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ON THE POSSIBILITY OF THE DIATOMIC HELIUM MOLECULE EXISTENCE

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The ground state energies of the helium dimers interacting via Lennard-Jones (12,6) pair potential in two dimensions are evaluated by means of variational calculus. The Ljoljc type of pair function is employed. The self-bound states of dimers ^4He —^4He and ^3He —^4He are found, while the binding of the dimers ^3He —^3He is not obtained.

1. Introduction

Regarding the recent investigations which refer to the nonrelativistic quantum theory of the liquids there arises a problem of defining the bound state of smaller number of atoms[1,2]. The microscopic theory of the quantum liquids regularly includes approximations, related to the consideration of an immense number of particles, which cannot usually be evaluated. Therefore one tries to start from a correct description of a smaller number of particles, this being quite possible due to the modern calculational techniques, and then to include the results in the formalism for describing a system of a great number of particles.

With regard to the above the consideration of binding a few atoms of helium represents an initial problem.

Some interesting conclusions in the context of this problem are the consequences of the results of the many-body theory. Namely, in the model of the semi-free gas of the liquid helium [3,4,5] the energy per particle of the ground state of the liquid ^{4}He and ^{3}He the following expressions, representing the series in density, have been obtained:

$$\frac{E}{N} = \varrho I_1 + \varrho^2 I_2 + \dots, \text{ for } {}^4\text{He}$$

$$\frac{E}{N} = \varrho^{2/3} I_1^F + \varrho I_2^F + \dots, \text{ for } {}^3\text{He}.$$

As $I_1 < 0$, and $I_1^F > 0$, it means that for $\varrho \to 0$ the energy per particle for the liquid ^{4}He remains negative, and for the liquid ^{3}He, in the same limit, positive. Such a different behaviour of the boson and fermion system should be evident in the case of a small number of particles as well.

All the inert gases, except helium, form experimentally observable dimers[6]. E. Feenberg seems to have been the first to assume the possibility of the existence of the dimer ^{4}He[7]. The problem of binding a few atoms of helium has been generally very intensively investigated during the last ten years. While trying to find the conditions of the existence of the dimers $(^4\text{He})_2$ and $(^3\text{He})_2$ A. Bagchi[8] considered these systems on the two-dimensional surface, and found by numerical solution of the Schrödinger's equation, the bound state of dimer ^{4}He with the binding energy $E = -0.035 \cdot 10^{-16}$ ergs. Qualitatively the same result in the two-dimensions was later confirmed by Siddon and Schick[9] and they have found that $E = -0.032 \cdot 10^{-16}$ ergs, as well as by Cabral and Bruch[10], who obtained for the energy of the same dimer $E = -0.030 \cdot 10^{-16}$ ergs.

The second type of conditions establishing the dimer $(^4\text{He})_2$ is represented by the liquid helium in which the dimer is immersed[11]. The improved calculations in such conditions are presented in Ref. 12, where the dimer ^{4}He—^{4}He is found to be stable, while the pairs of the atoms ^{3}He—^{3}He and ^{3}He—^{4}He are not bound.

Let us state here also some interesting calculations for the trimers of helium in the two[10] and three dimensions[13]. The trimer ^{4}He is bound in two and three dimensions; the binding energies being:

$$E = -0.155 \cdot 10^{-16} \text{ ergs, for two dimensions}$$

and

$$E = -0.069 \cdot 10^{-16} \text{ ergs, for three dimensions.}$$

It is interesting to note that the binding energy of the trimer ^{4}He in two dimensions is greater by a factor 2.24 from the one in the three dimensional space. The same situation should be expected for the dimers. As far as we know the problem of binding two atoms of ^{4}He has not been solved yet [14,15]. The trimer ^{3}He does not seem to be bound either in two or three dimensions[10]. As we expect that the above qualitative picture holds for dimers, it means that the results stated for the dimers ^{3}He in the Refs. 8 and 9 are not likely to be correct.

In this paper we firstly present the calculation of the binding energy of the helium dimer based on the variational function[16] employing the Lennard-Jones potential and then discuss the obtained results.

2. *Energies of binding two atoms of helium in two dimensions*

From the variational ansatz for two particles

$$E_0 \leqslant E = \frac{< \Phi(1,2) | H(1,2) | \Phi(1,2) >}{< \Phi(1,2) | \Phi(1,2) >}, \tag{1}$$

taking for the symetric wave function the Ljolje type two particle wave function[16]

$$\Phi(1,2) = \Phi_B(1,2) = e^{-(a/r_{12})^{\beta} - s r_{12}} \tag{2}$$

and the antisymetric $\Phi_F = \Phi_B \cdot S(1,2)$, where $S(1,2)$ is the antisymetric spin function of the two atoms ^{3}He

$$S(1,2) = 2^{-1/2} \{\chi_{1/2}(s_1)\,\chi_{-1/2}(s_2) - \chi_{1/2}(s_2)\,\chi_{-1/2}(s_1)\},$$

we get for the energy of two particles in two dimensions

$$E = E_k + E_p. \tag{3}$$

In the above relation the expressions for the kinetic and potential energy have the following form:

$$E_k = \frac{1}{I}\Big\{-(\hbar^2/2\mu\, a^2)\int \Phi^2(1,2)\,[\beta^2 (a/r_{12})^{2\beta+2} - \beta^2 (a/r_{12})^{\beta+2} - 2\beta a s\,(a/r_{12})^{\beta+1} - a s\,(a/r_{12}) + a^2 s^2]\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\Big\}$$

and

$$E_p = \frac{1}{I}\int \Phi^2(1,2) \cdot 4\,\varepsilon\,(\sigma/r_{12})^6\,[(\sigma/r_{12})^6 - 1]\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2$$

with

$$I = \int \Phi^2(1,2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2$$

where the reduced masses for the single pairs of atoms are:

$\mu = m^4{}_{\mathrm{He}}/2 = 3.312 \cdot 10^{-24}$g, for ^{4}He — ^{4}He,

$= m^3{}_{\mathrm{He}}/2 = 2.50 \cdot 10^{-24}$g, for ^{3}He — ^{3}He,

$= m^3{}_{\mathrm{He}}\, m^4{}_{\mathrm{He}}/(m^3{}_{\mathrm{He}} + m^4{}_{\mathrm{He}}) = 2.852 \cdot 10^{-24}$g, for ^{3}He — ^{4}He.

For the interaction potential we have chosen the Lennard-Jones one with De Boer-Michels's parameters $\varepsilon = 14.1077 \cdot 10^{-16}$ ergs and $\sigma = 2.556 \cdot 10^{-8}$ cm. α, β and s are the variational parameters. Choosing $\beta = 5$, which has proved good in the earlier analyses[17,18] in the many-body theory, and by minimizing the expression (3) with regard to the parameters α and s, the numerical calculation of the integral has been derived with the necessary accuracy. The results of the calculation are presented in the table and qualitatively in the figure. Thus binding energies are as follows:

$E = -0.0286 \cdot 10^{-16}$ ergs, for ^{4}He — ^{4}He, with parameters $\alpha = 2.58 \cdot 10^{-8}$cm and $s = 0.075 \cdot 10^8$ cm^{-1},

$E = -0.00057 \cdot 10^{-16}$ergs, for ^{3}He — ^{4}He, with parameters $\alpha = 2.58 \cdot 10^{-8}$ cm and $s = 0.018 \cdot 10^8$ cm^{-1}.

The bound state has not been found for two atoms ^{3}He — ^{3}He. The calculations have been carried out also for one and for three dimensional system of the two atoms ^{4}He. The bound state has not been found in either case.

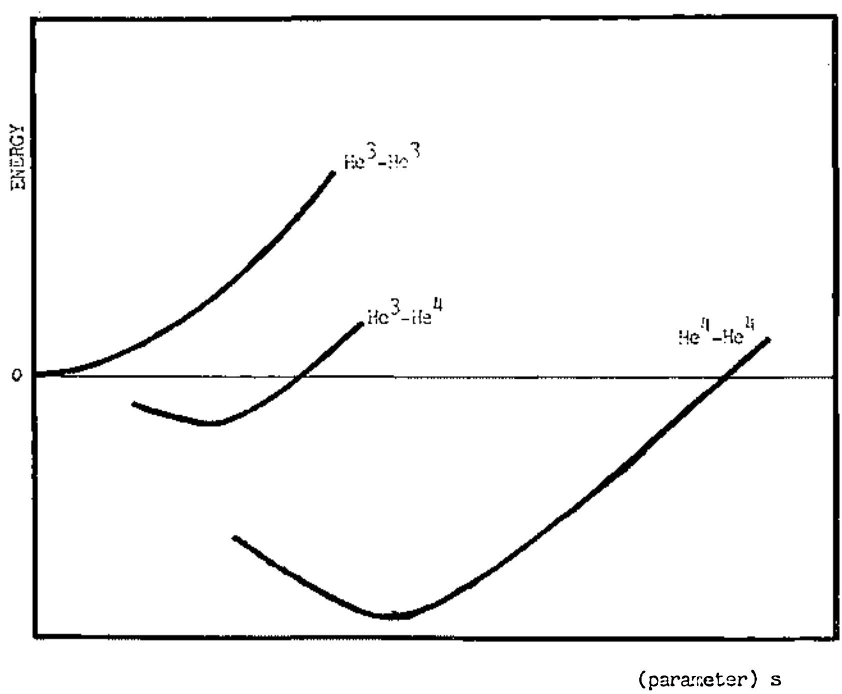

Fig. 1. Energy of the Lennard — Jones (12,6) helium dimers in two dimensions as a function of the variational parameter s.

TABLE 1.

Dimer	a_{min}	$s \cdot 10^{-8}$ cm^{-1}	I	$E_k \cdot 10^{16}$ erg s	$E_p \cdot 10^{16}$ erg s	$E \cdot 10^{16}$ erg s
		.02	92.9290	0.0355	−0.04178	−0.00628
		.03	40.9013	0.0753	−0.0872	−0.01185
		.04	22.6882	0.12697	−0.1445	−0.01753
$^4He-^4He$		.05	14.2783	0.1886	−0.2112	−0.02255
		.06	9.72573	0.25906	−0.28536	−0.02639
		.07	6.99319	0.33711	−0.36543	−0.02832
		.071	6.7822	0.345302	−0.3737	−0.02841
	2.58	.073	6.38629	0.36188	−0.390408	−0.028527
		.075	6.02207	0.37872	−0.407279	−0.028558
		.077	5.688628	0.395814	−0.424314	−0.028499
		.08	5.22978	0.42192	−0.45016	−0.028237
		.09	4.02906	0.51275	−0.538522	−0.02577
		.1	3.17708	0.608986	−0.629677	−0.02069
		.11	2.55247	0.710106	−0.722917	−0.01281
		.2	0.57134	1.78294	−1.5816	0.2013
		.3	0.171263	3.19828	−2.43086	0.76742
		.4	0.062919	4.75914	−3.07288	1.68626
		.5	0.025836	6.42302	−3.46997	2.95305
		.6	0.011393	8.16664	−3.60563	4.56101
		.011	302.372	0.01351	−0.01387	−0.000357
		.021	256.064	0.01583	−0.01624	−0.000406
		.013	219.233	0.01835	−0.0188	−0.000450
		.014	189.567	0.02107	−0.02156	−0.000489
$^3He-^4He$		.015	165.388	0.02398	−0.0245	−0.000521
		.016	145.759	0.027010	−0.02756	−0.000553
		.017	129.04	0.030302	−0.030869	−0.000567
	2.58	.018	115.020	0.033764	−0.034337	−0.000573
		.019	103.151	0.037392	−0.037963	−0.000570
		.021	84.2406	0.04517	−0.0457	−0.000527
		.031	38.2571	0.092935	−0.092446	0.004885
		.041	21.5613	0.15413	−0.15079	0.003344
		.061	9.39012	0.309557	−0.29312	0.01643
		.071	6.7822	0.401033	−0.3737	0.02732
		.091	3.9307	0.60641	−0.54752	0.05888
		.101	3.10587	0.71877	−0.638918	0.079855
		0.004	1289.35	0.003803	−0.00338	0.000422
		0.008	512.053	0.009209	−0.008224	0.000985
		0.01	349.404	0.01324	−0.011846	0.001394
$^3He-^3He$		0.012	249.722	0.018216	−0.01629	0.001922
		0.014	185.745	0.024116	−0.02153	0.002584
		0.018	113.021	0.038514	−0.03419	0.004316
		0.044	18.3349	0.19876	−0.16928	0.02948
	2.6	0.05	14.0496	0.24908	−0.210147	0.03893
		0.06	9.5675	0.34195	−0.28406	0.05789
		0.07	6.87758	0.44487	−0.36393	0.080943
		0.074	6.0972	0.48858	−0.39726	0.091321
		0.078	5.43549	0.533657	−0.43129	0.10236
		0.08	5.1418	0.55668	−0.44854	0.10814

Energy of the Lennard-Jones (12,6) helium dimers in the two dimensions as a function of the variational parameters: s — parameter; a_{min} — the value of the variational parameter a for which the energy minimum is obtained; E_k, E_p and E are the kinetic, potential and total energy and I — normalization integral.

3. *Discussion*

From the previously presented results it can be concluded that the two atoms of ^{4}He and the two atoms ^{3}He — ^{4}He in two dimensions have the bound states, i.e. form molecules. On the contrary the two atoms ^{3}He do not form a bound state in two dimensions at all. These results are completely in accordance with the conclusions from the Ref. 10. However, the results concerning ^{3}He have not confirmed the results from Refs. 8 and 9, where the existence of the stable state of ^{3}He has been stated. Nevertheless, our conclusions for the dimer ^{3}He have been confirmed in most papers, so that the calculations[8,9] for the dimer ^{3}He are not likely to be numerically correct.

With regard to the three-dimensional motion of the two atoms ^{4}He the bound state has not been stated for the employed form of the wave function (2), what is in accordance with the calculations from Ref. 19 carried out for the Yntema--Schneider's potentiəl. Similary, the bound state has not been found for the one--dimensional motion of the atom ^{4}He.

The maximum of the wave function of the molecule $(^4\text{He})_2$ is found for $r_{12} = 4.436 \cdot 10^{-8}$ cm. If we assume the existence of the liquid film with the səme particle spacing, then we obtain the density $\varrho = 0.0647 \cdot 10^{16}\,\text{cm}^{-2}$. When comparing this result with the actually calculated density for the liquid film ^{4}He on the absolute zero[20,21] of $\varrho = 0.035 \cdot 10^{16}\,\text{cm}^{-2}$, we can come to the conclusion that in the two dimensional many particle system the particles are farther apart than in the molecule $(^4\text{He})_2$. This fact points to the direction in which to expect the changes of the two-particles function which pretends to describe a great number of the helium atoms.

References

1) K. Ljolje, private comunication;
2) S. Kilić and M. Ristig, Il nuovo cimento **39** (1977) 248;
3) K. Ljolje, Fizika **1** (1968) 11;
4) S. Kilić, Fizika **2** (1970) 105;
5) S. Sunarić, M. S. A. thesis, Sarajevo 1969 (unpublished);
6) Y. Tanaka and K. Yoshino, J. Chem. **57** (1972) 57;
7) E. Feenberg, Amer. J. Phys. **38** (1970) 684;
8) A. Bagchi, Phys. Rev. **A3** (1971) 1133;
9) R. L. Siddon and M. Schick, Phys. Rev. **A9** (1947) 907;
10) F. Cabral and L. W. Bruch, preprint 1979;
11) E. Blaisten — Barajos, O. Novaro and O. Sinanoglu, Molec. Phys. **31** (1976) 1941;
12) E. Blaisten — Barajos, O. Novaro and L. W. Bruch, Molec. Phys. **37** (1979) 599;
13) L. W. Bruch and I. J. Mc Gee, J. Chem. Phys. **59** (1973) 409;
14) C. Poulat, S. Y. Larsen and O. Novaro, Molec. Phys. **30** (1975) 645;
15) R. S. Grace, W. M. Pope, D. L. Johnson and J. G. Skofronick, Phys. Rev. **A14** (1976) 1006;
16) K. Ljolje and S. F. Wang, Reports of the University of Illinois, (1962);
17) W. L. Mc Millan, Phys. Rev. **138** (1965) A442;
18) D. Schiff and L. Verlet, Phys. Rev. **160** (1967) 208;
19) S. Sunarić, Fizika **10** (1978) 113;
20) C. E. Campbell and M. Schick, Phys. Rev. **A3** (1971) 691;
21) K. S. Liu, M. H. Kalos and G. V. Chester, Phys Rev. **B13** (1976) 1971.

O MOGUĆNOSTI POSTOJANJA DVOATOMSKE MOLEKULE HELIJA

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Dan je varijacioni proračun energije vezanja dvaju atoma helija za dvodimenzionalno gibanje. Pokazano je da u ovim uvjetima postoji vezanje dimera $(^4He)_2$ i $^4He—^3He$ te da dimer $(^3He)_2$ nije vezan. Također je potvrđeno da sa Ljoljinom funkcijom za prostorno gibanje nema vezanja ni jednog para atoma helijevih izotopa.