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THE EFFECTS OF RETARDED FORCES IN HELIUM DIATOMIC MOLECULES

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The binding energies of helium-3 dimer, helium-4 dimer and ^{3}He $-\,^4$He molecule in the state $1\,^1$S – $1\,^1$S are calculated using the standard variational procedure. It is shown that the binding energy depends on the retardation long-range potentials. The expectation value of the internuclear distance for each complex is also derived.

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1. Introduction

There are several reasons for studying helium diatomic molecules. Many physical phenomena, like the superfluidity in the bulk and films, the diffraction in small helium clusters, are related to the behaviour of two helium atoms.

Helium diatomic molecules are also interesting as special physical systems. They exist at very low temperature, below 0.01 K. Two helium atoms, isotopes ^{3}He and ^{4}He, form three types of stable molecules in infinite and confined space: $(^3\text{He})_2$ dimer, $(^4\text{He})_2$ dimer and ^{3}He $-\,^4$He molecule [1]. In infinite space, there are three stable molecules of the two isotopes:

1. $(^3He)_2$ dimer, which is bound in two dimensions (2D) with the binding energy of –0.016 mK [1];

2. $(^4He)_2$ dimer, which is bound in three-dimensions (3D) with the binding energy of about –1.3 mK [1–4] and in 2D with the binding energy of –39.5 mK [1,5–8];

3. $^3He - ^4He$ molecule in 2D with the binding energy of –3.2 mK [1,5–8].

The expectation values of the internuclear distance of two atoms in the ground state are from about 1.5 nm up to 56.0 nm [1]. Thus, helium molecules are the largest of all two-body molecules in the ground state. They are of a great fundamental interest as the systems for testing long-range retardation effects – the Casimir forces [9–11]. Namely, the retardation changes the dispersion interaction at long range. The instantaneous atomic dipole (quadrupole) is modified during the time required for the photon to propagate to the other atom and back. Due to the retardation effects, the strength of the attraction is decreased at long range. Therefore, the binding energy of helium molecules is decreased and the expectation value of the distance between atoms is increased.

In this paper, we study the influence of the Casimir forces on the binding energy and on the average value of the internuclear distance of the helium molecules in infinite space (Sec. 2). In Sec. 3 we discuss our results.

2. *Binding energy of helium molecules*

In the calculation, we use a standard variational procedure. The following trial wave functions are employed [1,12]

$$\Psi(r_1, r_2) = \frac{1}{r_{12}} \exp[-(a/r_{12})^\gamma - s r_{12}], \tag{1}$$

in 3D, and

$$\Psi_0(r_1, r_2) = \frac{1}{\sqrt{r_{12}}} \exp[-(a/r_{12})^\gamma - s r_{12}], \tag{2}$$

in 2D, where r_{12} is the distance between atoms; a, s and γ are the variational parameters.

Analytic form of a trial wave function giving the binding of helium-3 dimer is unknown. In our variational calculation for trial wave function, we use a table of numbers which represents this function and which was found by Krotscheck and Zillich [1].

The Hamiltonian of two helium atoms is

$$\hat{H} \;=\; -\frac{\hbar^2}{2m_1}\Delta_1 - \frac{\hbar^2}{2m_2}\Delta_2 + \hat{V}(r_{12}) \;, \tag{3}$$

where m_1 and m_2 are the masses of the particles 1 and 2, respectively. For the potential describing the interaction between two helium atoms, we use HFD-B2(He) potential [13–

14]

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

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

where $x = r/r_m$,

$\varepsilon = 15.1044\ 10^{-23}$ J	$D = 1.4132$
$r_m = 2.970\ 10^{-10}$ m	$c_6 = 1.34920045$
$A = 192215.29$	$c_8 = 0.41365922$
$\alpha = 10.73520708$	$c_{10} = 0.17078164$
$\beta = -1.89296514.$	

Introducing (1) (or 2) and (3) into the variational *ansatz*

$$
E \leq \frac{\int \Psi^\star \hat{H} \Psi \, d\vec{r}}{\int \Psi^\star \Psi \, d\vec{r}}, \tag{4}
$$

one finds

$$
E \leq \varepsilon_k + \varepsilon_p, \tag{5}
$$

where the kinetic and potential energies are

$$
\varepsilon_k = \frac{I_k}{I_n}, \quad \varepsilon_p = \frac{I_p}{I_n}. \tag{6}
$$

The explicit forms of the integrals in 3D are

$$
I_n = \int_0^\infty \Psi^2 \mathrm{d}r\,, \qquad I_p = \int_0^\infty \Psi^2\, V(r)\, \mathrm{d}r\,, \tag{7}
$$

$$
I_k = -\frac{\hbar^2}{m} \int_0^\infty \Psi^2 \left\{ \left[\gamma \frac{a^\gamma}{r^{\gamma+1}} - s\right]^2 - \gamma(\gamma+1) \frac{a^\gamma}{r^{\gamma+2}} \right\} \mathrm{d}r \tag{8}
$$

After reducing the integrals to one-dimensional ones, Romberg integration with a high accuracy is applied. The parameters a, s and γ are obtained in a minimization procedure of the energy.

Using the same wave function, with the parameters derived in the above procedure, the expectation value of the internuclear distance is calculated using the same Romberg algorithm.

Retarded forces are introduced using the dispersion-retarded potential from Ref. 11

$$V_{d-r}(x) \;=\; -\frac{C_6 f_6(x)}{x^6} - \frac{C_8 f_8(x)}{x^8} - \frac{C_{10} f_{10}(x)}{x^{10}}, \tag{9}$$

where, in the state $1^1\mathrm{S}-1^1\mathrm{S}$, the values of the dispersion coefficients are $C_6 = 1.46108$, $C_8 = 14.1202$, $C_{10} = 183.744$ (in a.u.), and of the retardation coefficients $f_6(x)$, $f_8(x)$ and $f_{10}(x)$ are given in Table III of Ref. 11. The above dispersion-retarded potential is transformed into appropriate units and introduced in the potential energy. Repeating the same calculation as before, but with this new potential, one finds energies and expectation values which include the retardation.

In the case of helium-3 dimer, the wave function describing the retardation is unknown. In order to estimate the retardation also in this case, we use the table of the numbers representing this function without retardation [1].

The results are presented in Table 1.

TABLE 1. Kinetic (ε_k), potential (ε_p) and total energy (ε), expectation value of the internuclear distance ($< r >$) and its r.m.s. deviation Δr, and the variational parameters: a, γ and s; for each molecule, the numbers in the second line correspond to the retardation potential.

Mole-cule	ε_k (mK)	ε_p (mK)	ε (mK)	$< r >$ (nm)	Δr (nm)	a (nm)	γ	s $(\mathrm{nm})^{-1}$
$(^4\mathrm{He})_2$	107.99	–109.54	–1.54	4.801	4.426	0.274	4.49	0.113
in 3 D	103.42	–104.83	–1.41	4.925	4.547	0.275	4.43	0.11
$(^4\mathrm{He})_2$	377.46	–414.74	–37.28	1.558	1.201	0.2733	4.70	0.42
in 2D	377.46	–414.26	–36.80	1.558	1.201	0.2733	4.70	0.418
$(^3\mathrm{He})_2$	1.318	–1.335	–0.017	57.301	45.261			
in 2D	1.318	–1.333	–0.015					
$^3\mathrm{He}-^4\mathrm{He}$	85.74	–89.00	–3.26	5.439	5.053	0.2757	4.199	0.099
in 2D	85.74	–88.89	–3.15	5.439	5.053	0.2757	4.199	0.099

3. Discussion

Using the variational procedure with a good trial wave function and new data for the retarded potential calculated in Ref. 11, we were able to obtain quite new results. In particular, these results are related to the behaviour in 2D.

As is seen in Table 1, the variational calculation confirms all results known in the literature and some still unpublished [1].

Only the helium-4 dimer was observed experimentally in 3D so far. The difference between our binding energy of –1.4 mK and the one accepted in the literature is –0.1 mK, and we believe it is due to the uncertainty of the used potential. The exclusion of the retardation decreases the binding energy by 9.6%. The expectation value of the internuclear distance 4.92 nm and *r.m.s.* 4.55 nm are shorter by 2.6% and 2.7%, respectively, when the retardation is excluded.

Helium-4 dimer in 2D decreases the binding energy by 1.3%, while the mean value of the internuclear separation and of *r.m.s.* remains almost the same.

Helium-3 dimer and molecule ^{3}He $-$ ^{4}He are bound only in 2D. Helium-3 dimer, in which atoms are separated at the average distance of 57.3 nm, is the largest diatomic molecule. Although we use for helium-3 dimer wave function, which does not minimize the energy, we find the retardation effect on the binding energy of 11.5%. Of course this number should be still bigger.

The retardation effect on the binding energy in the molecule ^{3}He $-$ ^{4}He is 3.6%. Furthermore, the retardation doesn't influence at all the expectation value and *r.m.s.* of the internuclear spacing.

Generally, one may say that the retardation effects are smaller in 2D than in 3D.

We believe that in the following years all diatomic systems of helium atoms will be observed and the retardation effects will be measured.

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References

1) E. Krotscheck and R. Zillich, private communication (1998).

2) F. Luo, G. C. McBane, G. Kim, C. F. Giese and W. R. Gentry, J. Chem. Phys. **98** (1993) 3564;

3) F. Luo, C. F. Giese and W. R. Gentry, J. Chem. Phys. **104** (1996) 1151;

4) W. Schollkopf and J. P. Toennies, J. Chem. Phys. **104** (1996) 1155;

5) S. Kilić and S. Sunarić, Fizika **11** (1979) 225;

6) A. Bagchi, Phys. Rev. A **3** (1971) 1133;

7) R. L. Siddon and M. Schick, Phys. Rev. A **9** (1974) 907;

8) F. Cabral and L. W. Bruch, J. Chem. Phys. **70** (1979) 4669;

9) H. B. G. Casimir and D. Polder, Phys. Rev. **73** (1948) 360;
10) L. Spruch, Physics Today, November (1986); B. Gross Levi, Physics Today, April (1993);
11) M. K. Chen and K. T. Chung, Phys. Rev. A **53** (1996) 1439;
12) L. W. Bruch, preprint (1998);
13) R. A. Aziz and H. H. Chen, J. Chem. Phys. **67** (1977) 5719;
14) R. A. Aziz and M. J. Slaman, Metrologia **27** (1990) 211.

UČINCI ZAKAŠNJELIH SILA U HELIJEVIM DIATOMSKIM MOLEKULAMA

Primjenom standardnog varijacijskog postupka, izračunale su se vezne energije dimera helium-3 i helium-4, te molekule ^{3}He $-^4$He. Pokazuje se kako vezna energija ovisi o zakašnjenju dugodosežnih potencijala. Izvedene su i očekivane vrijednosti međunukleonskih razmaka za svaki spoj.