

Helium 4 Dimer in Nanotubes

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The ground state of the helium 4 dimer is considered using the Monte Carlo technique. In a cylinder with a hard core wall, binding depends on its radius. For a small radius binding occurs as in the one-dimensional case. With an increase of the radius, the binding becomes stronger, reaches its maximum value, and then slowly diminishes. In conical geometry, that may be realized as a generalization of a cylindrical one, this dependence of the binding energy on the radius might lead to an effective force which tends to move the molecule toward the region of minimal energy. Thus, in channels, with nonhomogeneous cross-sections, the particles move easier in dimer form. In addition, the square of the momentum and of the particle separation along the cylinder axis and in the plane perpendicular to it are calculated as well.

I. INTRODUCTION

Real physical systems almost always involve the study of particles in a confined geometry. We may imagine that the simplest geometries are defined by spheres in 3D (three-dimensions), circles in 2D, and straight lines in 1D. In these spaces two body problems, in which particles interact via the potential that depends only on the distance between them, can be reduced to one body problem and can generally be resolved by standard numerical procedures. In previous papers^{1–3} we indeed showed that it may be reduced to a one-dimensional Schrödinger equation. Spherically symmetric confined spaces are considered as models for the behavior of helium atoms in cavities in solid matrices or on a solid, corrugated substrate.

Probably the most important confined geometry is cylindrical. There are many physical situations that may be modeled by cylindrical geometry. Let us mention carbon nanotubes^{4–9} with a variety of diameters ranging from 7 to 40 Å.

Cylindrical geometry is not as simple as spherical geometry. Namely, transformation to relative coordinates in order to lower the number of independent variables below five is not possible. That is why in this geometry one has to employ a different numerical approach in studying the two-body problem. Furthermore, the values of some physically important quantities in cylindrical geometry, components of the square of the momentum for example, depend on direction.

Our goal in this paper is basically 2-fold. We wish to enlarge our knowledge of energetics of the diatomic helium molecule in this geometry and derive its dependence on the radius and length of the cylinder. On the other hand, we intend to study and develop tools, that are precise enough, for treating this and similar systems for future theoretical consideration.

As we showed earlier, for a sphere and circle, the binding energy increases in confined geometry. Dependence of the binding energy on geometry could be the basis for the

explanation of some phenomenological properties in molecular biology where proteins can change the diameters of channels.

Let us notice that in order to obtain the binding energy of two interacting particles in a confined geometry one must subtract the corresponding energy of two free particles in the same geometry.

Following in section II we define a trial wave function in cylindrical geometry with an infinite repulsive wall and find the expressions for the local energy and the square of the momentum along the axis of the cylinder and in the plane perpendicular to that axis. In section III we describe a method of numerical calculation and present the results. Section IV is devoted to the discussion of results and future prospects.

II. VARIATIONAL WAVE FUNCTION AND LOCAL QUANTITIES

The Hamiltonian of two helium atoms of mass m_1 and m_2 in a cylindrical tube with radius R and length L reads

$$H = -\frac{\hbar^2}{2m_1}\Delta_1 - \frac{\hbar^2}{2m_2}\Delta_2 + V(r_{12}) + V_{\text{ext}}(r_1) + V_{\text{ext}}(r_2), \quad (1)$$

where $r_{12} = |r_1 - r_2| = r$ is the particle separation, $V_{\text{ext}}(r_i)$ is the interaction potential between particle i and the tube, and $V(r_{12})$ is the interaction potential between particles. We neglect the details of the interaction between the cylindrical wall of the tube and the particles and simply assume a smooth and hard wall, i.e., the confining external potential is

$$V_{\text{ext}}(\rho) = \begin{cases} 0, & \text{for } \rho < R, 0 < z < L \\ +\infty & \text{otherwise} \end{cases}$$

where ρ and z are cylindrical coordinates of any particle. The smooth confining potential is a rather good approximation at least for ^4He atoms inside a carbon nanotube since the energy and the position of a ^4He atom changes by less than 1% if one considers the interactions with the individual carbon atoms inside the wall of the tube.⁵ For $V(r)$ we use the SAPT potential by Korona et al.^{10,11}

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$$V(r) = \epsilon V^*(r)$$

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

where

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

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

To study the lowest energy state of the system, we start with the variational wave function of the form¹

$$\Psi(r_1, r_2) = f(r_{12}) \phi(r_1) \phi(r_2) \quad (2)$$

where $\phi(r_i)$ is the ground-state wave function of the free particle i in the cylindrical well, i.e.

$$\phi(\rho, \varphi, z) = C J_0(K\rho) \sin(kz) \quad (3)$$

where J_0 is the Bessel function of the first kind and C is a normalization constant. The corresponding ground-state energy is

$$\epsilon = \frac{\hbar^2}{2m}(K^2 + k^2); \quad K = \frac{2.40483}{R}; \quad k = \frac{\pi}{L} \quad (4)$$

The interaction between particles is taken into account by a suitably chosen function of the relative coordinate

$$f = \frac{1}{r_{12}} \exp \left[- \left(\frac{a}{r_{12}} \right)^\gamma - s r_{12} \right] \quad (5)$$

where a , γ , and s are variational parameters to be determined by the minimization procedure and

$$r_{12} = [\rho_1^2 + \rho_2^2 - 2\rho_1\rho_2 \cos(\varphi_1 - \varphi_2) + (z_1 - z_2)^2]^{1/2}$$

is the distance between particles.

The usual procedure of separating the relative motion from the center of mass motion in a two-body problem is not feasible in this case due to the restrictive geometry. Namely, using the variational method, one can obtain an upper bound for the ground-state energy in the form of a five-dimensional integral in cylindrical coordinates. Since this integral is not well suited for standard numerical integration, we determine the ground-state energy directly by the Monte Carlo methods. Variational ansatz for the ground-state energy can be written in the form¹²

$$E[\Psi] \leq \frac{\int \Psi^2 E_L d^3r_1 d^3r_2}{\int \Psi \Psi d^3r_1 d^3r_2} \quad (6)$$

where the “local energy” E_L is

$$E_L = \frac{1}{\Psi} H \Psi \quad (7)$$

First, we use variational Monte Carlo (VMC) to perform the six-dimensional integration in (6) and to minimize $E[\Psi]$. In continuation, we employ diffusion Monte Carlo (DMC) to compute exact¹³ ground-state energies. The Monte Carlo (MC) estimate of the energy is

$$E = \lim_{M \rightarrow \infty} \frac{1}{M} \sum_{i=1}^M E_L(X_i) \quad (8)$$

where sample points $\{X_i\}$ are drawn from the probability density distribution. In VMC the points are sampled from Ψ^2 and in DMC from the mixed distribution¹² $\Psi \Phi_0$, where Φ_0 is the exact ground-state wave function. The expression for local energy (7) becomes

$$E_L = \epsilon_1 + \epsilon_2 + V(r_{12}) - \frac{\hbar^2}{2\mu} G(r) - \frac{\hbar^2}{2} N(r_1, r_2) \quad (9)$$

where

$$G(r) = \frac{\gamma^2 a^{2\gamma}}{r^{2\gamma+2}} - \frac{\gamma(\gamma+1)a^\gamma}{r^{\gamma+2}} - \frac{2s\gamma a^\gamma}{r^{\gamma+1}} + s^2$$

$$N(r_1, r_2) = \frac{2}{r} \left[\frac{\gamma a^\gamma}{r^{\gamma+1}} - \frac{1}{r} - s \right] \left\{ \frac{1}{m_1} \left[k(z_1 - z_2) \text{ctg}(kz_1) - \right. \right.$$

$$K \frac{J_1(K\rho_1)}{J_0(K\rho_1)} [\rho_1 - \rho_2 \cos(\varphi_1 - \varphi_2)] \left. \right] +$$

$$\frac{1}{m_2} \left[k(z_2 - z_1) \text{ctg}(kz_2) - \right.$$

$$\left. K \frac{J_1(K\rho_2)}{J_0(K\rho_2)} [\rho_2 - \rho_1 \cos(\varphi_2 - \varphi_1)] \right] \left. \right\}$$

and μ is the reduced mass of the system.

We also consider the square of the momentum along the z -axis, p_z^2 , and in the plane perpendicular to it, p_o^2 . Their local expressions read

$$p_z^2 = 2\hbar^2 k^2 [1 - \text{ctg}(kz_1) \text{ctg}(kz_2)] \quad (10)$$

$$p_o^2 = 2\hbar^2 K^2 \left[1 - \frac{J_1(K\rho_1) J_1(K\rho_2)}{J_0(K\rho_1) J_0(K\rho_2)} \cos(\varphi_1 - \varphi_2) \right] \quad (11)$$

J_1 is the Bessel function of the first kind.

III. CALCULATION METHOD AND RESULTS

We take an ensemble having 500 walkers. In the VMC calculation we begin with the random distribution of the walkers and move them in the space using the simple Metropolis algorithm. We have found that 20 000 steps, with 10 steps of thermalization, are sufficient to stabilize the energy. To completely examine all of the available space, we move the ensemble in such a way that the acceptance ratio is about 50%. The final configuration of walkers in the ensemble, as an output of the VMC, is employed in the DMC as a starting distribution. The beginning trial energy in the DMC calculation is also taken from the VMC calculation where it is obtained by the minimization of parameters in the wave function. This wave function is then used as the guiding wave function in the DMC. To allow the system to equilibrate we

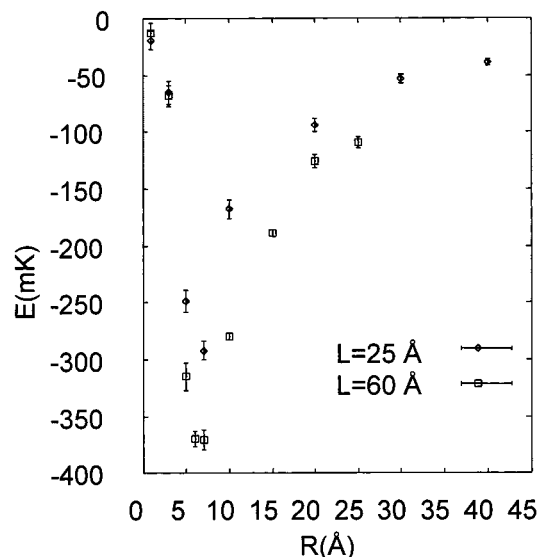


Figure 1. The binding energy E in mK vs the radius of the cylinder R in Å.

Table 1. Values of the Binding Energy (in K) of the Ratio of the rms of Components of the Momentum and Coordinates vs the Radius R (in Å) of the Cylinder and the Mean Value of the Particle Separation $\langle r \rangle$ (in Å) and the Ratio of the Length to Radius of Cylinder

R	E	$\sqrt{p_x^2/p_z^2}$	$\sqrt{r_o^2/r_z^2}$	$\langle r \rangle$	L/R
1	-0.012(8)	18.9	0.09	6.5	25
3	-0.068(9)	6.8	0.31	6.4	8.333
5	-0.315(12)	3.9	0.65	6.1	5.000
6	-0.370(7)	3.1	0.79	5.9	4.167
7	-0.371(9)	2.7	0.91	6.3	3.571
10	-0.280(1)	1.8	1.20	7.0	2.500
15	-0.189(3)	1.5	1.20	8.3	1.667
20	-0.126(6)	0.9	1.82	10.1	1.250
25	-0.109(5)	0.8	2.11	10.9	1.000

first move our ensemble up to 200 000 steps (with 10 steps of thermalization). The following 300 000–600 000 steps with the same thermalization are then used for the calculation. To eliminate the time step bias in DMC we perform the calculation for several small time steps (acceptance ratio greater than 99.5%).

The accuracy of the calculation is estimated in two ways. First, averaging over the blocks we find the standard deviation. Second, extrapolating to time step zero we obtain a deviation of the same order as the previous one.

For any pair of radius and length of a cylinder we obtain the minimum of the total energy, the standard deviation of the energy, the average particle separation, and the square of the momentum components. We consider the cylinders of two lengths: 25 and 60 Å. The values of radii and lengths are chosen to be close to some real examples. Energies for both cylinders are presented in Figure 1.

The ratio of the root-mean-square (rms) of the momentum components and the particle separation components, along with the axis of the cylinder and in the plane perpendicular to it, are given in Table 1 for the cylinder length 25 Å.

In a set of cylinders of the same volume, the energy of two free quantum particles is minimal for cylinders with a length-to-radius ratio of 1.847.¹⁴ To study the dependence of the dimer binding energy on this ratio, we take the cylinder volume $V = 625\pi$. Then we calculate the binding energy

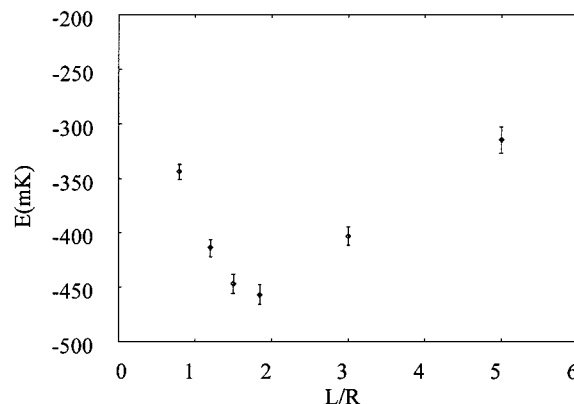


Figure 2. The binding energy E (in mK) as a function of the ratio of the length to radius of cylinders with the same volume of 625π . Two free particles have the minimum energy for cylinders with $L/R = 1.847$.

for different ratios of the length to radius for that volume. The results are shown in Figure 2.

IV. DISCUSSION AND FUTURE PROSPECTS

It may be noticed that for a fixed length of cylinder the binding energy of two particles depends on the radius of the cylinder. For the radius $R \rightarrow 0$, contrary to the case of a sphere and circle,¹ the binding energy is expected to be negative. It reaches the minimum value (maximal binding) at the radius R_m . With the enlargement of R the binding increases slowly. Now let us imagine a real physical space made of two joined cylinders with the same axis and different radii. Most of the time two noninteracting particles in such a space occupy the cylinder with the larger radius. Switching on the real interaction between particles, repulsive at small distances and attractive otherwise (for example Lennard–Jones), we may get the opposite situation. A system of two bound particles may prefer to stay in the cylinder with the smaller radius because its binding energy is greater in that space. A simple generalization of this could be a conical space. In such a space two bound particles will move toward the region of minimal energy. The total effect could be the continuous motion of two bound particles through the nanochannel. The force, which drives the system, is proportional to the gradient of the binding energy $E(R)$ along the axis of the cylinder.

The above result is very interesting. It opens a new problem which should be studied quantitatively in the future.

Dependence of the binding energy on the length of the cylinder shows the expected behavior. It is weaker for longer cylinders (except for the radii lower than about 3 Å).

To model a more realistic situation one may impose the periodic boundary conditions along the axis of the cylinder. In that case the wave function, describing a free particle in the cylinder, becomes

$$\phi(\rho, \varphi, z) = C J_0(K\rho) \exp(ikz) \quad (12)$$

where $k = 2\pi n/L$, $n = 0, 1, 2, \dots$ With this function the binding is generally weaker. If the cylinder is long enough, one obtains the same result as (3).

As shown in Table 1, cylindrical geometry is manifested in the values of the square of the momentum and particle separation components along the z axis and in the plane

perpendicular to it. The ratio of these two momenta depends on the relation between the radius and the length of the cylinder. For instance, for $R = 5 \text{ \AA}$ and $L = 25 \text{ \AA}$ square of the momentum along the z axis is 15.2 times lower than in the plane perpendicular to it. This gives us explicit information on the distribution of the kinetic energy in the tube.

The ratio of the rms of two components of the interparticle distance shows how a dimer occupies space in cylinders. Only the space along the axis is occupied in narrow cylinders.

In Figure 2 it is also interesting to notice how the interaction between particles is related to the cylinder parameters for which the maximal binding is obtained. Namely, the strongest binding is achieved for the value of $R/L \cong 1.847$, which is just the same as in the case of free particles (in the frame of calculation error).

Two other diatomic molecules of helium, $(^3\text{He})_2$ and $^3\text{He}-^4\text{He}$, are not studied. Although the helium 3 dimer is fermionic system, our experience¹⁻³ shows that, in comparison with helium 4, nothing will be changed qualitatively.

It is possible to compare our results with others only qualitatively. Namely, ^4He atoms in one dimension (1D)^{15,16,4} and tube⁴ have been considered as many body systems. Gordillo et al.⁴ obtained binding energy per particle of -0.0036 K at equilibrium density in 1D. In our case dimer binding energy in the cylinder with $R = 1 \text{ \AA}$ and $L = 25 \text{ \AA}$ is $-0.012(8) \text{ K}$.

The variational energies are 3–10% higher than the exact DMC energies, except for R less than 5 \AA where the difference between these energies starts to grow. A satisfactory optimization of variational parameters could not be achieved due to numerical instability of the VMC for small radii.

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