Some Relations for the Ground State Energy and Helium Diatomic Molecules

Srećko Kilić* and Leandra Vranješ

Faculty of Natural Science, University of Split, 21000 Split, Croatia

It is shown quite generally that the ground state energy of two atoms in infinite space, interacting *via* a spherical potential that depends only on the distance between particles, is the lowest in two dimensions. Using variational procedure, binding energies of helium diatomic molecules, in infinite and restricted spaces, are obtained as well. The results derived for helium atoms are in accord with the lemma.

Key words: ground state energy, helium diatomic molecules, spherical potential

INTRODUCTION

　　Many physical phenomena in nature are related to the behaviour of small systems of particles. Among them, in low temperature physics, are superconductivity, superfluidity and Bose-Einstein condensation. Specially interesting and important cases are systems in which particles are helium atoms: helium liquids, helium films, liquid drops, atoms in cavities in solid matrices and in nanotubes.

　　Consideration of small systems begins with the study of two atoms. They can be located both in restricted and unrestricted spaces: in 3 dimensions (3 D), 2 dimensions (2 D) and 1 dimension (1 D). Of course, the real physical world has been occurring in the finite 3 dimensional space. In making models of different physical situations we are led to consider 2 D and 1

---

* Author to whom correspondence should be addressed.

D space. In such circumstances, many physical effects are dominant in the relevant dimension.

In this paper, we prove a general lemma. It relates ground state energies of two particles in 1, 2 and 3 dimensions in infinite space. It is assumed that particles interact *via* spherical potential, depending only on the distance between them. Using variational procedure and employing the newest potential of the interaction between helium atoms,[1] the ground state energies of helium molecules are obtained. The consistency with the lemma is demonstrated.

RELATIONS BETWEEN GROUND STATE ENERGIES IN DIFFERENT DIMENSIONS

We consider the ground state of two particles that interact *via* a spherically symmetrical potential $\hat{V}(\vec{r}_1, \vec{r}_2)$, in one, two and three dimensional space. The Hamiltonian of the system in relative coordinates reads

$$\hat{H} = -\frac{\hbar^2}{2\mu}\Delta + \hat{V}(|\vec{r}_1 - \vec{r}_2|) \, , \tag{1}$$

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the particles, m_1 and m_2 are masses of the particles. In the ground state, only the »radial« part of the Hamiltonian is important and the operator Δ, in this case, has the form

$$\Delta_1 = \frac{\partial^2}{\partial r^2} \, , \qquad \text{in 1 D} \tag{2}$$

$$\Delta_2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} \, , \quad \text{in 2 D} \tag{3}$$

$$\Delta_3 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} \, , \quad \text{in 3 D} \, . \tag{4}$$

Inequalities between energies in different dimensions may be obtained by variational *ansatz*

$$E_n \leq \frac{\int \Psi_n^* \hat{H}_n \Psi_n \, r^{n-1} \, dr \, d\Omega^n}{\int \Psi_n^* \Psi_n \, r^{n-1} \, dr \, d\Omega^n} \, , \tag{5}$$

where $n = 1, 2, 3$ denotes the dimension of physical space and $d\Omega^1 = 1$, $d\Omega^2 = 2\pi$ and $d\Omega^3 = 4\pi$.

Since we are studying the ground state and having in mind the symmetry of the system, it is useful to write the trial wave functions in the form

$$\Psi_1(r) = \Psi_{10}(r)$$

$$\Psi_2(r) = \frac{1}{\sqrt{r}}\Psi_{20}(r)$$

$$\Psi_3(r) = \frac{1}{r}\Psi_{30}(r). \tag{6}$$

Introducing trial wave functions in the variational *ansatz* (5), one finds

$$E_1 \leq \frac{1}{I_1}\left[-\frac{\hbar^2}{2\mu} \int_0^\infty dr\,\Psi_1 \frac{d^2}{dr^2}\Psi_1 + \int_0^\infty dr\,\Psi_1^2 V(r) \right] \tag{7}$$

$$E_2 \leq \frac{1}{I_2}\left[-\frac{\hbar^2}{2\mu} \int_0^\infty dr\,\Psi_{20}\left\{\frac{d^2}{dr^2}\Psi_{20} + \frac{1}{4r^2}\Psi_{20}\right\} + \int_0^\infty dr\,\Psi_{20}^2 V(r) \right] \tag{8}$$

$$E_3 \leq \frac{1}{I_3}\left[-\frac{\hbar^2}{2\mu} \int_0^\infty dr\,\Psi_{30} \frac{d^2}{dr^2}\Psi_{30} + \int_0^\infty dr\,\Psi_{30}^2 V(r) \right] \tag{9}$$

where the normalization integrals read $I_n = \int_0^\infty dr\,\Psi_{n0}^2$, $n = 1, 2, 3$.

Relations (7), (8) and (9) are general. Assuming that Ψ_1 is the eigenfunction in one dimensional case and taking $\Psi_{20} = \Psi_1$, from Eqs. (7) and (8), it follows

$$E_2 < E_1 - \frac{1}{I_1}\frac{\hbar^2}{2\mu}\int_0^\infty dr\,\frac{1}{4r^2}\Psi_{20}^2 \,; \tag{10}$$

which means $E_2 < E_1$.

If it is supposed that $\Psi_{30} = \Psi_{20}$, where Ψ_2 is the eigenfunction in 2D, then from Eqs. (8) and (9) one finds

$$E_3 < E_2 + \frac{1}{I_2}\frac{\hbar^2}{2\mu}\int_0^\infty dr\,\frac{1}{4r^2}\Psi_{20}^2\,. \tag{11}$$

On the other hand, if Ψ_3 is the eigenfunction in 3D and $\Psi_{20} = \Psi_{30}$, then

$$E_3 > E_2 + \frac{1}{I_3}\frac{\hbar^2}{2\mu}\int_0^\infty dr\,\frac{1}{4r^2}\Psi_{30}^2\,. \tag{12}$$

The last two inequalities may be joined

$$E_2 + \frac{1}{I_3}\frac{\hbar^2}{2\mu}\int_0^\infty dr\,\frac{1}{4r^2}\Psi_{30}^2 < E_3 < E_2 + \frac{1}{I_2}\frac{\hbar^2}{2\mu}\int_0^\infty dr\,\frac{1}{4r^2}\Psi_{20}^2\,. \tag{13}$$

From the above relation it follows that $E_2 < E_3$. In a similar considera-tion, $E_3 = E_1$ follows from Eqs. (7) and (9). In this way, it is proved that the binding energy of two interacting particles is the lowest in 2D. The result is independent of the statistics of the particles.

GROUND STATE ENERGY OF DIATOMIC HELIUM MOLECULES

To describe physical systems that contain helium, many potentials be-tween atoms have been obtained. One of the best is the *ab initio* SAPT po-tential by Korona *et al.*;[1] its enlarged forms by Janzen and Aziz[2] are SAPT1 and SAPT2, which comprise retardation effects. Since the SAPT potential is so precise, it is expected that the effect of retardation forces can be examined experimentally. It reads

$$V(r) = \varepsilon V^*(r) \tag{14}$$

$$V^*(r) = A e^{-\alpha r + \beta r^2} - B\sum_{n=3}^{8} f_{2n}(b,r)\frac{c_{2n}}{r^{2n}} , \tag{15}$$

where

$$f_{2n}(b,r) = 1 - e^{-br}\sum_{k=0}^{2n}\frac{(br)^k}{k!} \tag{16}$$

and

$\varepsilon = 10^8$ mK $\qquad c_6 = 0.03207856$ Å^6
$A = 20.7436426 \qquad c_8 = 0.08680214$ Å^8
$B = 3.157765 \qquad c_{10} = 0.31625734$ Å^{10}
$\alpha = 3.56498393$ Å$^{-1} \qquad c_{12} = 1.57407624$ Å^{12}
$\beta = -0.22141687$ Å$^{-2} \quad c_{14} = 10.31938196$ Å^{14}
$b = 3.68239497$ Å$^{-1} \qquad c_{16} = 86.00126516$ Å^{16}.

Let us first calculate the binding energy of two helium atoms in infinite space. For the ground state, we found that a good analytic form of Eq. (6) in all dimensions is

$$\Psi_{0i}(r) = \exp\left[-\left(\frac{a}{r}\right)^{\gamma} - sr\right], \tag{17}$$

where $i = 1, 2, 3$; a, γ and s are variational parameters and, of course, have different minimization values in 3D (1D) and 2D. The same form of pair cor-relations in 3 D has recently been used by Bruch[3] to examine the properties of boson trimers. In 2D, we use the form employed in Ref. 4 which provides a slight improvement over the variational wave function introduced in Ref.

TABLE I

Binding energies in infinite space (in mK) of helium molecules in 2 D and for dimer $(^4\text{He})_2$ in 3 D (second line), derived by numerical solving of the Schrödinger Eq. and in variational procedure; variational values are in round brackets; parameters: a (in Å), γ (dimensionless) and s (in Å^{-1}) are shown for the SAPT potential only. Note that our variational wave function is not flexible enough to predict the bound state of the $(^3\text{He})_2$ dimer in 2 D and that molecules $(^3\text{He})_2$ and $^3\text{He} - {}^4\text{He}$ are not bound in 3 D.

Molecule	HFD-B3-FCI1[a]	SAPT[b]	a	γ	s
$(^4\text{He})_2$	−39.4 (−37.7)	−40.7 (−39.93)	2.758	4.408	0.047
	−1.559 (−1.480)	−1.871 (−1.762)	2.737	4.49	0.012
$(^3\text{He})_2$	−0.016	−0.02			
$^3\text{He} - {}^4\text{He}$	−4.0 (−3.21)	−4.3 (−3.51)	2.761	4.173	0.011

[a]Ref. 6
[b]Ref. 1

5. The binding energy and parameters are obtained by a minimization procedure. The results are shown in Table I. To evaluate our variational calculation, and compare the results, the corresponding numerical solutions of Schroedinger equation are presented for HFD-B3-FCI1 (Ref. 6), and SAPT potentials as well.

Second, we concentrate on two helium atoms confined by a hard-walled spherical potential in 3D and circular in 2D. As it was demonstrated in Ref. 4 good variational wave functions of the ground state are

$$\Psi_{03}(r;d) = \Psi_{03}(r)j_0(\pi r/d) \tag{18}$$

in 3D, and

$$\Psi_{02}(r;d) = \Psi_{02}(r)\,J_0(2.404826r/d) \tag{19}$$

in 2D. d is the diameter of the sphere and of the circle. j_0 is the spherical Bessel function and J_0 is the zeroth-order Bessel function. Like in infinite space, the ground state energy of the non-interacting system must be subtracted. The energy of two free particles is $\dfrac{C_i}{d^2}$, $i = 2, 3$, where $C_2 = \hbar^2(2.404826)^2/2\mu$ in 2D and $C_3 = \hbar^2\pi^2/2\mu$ in 3D. The results for $d = 50$ Å and $d = 100$ Å are presented in Table II.

DISCUSSION

Let us mention that only the helium 4 dimer in 3 D has been observed experimentally[7–9] to date.

TABLE II

Binding energies (in mK) of helium molecules in a sphere (3 D, first line) and in a circle (2 D, second line) derived in variational procedure for the SAPT potential; the diameters of both confinements are $d = 50$ Å and $d = 100$ Å; parameters: a (in Å), γ (dimensionless) and s (in Å^{-1}) are shown for $d = 50$ Å.

Molecule	50	100	a	γ	s
$(^4\text{He})_2$	−138.713	−40.650	2.753	4.41	−0.013
	−61.660	−52.133	2.767	4.36	0.02
$(^3\text{He})_2$	−67.086	−10.191	2.782	3.91	−0.058
	73.159	14.827	2.798	3.87	−0.029
$^3\text{He} - ^4\text{He}$	−94.354	−19.936	2.774	4.10	−0.042
	16.718	−7.264	2.794	4.04	−0.011

As it is seen from Table I, the binding energies for all helium molecules are consistent with the lemma. Moreover, neither of the lighter molecules are bound in 3 D. Two particles may be kept in 2 D space by an external potential. This can be realized, for example, in a space between two close, parallel big plates. Similarly, the interior of a long and thin cylinder may represent 1D space. Of course, these »confining« external potentials are not included in the binding energies cited in Table I.

Since in a restricted geometry (in our case, sphere and cylinder) the external potentials are partly included, the lemma cannot be valid. Of course, it is correct in this case as well if parameters of the geometry (for instance in our case, the sphere or cylinder diameter) are much bigger than the effective range of the interaction potential. Such behaviour can be recognized in Table II. From the »exact« numerical solution of the Schrödinger equation,[4] we know that all combinations of two helium atoms are bound in finite space (in the above sense); the same is true of infinite space, except for two atoms of ^{3}He and one atom ^{3}He and one atom ^{4}He, which are not bound in 3D. Let us note that our trial function in the case of $(^3\text{He})_2$ is not good enough to reproduce binding in 2D in either infinite or finite space. As the comparision with numerical solution shows, it is quite good for other cases.

The zero point energy of the relative motion may be obtained by calculating the root-mean-square deviation Δr (rms). For the helium 4 dimer in 3D, it was found numerically[4] that the expectation value of the coordinate $<r> = 47.8$ Å and $\Delta r = 44.3$ Å, which leads to uncertainty in energy 2.05 mK. Thus, we may conclude that the zero-point energy of relative motion is of the order of binding energy of the helium 4 dimer. The corresponding de Broglie wavelength and the mean speed are then 556.7 Å and 4.75 m/s, re-

spectively. It is shown that in confined space the root-mean-square deviation Δr depends almost linearly on the diameter of the »box«. This dependence disappears for the helium 4 dimer for diameters greater than about 28 $\mathring{A}$ in 2D and 100 $\mathring{A}$ in 3D. Thus, the de Broglie wavelength of the zero-point relative motion dependens on the diameter of the »box« and increases with it up to the value that it has in infinite space. Let us mention that the above consideration does not include the centre of mass motion.

It seems that the interior of a cylinder is the form that could be the easiest to realize in an experiment. Although we have not solved this problem theoretically, the main energetic characteristics are given by our spherical-models in 3D and 2D.

Finally, we mention that our calculation in finite space is an approximative one. Namely, we assumed that the centre of the mass of two particles was located in the centre of space symmetry. It was shown in Ref. 4 that this approximation gives the general features of the systems considered.

A further approximation has been performed in using the same form of the potential in all dimensions. Potential (Eq. (14)) has been obtained for a pure physical situation in 3D. We expect that our approximation is valid for physical situations in which two- or one- dimensional motions are dominant, like in films and nanotubes.

REFERENCES

1. T. Korona, H. L. Williams, R. Bukowski, B. Jeziorski, and K. Szalewicz, *J. Chem. Phys.* **106** (1997) 5109–5122.
2. A. R. Janzen and R. A. Aziz, *J. Chem. Phys.* **107** (1997) 914–919.
3. L. W. Bruch, *J. Chem. Phys*. **110** (1999) 2410–2413.
4. S. Kilić, E. Krotscheck, and R. Zillich, *J. Low Temp. Phys.* **116** (1999) 245–260.
5. S. Kilić and S. Sunarić, *Fizika* **11** (1979) 225–231.
6. R. A. Aziz, A. R. Janzen, and M. R. Moldover, *Phys. Rev. Lett.* **74** (1995) 1586–1589.
7. F. Luo, G. C. McBane, G. Kim, C. F. Giese, and W. R. Gentry, *J. Chem. Phys.* **98** (1993) 3564–3567.
8. F. Luo, C. F. Giese, and W. R. Gentry, *J. Chem. Phys.* **104** (1996) 1151–1154.
9. W. Schollkopf and J. P. Toennies, *J. Chem. Phys.* **104** (1996) 1155–1158.

SAŽETAK

Neke relacije za energiju osnovnog stanja i
helijeve dvoatomne molekule

Srećko Kilić i Leandra Vranješ

Sasvim općenito je dokazana lema po kojoj je energija osnovnog stanja dvaju atoma u beskonačnom prostoru najniža u dvije dimenzije. Pri tome se pretpostavlja da atomi međudjeluju sferno simetričnim potencijalom koji zavisi samo o udaljenosti između čestica. Nadalje, koristeći se varijacijskim postupkom određena je energija vezanja helijevih dvoatomnih molekula u beskonačnom i ograničenom prostoru. Dobiveni rezultati u skladu su s izvedenom lemom.