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The article by Thorne Lay and Hiroo Kanamori is an interesting one. It discusses the energy released by the 1994 Northridge earthquake. The authors estimate that the earthquake released about 100 megajoules of energy. This is a very large amount of energy. For comparison, the energy released by a 100-megaton explosion is about 100 megajoules. The authors also discuss the energy released by the 1964 Chilean earthquake. They estimate that this earthquake released about 100 megajoules of energy. This is also a very large amount of energy. The authors conclude that the energy released by earthquakes is much larger than the energy released by nuclear weapons. This is a very important point. It shows that the energy released by earthquakes is a natural phenomenon and not a man-made one. This is a very important point. It shows that the energy released by earthquakes is a natural phenomenon and not a man-made one.

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By the act of hitting a ball with a bat, one calculates the force energy to deliver the ball to its new location, but one must also take into account that the ball extended its energy release to that which became struck by the ball as its momentum ceased and passed energy to the struck item. Therefore the parameters of the damage extend into the future when the received energy to that pushed upon later becomes released in a new event. Perhaps calculations of one added that in while another's calculations did not. E.M.C.
Written by Edgar McCarroll, 14 July 2012 19:59

The structure of a weakly bound ionic trimer: Calculations for the ${}^4\text{He}_2\text{H}^-$ complex

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The weakly bound diatomic systems ${}^4\text{He}_2$ and ${}^4\text{HeH}^-$ have been found able to support only one bound state for $J=0$, although the latter also supports an additional bound state for $J=1$. In the present paper we, therefore, study the structure of the bound states which might exist for the weakly bound triatomic ${}^4\text{He}_2\text{H}^-$, in its $J=0$ state, by describing the full potential as a simple addition of two-body (2B) interactions. We carry out bound state calculations using both Jacobi coordinates within a discrete variable representation (DVR) and pair coordinates with a distributed Gaussian function (DGF) expansion. The system is shown to possess two bound states with respect to its lower dissociation threshold and two further “ghost” states before the complete break-up threshold. The spatial structures of such states and of the floppy complex are analyzed in detail, as is the possibility of detecting Efimov-type states in such a weakly bound aggregate. Finally, the inclusion of three-body (3B) forces in the description of the full interaction and its effect on the number of possible bound states is also discussed. © 2001 American Institute of Physics.

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I. INTRODUCTION

The experimental use of supersonic jets has been very successful over the last two decades in generating beams of cold, and nearly isolated, molecules,^{1–3} thereby providing a great deal of information on the energetics and structural properties of very weakly bound molecular species. The ability to cool molecules below 1 K indeed facilitates the exploration of ultracold molecular physics and ultracold collisions, as has been shown by recent research.^{4–7} As an example of it, small bosonic helium clusters, ${}^4\text{He}_N$, have been the subject of many experimental and theoretical studies and the existence of weakly bound ${}^4\text{He}$ dimers has been suggested over the years by independent experiments.^{8,9} The more recent transmission grating observations¹⁰ also provide a promising technique to study ${}^4\text{He}_N$ clusters with N up to about 20–30 atoms, thereby indicating in a quantitative way the relative stabilities of these very weakly molecular species.

The interest on the properties of such “molecules” is

both experimental and theoretical in nature, since the possibility of proving the existence of polyatomic aggregates with several atoms hinges on our capability of also showing, via computational modeling, the specific features of these unusual bound species and the expected values of the binding energies for their ground and excited states. An illuminating review of such methods¹¹ and some of the results for specific cases^{12,13} have been already published in recent years and we, therefore, refer any interested reader directly to them without giving here any further detail.

Among the variety of studied systems the clusters of ${}^4\text{He}$ possess a rather rich and intriguing set of properties related to their very weak interaction forces and to their weak response to external fields induced by additional atomic and molecular “impurities.” The latter species, in fact, could be added to the initial helium cluster by taking advantage of the ease with which these aggregates can pick up one or more of such impurities.¹⁴ In the present study we specifically intend to analyze in some detail the structural consequences of adding to the simplest ${}^4\text{He}$ cluster, the helium dimer, one of the ionic impurities which has been already shown to interact with one ${}^4\text{He}$ atom through a very weak potential, i.e., the H^- impurity.¹⁵

The problem here, in fact, is to analyze the overall spatial shape of this special triatomic ion and to establish the number and nature of the bound states of this system in order to relate the present findings with those already obtained and discussed by us for another impurity that shows similarly

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weak interactions with ${}^4\text{He}$ and ${}^4\text{He}_2$: the Li atomic species.^{16,17}

The present study is organized as follows: The next Sec. II briefly describes the interaction potentials which we employ in this work while Sec. III reviews the computational methods used to obtain the bound states and the spatial features of the triatomic ion. Section IV reports the results and analyzes them in some detail, while in Sec. V we discuss the consequences of scaling the strength of the potential-energy surface in the search for Efimov-type states. Since the number of bound trimer states can change with the potential, in Sec. VI we report some preliminary *ab initio* calculations of the full interaction when the 3B effects are also included. Our conclusions are finally summarized in Sec. VII.

II. THE POTENTIAL-ENERGY SURFACE (PES)

The study of the ${}^4\text{HeH}^-$ interaction has been recently revived because of the corresponding interest in the isoelectronic ${}^4\text{He}_2$ dimer and, as mentioned before, its bound state features. The negative ionic character of ${}^4\text{HeH}^-$, however, leads to a very different two-body (2B) interaction with respect to the neutral dimer and, therefore, to a very different potential-energy curve. Since the H atom has a sizeable electron affinity (0.7542 eV) while the He^- system is unstable, the two-particle system will preferably have $\text{He}+\text{H}^-$ as its lower dissociating threshold for the ground electronic state.¹⁵ Hence, the charge-induced interaction at large distances will behave as proportional to R^{-4} and, therefore, will go to zero more slowly than the dispersion interaction in ${}^4\text{He}_2$.

The recent full-configuration-interaction (FCI) calculations¹⁵ on the 2B potential have produced a very accurate description of it, suggesting a rather small well depth of the potential ($\sim 4.0\text{ cm}^{-1}$), a large value of the distance where the minimum is located (about 13 bohr) and a very long tail for the vibrational ground-state wave function. The calculations also showed the presence of an excited rotational state with $J=1$ in addition to the single bound state found for $J=0$.

Another recent calculation on the same system¹⁸ adopted instead a model potential approach and assumed the full ${}^4\text{HeH}^-$ interaction to consist of the pair interactions between the extra electron and the two atomic partners. The authors of Ref. 18, therefore, solved the one-electron diatomic molecular ion, within the Born–Oppenheimer (BO) approximation, by using spheroidal coordinates to obtain a two-dimensional eigenvalue equation at each internuclear separation R and by then solving the ensuing equation with the use of two-dimensional B-Spline functions.¹⁸ Because of the marked differences between the two methods, the computed data do not agree quantitatively with each other although the qualitative conclusions are very similar. We summarize in Table I the results given by the two methods for the properties of this dimer. In the present work we have used for the ${}^4\text{He}-\text{H}^-$ interaction the FCI calculations via the analytical fit employed by Casalegno *et al.*¹⁹ in recent Monte Carlo (MC) calculations for $(\text{He})_N\text{H}^-$ clusters. For the ${}^4\text{He}_2$ interaction potential we have adopted the one proposed by Aziz and Slaman²⁰ as in our previous calculations.^{16,17,21,22}

TABLE I. Computed properties of the ${}^4\text{HeH}^-$ interaction potentials from Refs. 15 and 18.

2B property	Ref. 15	Ref. 18
$R_{\min}/\text{bohr}$	12.88	11.5
D_e/cm^{-1}	3.22	4.99
$\epsilon_0^{J=0}/\text{cm}^{-1}$	-0.4000	-0.952
$\epsilon_0^{J=1}/\text{cm}^{-1}$	-0.0447	-0.393
$\langle R \rangle^{J=0}/\text{bohr}$	22.54	17.9
$\langle R \rangle^{J=1}/\text{bohr}$	...	20.2

We report in Fig. 1 the relative shapes and strength values of the 2B potentials considered here: The HeH^- interaction is clearly shallower and more repulsive than the corresponding HeHe potential, as already seen by previous work.^{15,18,23} However, the different shape of the long-range tail of the 2B interaction makes the HeH^- potential capable of supporting a more strongly bound state which is more “compact” in space, albeit still very diffuse, than the corresponding bound state of ${}^4\text{He}_2$.²¹

The simplest construction of a three-body (3B) interaction potential for the trimer is to treat the system as a sum of 2B interactions between partners

$$V(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = [V_{\text{HeH}^-}(\mathbf{R}_1) + V_{\text{HeH}^-}(\mathbf{R}_2) + V_{\text{HeHe}}(\mathbf{R}_3)]. \quad (1)$$

Due to the relative weakness of each 2B potential this may not be an unrealistic ansatz. It is the one which has been used in all the previous calculations for this trimer.^{19,23}

FIG. 1. Representation of the atom–atom potentials employed in the present work. Distances in Å and potential values in cm^{-1} . See text for the references associated to each potential curve.

FIG. 2. Two-dimensional energy levels for the potential of Eq. (1), using Jacobi coordinates for the complex. The energy values are given in cm^{-1} .

In Fig. 2 we present the potential-energy maps obtained from our potential via Eq. (1) for the range of available (R, r, θ) values as given by writing 2B interactions within a Jacobi coordinate representation. One clearly sees there the existence of symmetric, D_{2h} , minima corresponding to the H^- partner located between 7 and 8 Å away from the midpoint of the He_2 diatomic. However, as we shall further discuss below, the overall weakness of the full interaction and the high delocalization of the bound atomic partners makes it very difficult to analyze the spatial structure of this very floppy triatomic within the conventional language of rigid molecular structures.

III. CALCULATION OF THE BOUND STATES

One could approach the construction of the relevant, total Hamiltonian within a Born–Oppenheimer (BO) picture as being given through the Jacobi coordinates described before, whereby the H^- partner is viewed as weakly bound to an equally weakly bound $^4\text{He}_2$ molecule. One can then employ

the PES of Fig. 2 over a broad range of coordinates and a rather dense grid of radial and angular values, hence realistically map the physical space within which one expects the present triatomic molecule to be located.

As is well known, Light and co-workers^{24,25} have pioneered the use of the so-called discrete variable representations (DVR's) in quantum-mechanical problems, a powerful device which becomes applicable whenever the following conditions are satisfied: (i) There exists a basis set $\{\varphi_n(x); n=1, N\}$ onto which one can expand the wave function of the system, and (ii) a (Gaussian) quadrature rule consisting of a set of quadrature points $\{x_n; n=1, N\}$ and weights $\{w_n; n=1, N\}$ can be used to compute matrix elements of the relevant operators within the above basis. Whenever such conditions are satisfied, there exists an isomorphism between the finite basis representation (FBR) into $\{\varphi_n\}$ and a discrete representation of coordinate eigenfunctions based on the quadrature points. The quadrature points thus become the eigenvalues of the FBR of the coordinate operator so that the corresponding eigenvector matrix

specifies the chosen transformation between the coordinate eigen- functions and the original basis functions.^{26,27}

We have, therefore, carried out calculations of the bound states for the ${}^4\text{He}_2\text{H}^-$ system by using spherical oscillators to represent the radial basis and Legendre polynomials for the angular basis.^{24,28} In order to reach numerical convergence, we employed 100 functions along the He–He distance (with r going from 0 to 80 Å), also 110 functions along R , which was varied between 0 and 90 Å, and 24 angular values between $\theta=0^\circ$ and 90° . The details of the numerical implementation have been given before²⁵ and will not be repeated here as we have followed the same procedure.

An alternative approach to the problem consists in using atom–atom pair coordinates $\{R_1, R_2, R_3\}$, with the Hamiltonian written down in terms of 2B interaction potentials

$$H = T + \sum_{i=1}^3 V(R_i), \quad (2)$$

the volume element being $R_1 R_2 R_3 dR_1 dR_2 dR_3$. The corresponding kinetic-energy operator for a system of two identical particles and a third different partner can be written as¹⁶

$$T^S = -\frac{\hbar^2}{2\mu} \left\{ \frac{1}{R_1^2} \frac{\partial}{\partial R_1} R_1^2 \frac{\partial}{\partial R_1} + \frac{1}{R_2^2} \frac{\partial}{\partial R_2} R_2^2 \frac{\partial}{\partial R_2} + \frac{2}{R_3^2} \frac{\partial}{\partial R_3} R_3^2 \frac{\partial}{\partial R_3} + \frac{R_1^2 - R_2^2 + R_3^2}{R_1 R_3} \frac{\partial^2}{\partial R_1 \partial R_3} + \frac{R_2^2 - R_1^2 + R_3^2}{R_2 R_3} \frac{\partial^2}{\partial R_2 \partial R_3} \right\} \\ - \frac{\hbar^2}{m_H} \left\{ -\frac{1}{R_3^2} \frac{\partial}{\partial R_3} R_3^2 \frac{\partial}{\partial R_3} + \frac{R_1^2 + R_2^2 - R_3^2}{2R_1 R_2} \frac{\partial^2}{\partial R_1 \partial R_2} - \frac{R_1^2 - R_2^2 + R_3^2}{2R_1 R_3} \frac{\partial^2}{\partial R_1 \partial R_3} - \frac{R_2^2 - R_1^2 + R_3^2}{2R_2 R_3} \frac{\partial^2}{\partial R_2 \partial R_3} \right\}, \quad (3)$$

where $\mu = m_H \cdot m_{\text{He}} / (m_H + m_{\text{He}})$. The inclusion of the scale factor $(R_1 R_2 R_3)^{1/2}$ in order to get the standard normalization of the total wave function $\Psi(R_1, R_2, R_3)$ leads to the final Hamiltonian expression which we have given in detail elsewhere for the case of zero total angular momentum.¹⁷ As in our previous work, we have expanded the wave function in terms of a set of distributed Gaussian functions²⁸ (DGF's) which take into account the proper symmetry of the system.^{16,17}

After careful numerical tests, we have finally employed a basis of 22 Gaussian functions which depend on each atom–atom pair coordinate and are centered as follows: 3, 3.7, ..., 12.1, 13, 14, ..., 17, 20, 23, and 26 Å. They are given by

$$\varphi_p(R_i) = \left(\frac{2A_p}{\pi} \right)^{1/4} e^{-A_p(R_i - R_p)^2}, \quad (4)$$

where R_p is the center of the p th Gaussian, the corresponding width being controlled by

$$A_p = \frac{4\beta}{(R_{p+1} - R_{p-1})^2} \quad (5)$$

with a selected optimal β value of 1.05.

The total wavefunction for the nuclear part of the triatomic system is expanded over a basis function set ϕ_j as

$$\Psi_k(R_1, R_2, R_3) = \sum_j a_j^{(k)} \phi_j(R_1, R_2, R_3), \quad (6)$$

where each ϕ_j function is a Hartree-type product of three φ Gaussian functions

$$\phi_j(R_1, R_2, R_3) = N_{lmn}^{-1/2} \sum_{P \in S_2} P[\varphi_l(R_1) \varphi_m(R_2)] \varphi_n(R_3). \quad (7)$$

Here, as in Eq. (6), j stands for a collective index $j = (l \leq m, n)$ and R_3 represents the He–He distance within the trimer. In turn, the N normalization factors become

$$N_{lmn} = 2s_{nn}(s_{ll}s_{mm} + s_{lm}^2), \quad (8)$$

with the s_{ij} 's being the overlap integrals

$$s_{ij} = \langle \varphi_i | \varphi_j \rangle. \quad (9)$$

In order to satisfy the triangular constraint for the molecular geometries, $|R_1 - R_2| \leq R_3 \leq (R_1 + R_2)$, then one accepts in Eq. (6) only those three-function products for which the centers of the corresponding DGF's satisfy the requirements: $R_n \leq R_l + R_m$ and $R_m \leq R_l + R_n$. Under such conditions, the selected 22 DGF's on each coordinate generate a basis of Hartree products for expansion (6) that amounts for a total of 3060 ϕ_j 's as defined in Eq. (7). In this way, the deviation from the triangular requirement, as we defined in Ref. 22, is estimated to be lower than 1%.

The advantage of using pair coordinates consists on the fact that a variety of spatial indicators, which help us to better describe the diffuse and floppy nature of trimers, can be readily estimated. In particular, it is possible to tackle the study of the spatial positioning of the partner atoms with respect to the center-of-mass (c.m.) or to the geometrical center (GC) of the trimer molecule. Thus, the distances of the three atoms to the c.m., in terms of the interparticle coordinates, are

$$r_{\text{H-CM}} = \frac{m_{\text{He}}}{M} \sqrt{2R_1^2 + 2R_2^2 - R_3^2}, \quad (10)$$

$$r_{\text{He}_1\text{-CM}} = \frac{1}{M} \sqrt{m_H m_{\text{He}} m_0 (m_{\text{He}}^{-1} R_1^2 - m_0^{-1} R_2^2 + m_H^{-1} R_3^2)}, \quad (11)$$

$$r_{\text{He}_2\text{-CM}} = \frac{1}{M} \sqrt{m_{\text{H}} m_{\text{He}} m_0 (m_{\text{He}}^{-1} R_2^2 - m_0^{-1} R_1^2 + m_{\text{H}}^{-1} R_3^2)}, \quad (12)$$

where $M = 2m_{\text{He}} + m_{\text{H}}$, $m_0 = m_{\text{He}} + m_{\text{H}}$, and the He atoms have been labeled 1 and 2. Similarly, the distances of the three atoms to the GC can be written as

$$r_{\text{H-GC}} = \frac{1}{3} \sqrt{2R_1^2 + 2R_2^2 - R_3^2}, \quad (13)$$

$$r_{\text{He}_1\text{-GC}} = \frac{1}{3} \sqrt{2R_1^2 - R_2^2 + 2R_3^2}, \quad (14)$$

$$r_{\text{He}_2\text{-GC}} = \frac{1}{3} \sqrt{-R_1^2 + 2R_2^2 + 2R_3^2}. \quad (15)$$

The corresponding expectation values, therefore, require the evaluation of integrals of the form

$$\begin{aligned} \langle \Psi_k | r_{\text{X-C}} | \Psi_k \rangle &= \sum_{jj'} a_{jj'}^{(k)} \langle \phi_j | r_{\text{X-C}} | \phi_{j'} \rangle \\ &= \sum_{jj'} a_{jj'}^{(k)} \sum_{pp'} \mathcal{N}_{jj'}^{-1/2} \langle P[\varphi_l \varphi_m] \varphi_n | r_{\text{X-C}} \\ &\quad \times | P'[\varphi_l' \varphi_m'] \varphi_{n'} \rangle, \end{aligned} \quad (16)$$

where $r_{\text{X-C}}$ is the corresponding distance between the atom X and the center C (CM or GC) of the system, $a_{jj'}^{(k)} = a_j^{(k)} a_{j'}^{(k)}$ and $\mathcal{N}_{jj'} = N_{lmn} N_{l'm'n'}$. The integrals between the DGFs can be accurately computed by using

$$\langle \varphi_l \varphi_m \varphi_n | r_{\text{X-C}} | \varphi_l' \varphi_m' \varphi_{n'} \rangle \approx r(R_1^\dagger, R_2^\dagger, R_3^\dagger) s_{ll'} s_{mm'} s_{nn'}, \quad (17)$$

$r(R_1^\dagger, R_2^\dagger, R_3^\dagger)$ is here the distance evaluated at the centers $R_1^\dagger$, $R_2^\dagger$ and $R_3^\dagger$ of the Gaussian functions obtained as the product of the two Gaussian φ -functions associated to each coordinate.

In a similar way, as discussed earlier by us,²² the expectation values for the cosine of the angle associated to each X atom, $\langle \cos \theta_X \rangle$, and higher moments, $\langle \cos^n \theta_X \rangle$, can be easily estimated. Another significant quantity is the root-mean-square (rms) value of the area “covered” by the trimer, $\sqrt{\langle S^2 \rangle}$, where S^2 can be expressed as

$$S^2 = \frac{1}{8} (R_1^2 R_2^2 + R_1^2 R_3^2 + R_2^2 R_3^2) - \frac{1}{16} (R_1^4 + R_2^4 + R_3^4). \quad (18)$$

Finally, an additional indicator of the contribution of each triangular structure, j , to the corresponding k th bound state is provided by a pseudo-weight defined as²²

$$P_j^{(k)} = a_j^{(k)} \langle \Psi_k | \varphi_j \rangle, \quad (19)$$

this piece of information is typical of the DGF variational approach and will be used extensively below to draw physical information on the shapes of the floppy triatomic complex.

IV. COMPUTATIONAL RESULTS

As mentioned before, several calculations have been carried out recently on the structure of the bound states supported by the ${}^4\text{He}_2\text{H}^-$ triatomic complex^{19,23} and, therefore, it also becomes of interest to compare the earlier findings with the present results. Recent variational and diffusion Monte Carlo calculations (VMC and DMC)¹⁹ have been

TABLE II. Calculated ${}^4\text{He}_2\text{H}^-$ bound states, in cm^{-1} , using the methods of this work. For comparison, earlier results are also presented (columns 1–3).

k	Hyperspherical ^a	VMC ^b	DMC ^b	DVR ^c	DGF ^c
0	−1.1885	−1.0565	−1.0912	−1.0989	−1.0902
1	−0.5421			−0.8563	−0.8478
2	−0.0037			−0.3239	−0.3261
3				−0.0911	−0.0821

^aFrom Ref. 18.

^bFrom Ref. 19.

^cPresent calculations.

based on the same potential form as that used by us in Eq. (1), that is, the same 2B potential to describe ${}^4\text{HeH}^-$ but a slightly different ${}^4\text{He}_2$ potential.²⁹ The potential used here for the 2B He–He interaction,²⁰ however, differs very little from the latter and, therefore, it is expected to yield a substantially similar PES for the triatomic complex.

We report in Table II a summary of the eigenvalues found for the present trimer in its $J=0$ state using the various methods discussed above. Since the dissociation threshold of the ${}^4\text{He}_2$ system is $\sim -0.001 \text{ cm}^{-1}$, while that for the ${}^4\text{HeH}^-$ system is $\sim -0.4 \text{ cm}^{-1}$, it follows that only the first two energy levels are bound with respect to both asymptotes, while those for $k=2$ and 3 are bound only with respect to the higher energy threshold of ${}^4\text{He}_2$ dissociation but are ghost states with respect to ${}^4\text{He}$ release

We clearly see in Table II how the differences representing the ${}^4\text{HeH}^-$ potential cause very marked energy differences within the binding energies of the triatomic system: Both the number and positions of the bound states found with hyperspherical coordinates within the adiabatic approximation²³ differ markedly from ours.

On the other hand, the present calculations which use two entirely different approaches, the DVR treatment and the DGF expansion, are seen to be in very good agreement with each other: In fact, the present bound states supported by the triatomic complex agree within 1% of each other. This indicates convergence of the two methods to the same set of results. The earlier Monte Carlo calculations¹⁹ could only

TABLE III. Average magnitudes of the triatomic complex when using the DGF expansion of the present work. Energy in cm^{-1} , distances in Å. In parentheses, fluctuation values of the corresponding quantities. In the last row, the rms of the area, $\sqrt{\langle S^2 \rangle}$ is expressed in Å².

$k=$	0 ^a	0	1	2
$E=$	−1.0912	−1.0902	−0.8478	−0.3261
r_{HeH^-}	11.11	10.92(3.37)	11.10(3.68)	13.97(5.77)
r_{HeHe}	7.86	9.63(4.90)	14.77(6.70)	21.71(7.50)
$r_{\text{He-CM}}$	5.25	4.95(2.45)	7.46(3.31)	10.90(3.77)
$r_{\text{H-CM}}$	6.88	8.39(3.10)	6.62(3.49)	7.92(3.66)
$\cos \theta_{\text{He}}$	...	0.40(0.47)	0.64(0.44)	0.73(0.33)
$\cos \theta_{\text{H}}$	...	0.51(0.54)	−0.05(0.70)	−0.22(0.55)
$\text{rms}(S)$	...	43	53	91

^aFrom Ref. 19.

FIG. 3. Computed radial distributions along the internal coordinates of the triatomic complex obtained from the variational DGF expansion discussed in the main text. The distributions refer to the ground state of the complex.

produce the ground-state energy but their results also turn out to be very close to ours, in particular their DMC results.¹⁹

In Table III we list several properties of the bound states of the trimer obtained by using the DGF method. The following comments are in order:

- (i) We report results for three bound levels in spite of the fact that only the first two are lower than both dissociation thresholds. The reason to include the third (*ghost*) level is its proximity in energy to the HeH^- dimer;
- (ii) the floppiness of the molecular structure is clearly visible from the large fluctuation values displayed by radial and angular quantities: The triatomic structure is obviously not given by a unique, rigid molecular structure. The rms of the area also gives an indication on the size of the triatomic cluster. The corresponding areas found for the different bound states are of the order of those reported for the ground state of the LiHe_2 system;^{16,17}
- (iii) for $k=0$, the bond distances are not very different between the three particles, although the H^- is found to be at a larger distance from any He atom than either of the helium partners. This is in qualitative agreement with the results of Ref. 19 which are reported in the first column of the table. This situation is just the opposite to the $k=1, 2$ cases, where the He–He distance becomes the largest;
- (iv) due to the large fluctuations in the cosine of bond angles, very high moments become necessary to describe the corresponding distributions, showing again the strongly floppy character of this cluster. One should also notice that the states with $k=1, 2$ chiefly correspond to a bending excitation of the θ_{H^-} angle. In particular, the $k=2$ state presents a marked linear geometry in which the hydrogen is placed in between the helium atoms.

FIG. 4. Families of triangular configurations obtained from the dominant Hartree-type basis functions, Eq. (7), employed for the ground state of the complex. Their corresponding pseudoweights are given in Table IV.

The ground-state ($k=0$) pair distributions are given in Fig. 3. One clearly sees there the agreement with what we have mentioned above and found by the VMC–DMC calculations of Ref. 19: The distribution of H^- with respect to either ^4He atoms peaks much further out than the pair ^4He – ^4He distribution. Our current calculations that used a DMC approach to obtain radial observables for clusters with a larger number of He atoms indeed appear to confirm the present findings.³⁰

The use of the pseudo-weights defined in Eq. (19) further allows us to obtain a more appealing pictorial view of the possible geometries which contribute to the description of the present system. A summary of the leading triangular configurations is reported in Fig. 4, while their relative importance is listed in Table IV for the ground, $k=0$ level. Such configurations were selected taking into account the centers of the Gaussian functions and allowing a tolerance given by the grid step. We see that the scalene configurations (marked *S* in Table IV) provide by far the largest contribution to the description of the system, ($\sim 60\%$). However, the two isosceles structures [marked $I^{(1)}$ and $I^{(2)}$ in Fig. 4 and Table IV] also provide sizeable contributions, accounting for $\sim 25\%$, while the equilateral structure is almost negligible.

TABLE IV. Computed sum of pseudo-weights, Eq. (21), for the different configurations collected in Fig. 5, corresponding to the ground trimer state. The Σ runs over all the triangle structures belonging to a given configuration. The highest contributing structure to each family of configurations is also listed in terms of pair coordinates, R_i , defining the Gaussian centers, as well as the corresponding atom distances from the GC, $r_{\text{X-GC}}$. All distances in Å.

	$\Sigma_j P_j^{(0)} (\%)$	R_1	R_2	R_3	$r_{\text{H}^- \text{GC}}$	$r_{\text{He}_1 \text{GC}}$	$r_{\text{He}_2 \text{GC}}$
$C^{(1)}$	4.77	7.9	9.3	17.0	1.0	8.3	8.7
$C^{(2)}$	6.14	8.6	13.0	5.1	7.1	1.8	5.9
$I^{(1)}$	13.42	7.9	8.6	4.4	5.3	3.1	3.7
$I^{(2)}$	12.46	8.6	10.0	7.9	5.6	4.4	5.3
<i>E</i>	1.09	7.9	8.6	7.9	4.8	4.4	4.8
<i>S</i>	62.13	8.6	10.0	4.4	6.0	3.1	4.3

Finally, it is interesting to note that the collinear structures roughly weight 10% and, therefore, also play a role.

To carry out this analysis even further, we present in Table IV, for the $k=0$ state, the values of the atom-atom distances and of the partner distances from the GC shown by the dominant configuration which occurs within each family of triangles analyzed in the table and shown in Fig. 4. By looking at the r_{H^-GC} distance in the most important triangular configurations (S , $I^{(1)}$, and $I^{(2)}$), one immediately realizes the agreement with the maximum of the radial distribution reported in Ref. 19 which was found at $r_{H^-GC} \sim 5.82$ Å. Furthermore, we see that the distances of H^- from the GC, which correspond to keeping it closer to GC, ($C^{(1)}$) or further away, ($C^{(2)}$) than the two helium atoms, indeed belong to configurations where the overall shape of the complex tends to be quasilinear. They have a very small but finite probability, in agreement with the conclusion reported by Ref. 19. Moreover, the average of the distances defined in Eqs. (13)–(15), $\langle r_{X-GC} \rangle$, become 6.30 Å for H^- and 5.89 Å for the He atom, the fluctuations being 2.33 and 2.40 Å, respectively. Thus, these results suggest that the dominant configurations indeed correspond to the helium atoms being closer to the GC than the H^- impurity, as obtained by the Monte Carlo calculations¹⁹ and indicated by our radial distributions of Fig. 3.

V. POTENTIAL SCALING AND EFIMOV STATES

As discussed in our previous work,^{16,17,21,22} one of the additional interests for the weakly bound three-body aggregates relates to the earlier studies in nuclear physics carried out by Efimov.³¹ In this context, a special effect was suggested to occur whenever each dimer involved in the triatomic species has no bound states but does exhibit a zero resonance. The ensuing Efimov effect amounts to a situation where the 3B system can now support infinitely many bound states which can accumulate at the dissociation threshold. The corresponding total wave function for the system thereby acquires a very extended spatial distribution over the fairly compact range of action of the full 3B interaction given by a sum of 2B potentials. In the case of an identical particle system (with, therefore, only one 2B potential involved) one can gauge the features of the full interaction by introducing a strength parameter λ . In contrast with the standard, expected behavior of common bound states, the Efimov-type states gradually disappear with increasing λ .

The purpose of this section is to analyze the feasibility of the existence of Efimov-type states in this trimer. The usual procedure is to vary λ and then to estimate the number, $N_E(\lambda)$, of such diffuse states through the following expression:³¹

$$N_E(\lambda) = \frac{1}{\pi} \ln \frac{|a_0(\lambda)|}{r_0(\lambda)}, \quad (21)$$

where a_0 is the scattering length at zero energy for s -wave scattering, and r_0 the effective range of the λ -scaled 2B interaction. Only when N_E is found to be close to or greater than unity the 3B system would be expected to show the presence of Efimov states. This prescription works fairly

FIG. 5. Effects of potential scaling on the $^4\text{HeH}^-$ properties: Behavior of its $J=0$ bound state and the s -wave scattering length as a function of the λ values.

well in the case of boson helium trimers,^{21,22,32} as well as in the $^6\text{Li}^4\text{He}_2$ system.¹⁶ However, the isotopic counterpart system, $^7\text{Li}^4\text{He}_2$, shows the presence of an Efimov-type state for λ values close to one in spite of a value of $N_E \sim 0.4$ found for the $^7\text{Li}^4\text{He}$ dimer.¹⁶

One way of extracting a_0 and r_0 is to fit the behavior of the phase-shift to the expression³³

$$\kappa \cot \eta_0(\kappa) = -a_0^{-1} + \frac{1}{2} r_0 \kappa^2 + O(\kappa^4), \quad (22)$$

where $\eta_0(\kappa)$ is the s -wave phase-shift, estimated through a Numerov propagation in the continuum, at the collision wave-vector κ . In the present situation for the $^4\text{HeH}^-$ potential, however, the simple definition of above does not apply since r_0 cannot be defined for a potential falling off to zero as r^{-4} like in this case.³⁴ By using the modified effective range theory, however, the scattering length has still physical meaning,^{35,36} and can be obtained by reaching numerical convergence for the s -wave phaseshift calculations as κ goes to zero. In the present case, when $\lambda=1.0$, a value of $+0.303$ Å was found for a_0 .

The calculated dependence of a_0 on a range of λ values for the $^4\text{HeH}^-$ dimer is reported in Fig. 5, where the results clearly show that the criticality needed for the presence of Efimov-type states occurs with a modified 2B potential the strength of which has become unrealistically small ($\lambda \sim 0.34$). It, therefore, follows that the present triatomic complex does not seem to show Efimov-type diffuse states unless its overall strength is unrealistically reduced.

Another feature of the diffuse bound states of the 3B systems, when analyzed in terms of 2B potential details, involves the location of halo states, i.e., of the presence of “local” 3B bound states when neither of the 2B potentials supports, when alone, either bound states or zero-energy resonances. In the present case we know that the helium dimer potential already does not support anymore a bound state for $\lambda < 1$ but very close to it. On the other hand, a very strong variation of the 2B potential of the ionic dimer within

FIG. 6. Dependence of the complex bound state energies on the global strength of the PES as defined by Eq. (23). See main text for meaning of symbols. All energies are in cm^{-1} .

the trimer is necessary for its bound state to disappear (e.g., see Fig. 5). Through the onset of the dimer bound state, which in turn coincides with the critical behavior of the scattering length, we clearly see again that one needs to dramatically reduce the 2B potential strength in order to be able to locate halo states in the trimer system. Given the unrealistically reduced interaction, it is very unlikely that the “exact” interaction within the ${}^4\text{He}_2\text{H}^-$ complex could give rise to such a special type of bound state.

As was mentioned earlier,¹⁶ some caution about the reliability of the prediction of the number of Efimov-type 3B bound states from 2B properties, as given by Eq. (21), may be in order here. In Fig. 6 we show the energy dependence of all the relevant bound states by plotting the energy values, E_b , as a function of the λ parameter. The global prescription for scaling the strength of the 3B interaction is given as

$$V(R_1, R_2, R_3) \Rightarrow \lambda V(R_1, R_2, R_3) \\ = \lambda \left[V_{\text{He}_2}(R_3) + \sum_{i=1}^2 V_{\text{HeH}^-}(R_i) \right]. \quad (23)$$

We clearly see in Fig. 6 that, at least in the limited potential region where λ is varied at most by 20%, the first excited state below the ${}^4\text{HeH}^- + {}^4\text{He}$ dissociation channel, labeled as $E_{3B}^{(1)}$ in the figure, stays well below the dissociation threshold and never tends to disappear into the continuum of the first dissociation. The next excited state, labeled here as $E_{3B}^{(2)}$ is clearly above, but close to, the first threshold for dissociation and only crosses it in the vicinity of $\lambda=1.1$.

We also carried out a sort of two-dimensional analysis of the potential strength dependence of the bound states of the trimer complex, this time by varying separately the ${}^4\text{HeH}^-$ and HeHe diatomic potentials. The corresponding potential scaling, therefore, becomes

FIG. 7. Two-dimensional dependence of the complex second excited-state energy, $E_{3B}^{(2)}$, in comparison with the location of the lower dissociation threshold, $E_{\text{He}_2\text{H}^-}^{(0)}$. The upper three panels show their dependence on the variation of the strength parameter of the ${}^4\text{He}_2$ interaction at fixed values of the ${}^4\text{HeH}^-$ interaction, as given by Eq. (24). The lower three panels show the results for the potential changes of the ${}^4\text{HeH}^-$ interaction at fixed ${}^4\text{He}_2$ potential strength values.

$$V(R_1, R_2, R_3)$$

$$\Rightarrow [\lambda_1 V_{\text{He}_2}(R_3) + \lambda_2 V_{\text{HeH}^-}(R_1) + \lambda_2 V_{\text{HeH}^-}(R_2)], \quad (24)$$

and the results are reported in Fig. 7. The six panels show only the variation of the $E_{3B}^{(2)}$ in comparison with the first dissociative threshold, i.e., the E_{HeH^-} binding energy. In the upper three panels the strength of the ${}^4\text{HeH}^-$ 2B potential is kept fixed in each panel while the strength of the ${}^4\text{He}_2$ 2B potential is varied. The complementary changes are shown in the lower three panels of Fig. 7.

One clearly sees that the strengthening of the helium dimer potential changes rather little the overall binding energy of the 3B excited state which varies instead rather markedly as the HeH^- interaction changes its strength (lower panels). On the other hand, the increase of the weaker 2B potential strength by only 2% or 3% shifts very clearly the $E_{3B}^{(2)}$, as indicated in the upper three panels. One also observes there that the dependence of the binding energy on the strength of the He_2 potential is really very weak, as already surmised by the results of the lower panel. In all examples shown there is no appearance of Efimov-type features for the 3B excited state under consideration, as already expected by the previous scattering length calculations.

We can, therefore, say from the above results, that the possible consequence of strengthening the 2B forces in the calculation of the PES of the ionic trimer would be that of making the two, already existing, bound states of the trimer even more strongly bound and to induce the eventual appearance of an additional third bound state. It deserves, however, some consideration the further possibility of directly performing *ab initio* calculations of the full PES involving the additional 3B contributions in order to assess the reliability of the results obtained through the use of the simple pairwise interaction of Eq. (2).

VI. THE FULL TRIATOMIC INTERACTION

In order to have a better understanding of the full PES features, preliminary *ab initio* calculations have been performed using the basis set of Ref. 37, uncontracting the functions used there and adding a set of diffuse functions $[(2s,2p,2d)$ on He, $(6s,6p,6d)$ on H]. All calculations were performed using the MOLPRO chain, at coupled-cluster single double triple (CCSD-T) level, which means that the effect of triple excitations is taken into account in a perturbative way.³⁸ In a previous study of HeH^- it was noticed that, among the different perturbative treatments of triples available in MOLPRO, CCSD-T gives the results that were the closest to FCI.¹⁵

These full calculations have been carried out for selected geometries and started with the D_{2h} symmetry. The angle was then moved away from the T-shape geometry but for a limited range of He–He and He– H^- distances. Figures 8(a)–8(c) show a comparison between the selected points obtained from the full interaction and the same values from the surface as computed by using the simpler sum of Eq. (1). The three subfigures refer to three different values of the He–He distance and each of them shows four different panels at different values of the Jacobi angle and over the range of H^- distances taken from the midpoints of the $^4\text{He}_2$ dimers. The solid lines show the behavior of the potential when obtained as a sum of 2B interactions, while the dotted lines refer to the full (2B+3B) calculations. The following information could be gathered from the comparison:

- (i) In the region of quasi-collinear geometries (small θ values) the effects coming from the full interaction appear to be rather small as the dashed lines follow fairly closely the solid lines for all He–He distances;
- (ii) the onset of the repulsive wall and the location of the well are affected by 3B forces mostly in the region of triangular structures close to the isosceles geometry. In fact, the (2B+3B) calculations appear, in all panels with $\theta=60^\circ$ and 90° , to yield interaction potentials which have deeper wells and softer repulsive walls.

Although we are here talking about fairly small effects, they are rather marked at the geometries close to the T-shaped complex when one considers the weakness of the whole interaction. Thus, by carrying out our initial study via an overall PES obtained as a sum of 2B forces, we should be aware of the fact that we are possibly constructing interaction forces which are less attractive and more repulsive than

full calculations would indicate. From the model analysis of the previous section on the effects of λ scaling, however, we can already say that no more than one additional third state would become bound for a set of a more strongly interacting three particles. One should also note here that the exploratory calculations reported in this section do not intend to fully analyze the effects of 3B forces but simply to point out the likely corrections to the binding energy values which they are inducing in the present system.

VII. PRESENT CONCLUSIONS

In this work we have shown the structure of the bound states of a very floppy trimeric complex in its ground electronic state, the $^4\text{He}_2\text{H}^-$ complex, by using both Jacobi coordinates within a DVR representation and pair coordinates with a DGF expansion. Assuming a pairwise form of the overall PES, we have presently looked at the $J=0$ situation and found very good agreement between the two types of calculations: two bound states with respect to the lower dissociation threshold were found to exist. The lower bound state was also found to be in very good accord with other DMC calculations, thus providing an independent check for the present results, as seen in our Table II. Therefore, the remarkable convergence of results when using three, entirely different, computational methods, shows that the results from these methods have become highly reliable.

The use of a DGF expansion allows us to easily gain some further information on the spatial properties of the present complex since it gives us specific values for the radial size of the bound states, indication on the most preferred three-particle configurations which can describe the complex and possible comparisons with the results obtained from the DMC calculations of Ref. 19. The examination of our data *vis á vis* the suggestions made from DMC calculations, for the ground state, indicates once more good agreement between the two sets of results (e.g., see Table III). The most likely configuration turns out to be the scalene triangular shape followed by isosceles arrangements, with the H^- impurity outside the two ^4He atoms and further away. The probability of quasilinear structures, finally, is small but finite from both types of computations.

We have also looked into the likelihood for the present system to exhibit excited states with Efimov-type behavior as discussed by us in the case of other, very weakly bound, three particle complexes.^{16,17,21,22} For this purpose we have examined the critical behavior of the *s*-wave scattering length, at vanishing collision energies, for the $^4\text{HeH}^-$ potential as its strength is varied. We have found that the corresponding a_0 value appears to show criticality only for an unrealistically weakened 2B potential. The same potential is also shown to be able to possibly have *halo* states only when its strength is reduced by strong factors, hence making the above effects unlikely to occur for any realistic choice of the HeH^- interaction. We have also reduced the overall strength of the global pairwise potential and found that none of the bound states disappear through the threshold for the lower dissociation channel. We can conclude, therefore, that the $^4\text{He}_2\text{H}^-$ is very unlikely to show the presence of Efimov-type states.

FIG. 8. Computed full interaction at selected geometries, in Jacobi coordinates, for the ${}^4\text{He}_2\text{H}^-$ complex. (a) For the He-He distance of 5.0 bohr; (b) For an He-He distance of $6.0 a_0$ and (c) For an He-He distance of 7.0 bohr. The solid lines labeled "2B sum" refer to the potential from Eq. (1) while the dashed lines labeled "3B" report the full *ab initio* CCSD-T calculations.

On the other hand, one of the excited bound states is seen to cross the threshold for the lower dissociation channel at moderate strengthening values, $\lambda \sim 1.1$, suggesting that such a state could become an actual bound level if the 3B forces were to be properly included. The contribution of such forces on the full interaction has been analyzed at a preliminary level by carrying out additional CCSD-T calculations for a set of selected geometries of the three-particle complex. A comparison of such computations with the interaction obtained instead as a sum of 2B terms showed that, especially for the nuclear configurations near to the T-shape geometries, the 3B forces are not negligible and cause the correct interaction to be both more attractive in the well region and with a “softer” repulsive wall. Thus, we expect that the present pairwise PES is likely to be qualitatively correct, although room for improvement still exists at the quantitative level.

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- ¹e.g., see D. H. Levy, L. Wharton, and R. E. Smalley, in *Chemical and Biochemical Applications of Lasers*, edited by C. B. Moore (Academic, New York, 1977), Vol. 2.
- ²M. S. Beck, D. L. Morris, M. G. Livermann, and R. E. Smalley, *J. Chem. Phys.* **70**, 1062 (1969).
- ³J. P. Toennies and A. F. Vilesov, *Annu. Rev. Phys. Chem.* **49**, 1 (1998).
- ⁴A. Amirav, U. Even, J. Jortner, F. W. Birss, and F. A. Ramsay, *Can. J. Chem.* **61**, 278 (1983).
- ⁵S. Goyal, D. L. Schutt, and G. Scoles, *Phys. Rev. Lett.* **69**, 933 (1992).
- ⁶R. Frochtenicht, J. P. Toennies, and A. Vilesov, *Chin. Phys. Lasers* **229**, 1 (1994).
- ⁷A. Rionetti, D. Comparat, A. Crubellier, O. Dulieu, F. Masnou-Seeuws, and R. Pillet, *Phys. Rev. Lett.* **80**, 4402 (1998).
- ⁸F. Luo, G. C. Mc Bane, G. Kim, C. F. Giese, and W. R. Gentry, *J. Chem. Phys.* **98**, 3564 (1993).

- ⁹W. Schöllkopf and J. P. Toennies, *Science* **266**, 1345 (1994).
- ¹⁰W. Schöllkopf and J. P. Toennies, *J. Chem. Phys.* **104**, 1155 (1996).
- ¹¹K. B. Whaley, *Int. Rev. Phys. Chem.* **13**, 41 (1994).
- ¹²R. N. Barnett and K. B. Whaley, *J. Chem. Phys.* **96**, 2953 (1992).
- ¹³R. N. Barnett and K. B. Whaley, *Phys. Rev. A* **47**, 4082 (1993).
- ¹⁴See, e.g., A. Scheidermann, J. P. Toennies, and J. A. Northby, *Phys. Rev. Lett.* **64**, 1899 (1999).
- ¹⁵G. L. Bendazzoli, S. Evangelisti, and F. Passerini, *Chem. Phys.* **215**, 217 (1997).
- ¹⁶I. Baccarelli, G. Delgado-Barrio, F. A. Gianturco, T. Gonzalez-Lezana, S. Miret-Artés, and P. Villarreal, *Europhys. Lett.* **50**, 567 (2000).
- ¹⁷I. Baccarelli, G. Delgado-Barrio, F. A. Gianturco, T. Gonzalez-Lezana, S. Miret-Artés, and P. Villarreal, *Phys. Chem. Chem. Phys.* **2**, 4067 (2000).
- ¹⁸Y. Li and C. D. Lin, *Phys. Rev. A* **60**, 2009 (1999).
- ¹⁹M. Casalegno, M. Mella, G. Morosi, and D. Bressanini, *J. Chem. Phys.* **112**, 69 (2000).
- ²⁰R. A. Aziz and M. J. Slaman, *J. Chem. Phys.* **94**, 8047 (1994).
- ²¹T. Gonzalez-Lezana, J. Rubajo-Soneira, S. Miret-Artés, F. A. Gianturco, G. Delgado-Barrio, and P. Villarreal, *Phys. Rev. Lett.* **82**, 1648 (1999).
- ²²T. Gonzalez-Lezana, J. Rubajo-Soneira, S. Miret-Artés, F. A. Gianturco, G. Delgado-Barrio, and P. Villarreal, *J. Chem. Phys.* **110**, 9000 (1999).
- ²³Y. Li and C. D. Lin, *J. Phys. B* **32**, 4877 (1999).
- ²⁴J. C. Light, I. P. Hamilton, and J. V. Lill, *J. Chem. Phys.* **82**, 1400 (1985).
- ²⁵S. E. Choi and J. C. Light, *J. Chem. Phys.* **90**, 2593 (1989).
- ²⁶A. S. Dickinson and P. R. Certain, *J. Chem. Phys.* **49**, 4209 (1968).
- ²⁷I. P. Harris, G. G. Engerholm, and W. D. Gwinn, *J. Chem. Phys.* **43**, 1515 (1965).
- ²⁸We employed the DVR code published in J. Tennyson, J. R. Henderson, and N. G. Fulton, *Comput. Phys. Commun.* **86**, 175 (1995).
- ²⁹K. T. Tang, J. P. Toennies, and C. L. Yiu, *Phys. Rev. Lett.* **74**, 4571 (1995).
- ³⁰C. Di Paola, F. A. Gianturco, and F. Paesani (unpublished).
- ³¹See, e.g., V. Efimov, *Comments Nucl. Part. Phys.* **19**, 271 (1990), and references therein.
- ³²T. K. Lim, K. Duffy, and W. C. Dameyt, *Phys. Rev. Lett.* **38**, 341 (1977).
- ³³M. J. Jamieson and A. Dalgarno, *Phys. Rev. A* **51**, 2626 (1995).
- ³⁴N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon, Oxford, 1965).
- ³⁵T. F. O'Malley, L. Spruch, and L. Rosenberg, *J. Math. Phys.* **2**, 491 (1961).
- ³⁶L. Rosenberg, L. Spruch, and T. F. O'Malley, *Phys. Rev.* **119**, 164 (1960).
- ³⁷P. O. Widmark, P. A. Malmqvist, and B. Ross, *Theor. Chim. Acta* **77**, 291 (1990).
- ³⁸MOLPRO is a package of *ab initio* programs written by H. J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, A. Berning *et al.*