomic interaction is idealized as an attractive deltafunction on a sphere of radius  $r_0$ , viz.

$$V(r) = -\text{const} \delta(r - r_0). \quad (1)$$

The Schrödinger equation for the relative motion of the two helium atoms can be written

$$\frac{1}{2\mu} \left[ -\psi''(r_{12}) - \frac{2}{r_{12}} \psi'(r_{12}) + \frac{\lambda}{r_0} \delta(r_{12} - r_0) \psi(r_{12}) \right] = E \psi(r_{12}), \quad (2)$$

assuming a state of zero angular momentum. Here  $\mu = M/2$ , where  $M$  is the mass of a  $^4\text{He}$  atom, 7296.3 au. There exists just one bound state with (unnormalized) wave function given by

$$\psi_k(r) = \frac{\sinh \kappa r_{<} e^{-\kappa r_{>}}}{\kappa r_{<} \kappa r_{>}}, \quad (3)$$

where  $r_{>}$  and  $r_{<}$  are the greater and lesser of  $\{r_{12}, r_0\}$  and the parameters are related by

$$\frac{2\kappa}{1 - e^{-2\kappa r_0}} + \frac{\lambda}{r_0} = 0. \quad (4)$$

The ground-state energy is equal to  $E = -\kappa^2/2\mu = -\kappa^2/M$ . We equate this to the LM2M2 computed value [26],  $-4.148 \times 10^9$  hartree or  $-1.310$  mK, which determines the parameter  $\kappa = 0.005520 \text{ b}^{-1}$ .

The first obvious candidate for the bubble radius  $r_0$  would be the computed potential minimum, 5.61 b. This would be an appropriate choice for very heavy atoms. However, we obtain better results by using instead the maximum of the LM2M2 radial distribution function, namely  $r_0 = 13.15 \text{ b}$ .

We have this leeway since we are constructing an empirical approximation to the accurate potential. The larger value of  $r_0$  also takes account of the extensive delocalization of the wave function. With this parameter, we obtain a spectacular overlap integral of 0.99942 between the LM2M2 radial distribution function and that computed from Eq. (3). Using Eq. (4), we can now assign the value  $\lambda = -1.07434$ . In fact, a bound state does not exist for Eq. (2) unless  $\lambda < -1$ . For other isotopic variants,  $\lambda$  is approximately proportional to the reduced mass. This would imply for  $^4\text{He}^3\text{He}$  that  $\lambda_{43} \approx -0.9207$ , consistent with a nonexistent bound state. As we will see later, an even smaller negative value for  $\lambda_{43}$  is appropriate.

## Helium Trimers

The Schrödinger equation for a trimer with arbitrary masses and pairwise deltafunction interactions can be written (in atomic units  $\hbar = m = 1$ )

$$\left[ -\frac{1}{2M_1} \nabla_1^2 - \frac{1}{2M_2} \nabla_2^2 - \frac{1}{2M_3} \nabla_3^2 + \frac{\lambda_{12}}{2\mu_{12}r_0} \delta(r_{12} - r_0) + \frac{\lambda_{23}}{2\mu_{23}r_0} \delta(r_{23} - r_0) + \frac{\lambda_{31}}{2\mu_{31}r_0} \delta(r_{31} - r_0) \right] \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = E \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3), \quad (5)$$

where  $\mu_{ij} \equiv M_i M_j / (M_i + M_j)$ . Assuming zero translational and rotational energies, this can be reduced to an equation in the three interatomic coordinates [27]:

$$\left[ -\frac{1}{2\mu_{12}} \left( \frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}} \frac{\partial}{\partial r_{12}} \right) - \frac{1}{2\mu_{23}} \left( \frac{\partial^2}{\partial r_{23}^2} + \frac{2}{r_{23}} \frac{\partial}{\partial r_{23}} \right) - \frac{1}{2\mu_{31}} \left( \frac{\partial^2}{\partial r_{31}^2} + \frac{2}{r_{31}} \frac{\partial}{\partial r_{31}} \right) + \frac{r_{12}^2 - r_{23}^2 - r_{31}^2}{2M_1 r_{23} r_{31}} \frac{\partial^2}{\partial r_{23} \partial r_{31}} + \frac{r_{23}^2 - r_{31}^2 - r_{12}^2}{2M_2 r_{31} r_{12}} \frac{\partial^2}{\partial r_{31} \partial r_{12}} + \frac{r_{31}^2 - r_{12}^2 - r_{23}^2}{2M_3 r_{12} r_{23}} \frac{\partial^2}{\partial r_{12} \partial r_{23}} + \frac{\lambda_{12}}{2\mu_{12}r_0} \delta(r_{12} - r_0) + \frac{\lambda_{23}}{2\mu_{23}r_0} \delta(r_{23} - r_0) + \frac{\lambda_{31}}{2\mu_{31}r_0} \delta(r_{31} - r_0) \right] \Psi(r_{12}, r_{23}, r_{31}) = E \Psi(r_{12}, r_{23}, r_{31}). \quad (6)$$

Lacking exact solutions to Eq. (6), we consider variational approximations of the form

$$\Psi(r_{12}, r_{23}, r_{31}) = \phi_1(r_{12}) \phi_2(r_{23}) \phi_3(r_{31}), \quad (7)$$

where the “orbital functions”  $\phi_i(r_{ij})$  have the functional form of the dimer solutions Eq. (3), with the  $\kappa_{ij}$  now treated as variational parameters. Note that this function is totally symmetrical with respect to interchange of any two particles, as is appropriate for a Bose–Einstein system. One must not fail to account for the deltafunction contributions resulting from second derivatives at the cusps  $r_{ij} = r_0$ , whereby

$$\begin{aligned}\phi''(r_0) &= [\phi'(r_0^+) - \phi'(r_0^-)]\delta(r_{ij} - r_0) \\ &= \frac{2\kappa}{1 - e^{-2\kappa r_0}}\phi(r_0)\delta(r_{ij} - r_0).\end{aligned}\quad (8)$$

### Homonuclear Trimer

We have recently done a preliminary computation on the  ${}^4\text{He}_3$  trimer, with the objective of studying the origin of three-body forces [28]. The three orbital functions can then be chosen with the same parameter  $\kappa$ , now treated as variational parameter, such as to minimize

$$E(\kappa) = \frac{\int \Psi H \Psi d\tau}{\int \Psi^2 d\tau}.\quad (9)$$

We set the  $M_i$  in Eqs. (5) and (6) all equal to  $M({}^4\text{He})$  and the  $\mu_{ij} = M/2$ . Exploiting the equivalence of the three interatomic coordinates, the variational energy can be reduced to

$$E(\kappa) = \frac{3}{M} \left[ -\kappa^2 + \frac{T}{N} + \left( \frac{2\kappa}{1 - e^{-2\kappa r_0}} + \frac{\lambda}{r_0} \right) \frac{D}{N} \right].\quad (10)$$

We must evaluate the normalization integral

$$N = \int [\phi(r_{12})\phi(r_{23})\phi(r_{31})]^2 d\tau,\quad (11)$$

the kinetic energy

$$\begin{aligned}T &= \int \phi(r_{12})\phi(r_{23})\phi(r_{31}) \frac{r_{12}^2 - r_{23}^2 - r_{31}^2}{2r_{23}r_{31}} \\ &\quad \times \phi(r_{12})\phi'(r_{23})\phi'(r_{31}) d\tau,\end{aligned}\quad (12)$$

and the deltafunction integral

$$D = \int [\phi(r_{12})\phi(r_{23})\phi(r_{31})]^2 \delta(r_{12} - r_0) d\tau.\quad (13)$$

The integration element in  $r_{12}r_{23}r_{31}$ -space is given by

$$d\tau = 8\pi^2 r_{12} r_{23} r_{31} dr_{12} dr_{23} dr_{31}\quad (14)$$

with the limits  $r_{12} = \{|r_{31} - r_{23}|, r_{31} + r_{23}\}$ ,  $r_{23} = \{0, \infty\}$ ,  $r_{31} = \{0, \infty\}$ . It has been found to be computationally convenient to take all three integrals over  $\{0, \infty\}$  while enforcing the triangle inequalities with a product of Heaviside functions  $\theta(-r_{12} + r_{23} + r_{31})\theta(r_{12} - r_{23} + r_{31})\theta(r_{12} + r_{23} - r_{31})$ .

With the choice of parameters  $r_0 = 13.15$  b and  $\lambda_{44} = -1.07434$ , the wave function  $\phi(r_{12})\phi(r_{23})\phi(r_{31})$  is optimized for  $\kappa = 0.0099$ , giving a binding energy of 96.1 mK. This compares well with the best Faddeev result of 117 mK. The average internuclear distance  $\langle r_{12} \rangle$  is computed to be 24.3 b. An indication of the spread of the interatomic distribution is given by the standard deviation  $\sigma = [\langle r_{12}^2 \rangle - \langle r_{12} \rangle^2]^{1/2} = 17.2$  b.

An augmented variational computation verified the existence of an excited bound state. Following the method of Hylleraas, we consider the linear variational function

$$\begin{aligned}\Psi(r_{12}, r_{23}, r_{31}) &= \phi(r_{12})\phi(r_{23})\phi(r_{31}) \\ &\quad \times [c_0 + c_1(r_{12} + r_{23} + r_{31}) \\ &\quad + c_2(r_{12}r_{23} + r_{23}r_{31} + r_{31}r_{12}) \\ &\quad + c_3(r_{12}^2 + r_{23}^2 + r_{31}^2) + c_4r_{12}r_{23}r_{31}].\end{aligned}\quad (15)$$

This function, like Eq. (7), is symmetrical with respect to interchange of any two particles. The five roots of the secular equation give two bound states with energies  $-99.75$  and  $-2.412$  mK (plus three positive roots corresponding to unbound excited states). The Hylleraas computation thus gives a slightly improved ground state, with binding energy 99.75 mK. More significant, however, is the prediction of a weakly bound excited state. This evidently represents the Efimov state in the vicinity of 1–2 mK, as conjectured by several workers.

### Heteronuclear Trimers

The computations of Nielsen et al. [20] predict a marginally stable (ca. 10 mK)  ${}^4\text{He}_2{}^3\text{He}$  trimer species with an average of 28 b for the 4–4 separation and 38 b for each 4–3 separation. While the choice of the parameter  $\lambda_{44}$  is quite straightforward, given the dimer results, no corresponding assignment of  $\lambda_{43}$  can be made on the basis of our model. Based on the reduced mass ratio, we might approximate  $\lambda_{43} \approx -0.9207$ . This successfully accounts for the instability of the  ${}^4\text{He}{}^3\text{He}$  dimer, but this value is much too large when used in trimer computations. (We found, with some embarrassment, that this parameter choice implied that the 443 trimer was stable by 64 mK and that even the 433 trimer was weakly bound.)

Our strategy is instead to fit the approximate wave function

$$\Psi(r_{12}, r_{23}, r_{31}) = \phi_{44}(r_{12})\phi_{43}(r_{23})\phi_{43}(r_{31})\quad (16)$$

to the average 4–4 and 4–3 distances. With the parameters  $\kappa_{44} = 0.0092$  and  $\kappa_{43} = 0.0056$ , we obtain  $\langle r_{12} \rangle = 28.0$  and  $\langle r_{23} \rangle = \langle r_{31} \rangle = 38.1$ . The parameter  $\lambda_{43}$  can then be “tuned” to  $-0.77$  to give a binding energy of 11.4 mK, in approximate agreement with accurate computations. Clearly neither the 433 nor the 333 trimers should be stable.

## Summary

We have revised the pairwise deltafunction potential we previously employed [25] to obtain better estimates of the binding energy of the helium trimer. We now calculate binding energies of 96.1 and 11.4 mK for the ground states of  ${}^4\text{He}_3$  and  ${}^4\text{He}_2{}^3\text{He}$ , respectively. The isotopomers  ${}^4\text{He}{}^3\text{He}_2$  and  ${}^3\text{He}_3$  are found to be unbound, in agreement with other studies. The species  ${}^4\text{He}_3$  is characterized by  $\langle r_{ij} \rangle$  values of 24.3 b, while  ${}^4\text{He}_2{}^3\text{He}$  is characterized by values of 28.0 b for its  ${}^4\text{He}$ – ${}^4\text{He}$  separation and 38.1 b for each of its  ${}^4\text{He}$ – ${}^3\text{He}$  separations. The binding energy of the species  ${}^4\text{He}_3$  increases slightly to 99.8 mK when our simple product wave function is augmented by a Hylleraas-type correlation function, Eq. (14). The latter variational method also yields an excited state for  ${}^4\text{He}_3$  with a binding energy of 2.4 mK, comparable to values found by the Faddeev methods.

Table I summarizes the energies and geometric parameters for all predicted stable helium dimers and trimers. The  $\pm$  values represent standard deviations  $\sigma = ((r_{ij}^2) - \langle r_{ij} \rangle^2)^{1/2}$ .

Nielsen et al. [20] calculated expectation values of various operators related to geometrical structure from their numerical solutions of the Faddeev equations. Based on the LM2M2 dimer potential of

Aziz and Slaman [6a], they obtain mean particle radii from the center of mass of 49.0 and 10.2 b for  ${}^4\text{He}_2$  and  ${}^4\text{He}_3$ , respectively. These values correspond to particle separations of 98.0 and 17.7 b, respectively, compared with our mean values of 98.1 and 24.3 b, shown in Table I. For the  ${}^4\text{He}_2{}^3\text{He}$  mixed trimer, constructing a triangle from our  $\langle r_{ij} \rangle$  values, the mean radius from the center of mass is 19.9 b, virtually identical to the value of 20 b calculated by Nielsen et al., although their averaging procedure differs from ours. Thus our method yields trimers very similar in size to those obtained by the Faddeev methods.

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**TABLE I**  
**Helium dimers and trimers.**

Molecule	$-E$ (mK)	$\langle r_{ij} \rangle \pm \sigma$ (b)
${}^4\text{He}_2$	1.310	$98.1 \pm 90.6$
${}^4\text{He}_3$	99.8	$24.3 \pm 17.2$
${}^4\text{He}_3^*$	2.4	$103.6 \pm 53.6$
${}^4\text{He}_2{}^3\text{He}$	11.4	$28.0 \pm 21.6^a$ $38.1 \pm 34.9^b$

<sup>a</sup>  $\langle r_{44} \rangle$ .

<sup>b</sup>  $\langle r_{43} \rangle$ .

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