

## Energy States of Helium-4 Dimer

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It is shown that the binding energy of helium-4 dimer for the same class of potentials depends on the set of potential parameters used. The existence of one excited vibrational state of the dimer, which is related to one node of the radial wave function, is also proved for all used potentials. Excited state energy is about  $(-0,3 \text{ mK}) \cdot k_B$ . The expectation value of the internuclear distance is about  $49 \text{ \AA}$  in the ground state and  $679 \text{ \AA}$  in the excited state.

*Key words:* energy states, helium-4 dimer, internuclear distances

### INTRODUCTION

Many physical phenomena, like superfluidity in the bulk and films, scattering on superfluid droplets, diffraction of small helium clusters, are related to the behaviour of two helium 4 atoms. Two helium atoms, isotopes  $^3\text{He}$  and  $^4\text{He}$ , may form three types of stable molecules in a restricted space:  $(^3\text{He})_2$  dimer,  $(^4\text{He})_2$  dimer and  $^3\text{He}-^4\text{He}$ .<sup>1</sup> In unrestricted space, there are two stable molecules of two isotopes:

1.  $(^4\text{He})_2$  dimer, which is bound in three-dimension (3 D) with binding energy about  $(-1.3 \text{ mK}) \cdot k_B$  (Refs. 1–4) and in two-dimension (2 D) with binding energy  $(-39.5 \text{ mK}) \cdot k_B$  (Refs. 1, 5–8);
2.  $^3\text{He}-^4\text{He}$  molecule in 2 D with binding energy  $(-3.2 \text{ mK}) \cdot k_B$  (Refs. 1, 5–8).

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The expectation value of the internuclear distance of two atoms in ground state is 47.38 Å and the root mean square deviation is 43.63 Å.<sup>1</sup> Thus, helium molecules are the largest of all diatomic molecules in the ground state. They are of great fundamental interest as systems for testing long range retardation effects – Casimir forces.<sup>9–16</sup>

The question of the existence of bound excited states is still open.

In this paper, we study the possibility of bound excited states in unrestricted space.

A standard variational procedure is used in the calculation. The following trial wave function is employed:<sup>1,17</sup>

$$\Psi_0(r_1, r_2) = \frac{1}{r_{12}} \exp[-(a/r)^\gamma - sr_{12}] \quad (1)$$

where  $r_{12}$  is the distance between atoms;  $a$ ,  $s$  and  $\gamma$  are variational parameters. The simplest excited wave function describing a change of radial distribution may be written in the form

$$\Psi_1 = (1 - br_{12})\Psi_0(r_1, r_2) \quad (2)$$

where  $b$  is a parameter which defines the node of  $\Psi_1$  and it is obtained from the orthogonality condition  $\langle \Psi_0, \Psi_1 \rangle = 0$ .

Rotational excited states could be described by

$$\Psi_{1r} = \Psi_0(r_1, r_2) Y_l^m(\theta, \phi) \quad (3)$$

where  $Y_l^m(\theta, \phi)$  is the spherical harmonic.

The organization of the paper is as follows. In next section, we formulate the variational procedure and calculate the binding energy of helium-4 dimer in the ground and excited states and the expectation value and fluctuations in the internuclear spacing. Discussion and concluding remarks are contained.

### *Variational Calculation of the Ground and Excited States*

The Hamiltonian of two helium atoms is

$$\hat{H} = -\frac{\hbar^2}{2m_1} \Delta_1 - \frac{\hbar^2}{2m_2} \Delta_2 + \hat{V}(r_{12}) \quad (4)$$

where  $m_1$  and  $m_2$  are the masses of particles 1 and 2, respectively. Many forms of potential description of the interaction between two helium atoms are available in literature. We use the Aziz and Chen form<sup>18</sup>

$$V(x) = \varepsilon V^*(x),$$

$$V^*(x) = A e^{-\alpha x + \beta x^2} - \left[ \frac{c_6}{x^6} + \frac{c_8}{x^8} + \frac{c_{10}}{x^{10}} \right] F(x)$$

$$F(x) = \begin{cases} e^{-(D/x-1)^2}, & x < D \\ 1, & x \geq D \end{cases},$$

were  $x = r/r_m$  with three sets of parameters:<sup>18-22</sup> the »best« HFD-B3-FCI1, HFD-B2(He), and HFD-B(He) which are given in Appendix.

Introducing Eqs. (1) and (2) into variational *ansatz*

$$E_n \leq \frac{\int \Psi_n^* \hat{H} \Psi_n d\vec{r}}{\int \Psi_n^* \Psi_n d\vec{r}} \quad (5)$$

where  $n = 0, 1$  denotes the ground and excited state respectively, one finds

$$E_n \leq \varepsilon_{nk} + \varepsilon_{np}, \quad (6)$$

where kinetic and potential energy are

$$\varepsilon_{nk} = \frac{I_{nk}}{I_n}, \quad \varepsilon_{np} = \frac{I_{np}}{I_n}. \quad (7)$$

The explicit forms of the integrals are given in the Appendix as well.

The integrals have been reduced to one-dimensional ones and calculated by Romberg integration with high accuracy. Parameters  $\alpha$ ,  $s$  and  $\gamma$  are obtained by a minimization procedure. Since we use the variational algorithm, the results for the energy are always above the exact values. The results are shown in Table.

TABLE I

Values of the energy (kinetic  $\varepsilon_k$ , potential  $\varepsilon_p$ , and total  $\varepsilon$  in mK), of the expectation and deviation *rms* of the internuclear distance ( $\langle r \rangle$  and  $\Delta r$  in Å), of the variational parameters ( $a$  in Å,  $\gamma$  dimensionless and  $s$  in Å<sup>-1</sup>) and of the node distance  $b^{-1}$  in Å; the numbers in the first, second, and third lines, in each state, correspond to HFD-B3-FCI1, HFD-B2 and HFD-B potential, respectively

State	$\varepsilon_{0k}$	$\varepsilon_{0k}$	$\varepsilon_{0k}$	$\langle r \rangle$	$\Delta r$	$a$	$\gamma$	$s$	$b^{-1}$
ground	105.110	-106.603	-1.498	49.2	45.5	2.74	4.49	.01100	
	105.586	-107.122	-1.536	49.2	45.5	2.74	4.51	.01100	
	109.588	-111.593	-1.594	47.4	43.7	2.737	4.492	.01145	
excited	21.378	-21.676	-0.298	678.9	502.2	2.738	4.505	.00222	229.05
	21.665	-21.973	-0.308	669.9	495.7	2.7373	4.503	.00225	226.05
	22.078	-22.396	-0.318	655.6	485.1	2.737	4.488	.00230	221.22

## DISCUSSION AND CONCLUSION

The results of variational calculations show the existence of the ground state and one excited state of helium 4 dimer. The binding energy of about  $(-1.5 \text{ mK}) \cdot k_B$  in the ground state, after corrections of the potential and retarded forces could give the value of  $(-1.3 \text{ mK}) \cdot k_B$ , as stated in literature. The expectation value of the nuclear distance in the ground state is about  $49 \text{ \AA}$  and the deviation  $45 \text{ \AA}$ . We also calculated the correction due to retardation for the HFD-B2 potential, using data from the paper,<sup>16</sup> and found  $50.1 \text{ \AA}$  for the expectation value in the ground state.

Our result for the excited state is a novel one. From the Table it can be seen that all potentials lead to the binding energy of about  $(-0.3 \text{ mK}) \cdot k_B$ . Thus it is likely that this state is present for temperatures about five times than those for which the dimer is present in the ground state. In this state, the wave function has a node at a distance of about  $226 \text{ \AA}$  and gives about  $670 \text{ \AA}$  for the expectation of the nuclear distance. The retardation increases this value to  $685 \text{ \AA}$ . It means that the retardation effects are greater than in the ground state. The retarded correction of about 10% has been found in the ground state. Therefore, Casimir forces may change the excitation energy significantly.

We believe that precise direct numerical solving of Schroedinger equation will confirm this variational result.

It is interesting to note that we have found no bound rotational state.

*Appendix*

I. The following parameters of potentials are used:

## 1. HFD-B(He)

$$\begin{array}{ll}
 \varepsilon = 15.115444 \cdot 10^{-23} \text{ J} & D = 1.4826 \\
 r_m = 2.963 \cdot 10^{-10} \text{ m} & c_6 = 1.36745214 \\
 A = 184431.01 & c_8 = 0.42123807 \\
 A = 186924.404 & c_8 = 0.41495143 \\
 \alpha = 10.43329537 & c_{10} = 0.17151143 \\
 \beta = -2.07758779 &
 \end{array}$$

## 2. HFD-B2(He)

$$\begin{array}{ll}
 \varepsilon = 15.1044 \cdot 10^{-23} \text{ J} & D = 1.4132 \\
 r_m = 2.970 \cdot 10^{-10} \text{ m} & c_6 = 1.34920045 \\
 A = 192215.29 & c_8 = 0.41365922 \\
 A = 192215.29 & c_8 = 0.41365922 \\
 \alpha = 10.73520708 & c_{10} = 0.17078164 \\
 \beta = -1.89296514 &
 \end{array}$$

## 3. HFD-B3-FCI1

$$\begin{array}{ll}
 \varepsilon = 15.1265 \cdot 10^{-23} \text{ J} & D = 1.438 \\
 r_m = 2.9683 \cdot 10^{-10} \text{ m} & c_6 = 1.35186623 \\
 A = 186924.404 & c_8 = 0.41495143 \\
 A = 186924.404 & c_8 = 0.41495143 \\
 \alpha = 10.5717543 & c_{10} = 0.17151143 \\
 \beta = -2.07758779 &
 \end{array}$$

II. Integrals  $I_n$  and  $I_{np}$ ,  $n = 0, 1$ , related to the normalization and potential energy in the ground and excited states, read

$$I_n = \int_0^\infty \Psi_n^2 dr, \quad I_{np} = \int_0^\infty \Psi_n^2 V(r) dr \quad (8)$$

The integrals in kinetic energy are:

$$I_{0k} = -\frac{\hbar^2}{m} \int_0^\infty \Psi_0^2 \left\{ \left[ \gamma \frac{\alpha^\gamma}{r^{\gamma+1}} - s \right]^2 - \gamma(\gamma+1) \frac{\alpha^\gamma}{r^{\gamma+2}} \right\} dr \quad (9)$$

and

$$I_{1k} = -\frac{\hbar^2}{m} \int_0^\infty (1-br) \Psi_0^2 \left\{ (1-br) \left[ \gamma \frac{\alpha^\gamma}{r^{\gamma+1}} - s \right]^2 - \gamma(\gamma+1) \frac{\alpha^\gamma}{r^{\gamma+2}} - 2b \left[ \gamma \frac{\alpha^\gamma}{r^{\gamma+1}} - s \right] \right\} dr \quad (10)$$

for the ground and excited states, respectively.

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## SAŽETAK

### Energija veze dimera helija-4

*Srećko Kilić i Tullio Persi*

Pokazano je da energija veze dimera helija-4 za istu klasu potencijala ovisi o upotrijebljenim parametrima potencijala. Jedno ekscitirano energijsko stanje, povezano s jednim čvorom radialne valne funkcije, ostvaruje se u svim upotrijebljenim potencijalima; energija veze iznosi oko  $(-0,3 \text{ mK}) \cdot k_B$ . Srednja vrijednost udaljenosti atomskih jezgri iznosi oko  $49 \text{ \AA}$  u osnovnom, te  $679 \text{ \AA}$  u ekscitiranom stanju.