Helium Molecules Within Carbon Nanotubes

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Abstract

The ground state properties of ^3He and ^4He dimers and trimers in infinite carbon nanotubes are studied. The ground state eigen-functions of a helium atom in tubes of different radii are obtained numerically and then fitted by analytic expressions. Total wave function is assumed to be a product of Jastrow-Feenberg (JF) pair correlation and one particle functions. After extensive Monte Carlo (MC) calculation in two successive stages, VMC (simple variational MC) and DMC (diffusion MC) it is found that binding depends on the tube radius and it has the maximum for a certain tube width. This radius is between 5 and 7Å, and the average distance between atoms in such tubes is ranges from 5 to 10Å. The difference in binding between bosons and fermions disappears for $R \to 0$.

Key words: helium dimer and trimer; binding in carbon nanotubes

1. Introduction

Among many attractive properties of single-walled carbon nanotubes (SWNT), their quasi-one dimensional character (Q1D) is the most general. These objects usually have radii ranging from 3 to 20 Å and lengths about 1000 times longer. Therefore, helium atoms within SWNT at low enough temperatures represent Q1D quantum fluid. In strictly one dimensional (1D) space, ^4He atoms form a self bound liquid [1] which becomes solid at high density [2]. Many-body calculations of ^4He inside SWNT have been performed as well [2]. It has been found that binding energy is three times larger than on planar graphite.

In unrestricted 3D space, only ^4He forms dimers and trimers. Calculations in two-dimensions (2D) and in quasi-2D space [4] have shown that dimers and trimers of both helium isotopes have self bound states in such confined space. Helium molecules within SWNT have not been studied so far, and it is not known whether they make self-bound systems in that geometry. In two recent works [5], helium 4 dimer has been studied in one finite cylinder and in two finite coaxial adjacent nanocylinders with different radii and infinite walls . It has been shown that ground state binding energy depends on the radius of the cylinder. It is the strongest for a certain value of the radius. For smaller and greater radii, binding becomes weaker. Here, we report a MC calculation of the ground state energy and the structures of ^3He and ^4He dimers and trimers, in a space within SWNT.

2. Calculation, results and conclusion

We consider helium atoms as point particles interacting both via Korona et al. pair potential $V(r_{ij})$ [3], and with the carbon nanotube wall represented by Stan and Cole potential $V_{SC}(r_i)$ [6]. The hamiltonian then reads

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{n}\Delta_i + \sum_{i<j=1}^{n} V(r_{ij}) + \sum_{i=1}^{n} V_{SC}(r_i). \quad (1)$$

For $n = 2$ and $n = 3$, hamiltonian is adapted to the dimers and trimers respectively. As usual, to get the binding energy in confined space, we subtract the en-

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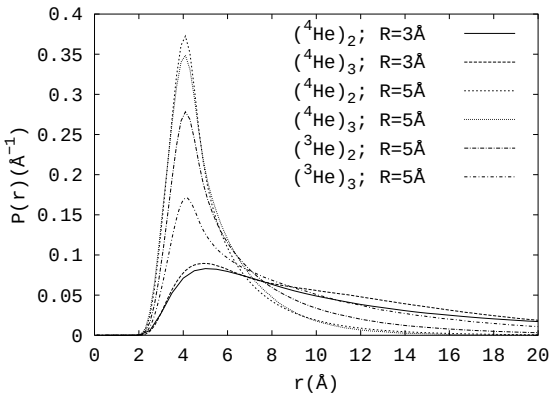

Fig. 1. The pair distribution functions for dimers and trimers in the nanotubes with R=3Å and R=5Å. $\int P(r)dr = 1$.

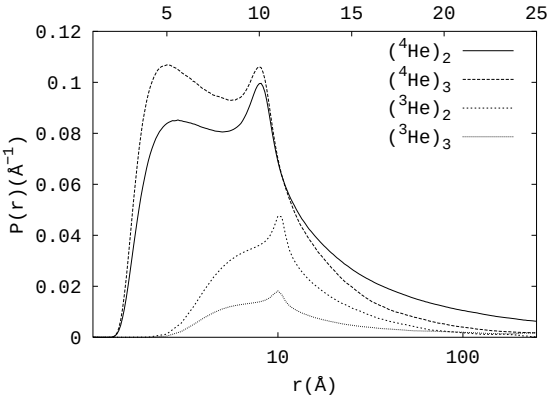

Fig. 2. The pair distribution functions for ^{4}He dimers and trimers (upper scale), and ^{3}He dimers and trimers (lower scale) in the nanotube with R=8Å .

ergy of noninteracting particles in that space. Trial wave functions for both dimers $n = 2$ (with corresponding mass) and for boson trimer $n = 3$ are

$$\Psi_0 = \prod_{i<j}^{n} F(r_{ij}) \prod_{i=1}^{n} \phi(r_i). \quad (2)$$

For ^3He trimer (spin 1/2) we take antisymmetric function

$$\Psi = \frac{2}{\sqrt{6}}[\alpha_1\alpha_2\beta_3(z_1 - z_2) + \beta_1\alpha_2\alpha_3(z_2 - z_3) + \alpha_1\beta_2\alpha_3(z_3 - z_1)]\Psi_0 \ , \quad (3)$$

where α is the spin-up, and β is the spin-down function. Two-body JF function is taken to be $F(r_{ij}) = exp[-(\frac{\alpha}{r_{ij}})^\gamma - sr_{ij}]$. One particle eigenfunctions $\phi(r_i)$ in the tube have been derived numerically and then fitted by analytic expressions. They are: $\phi(r_i) = exp[-a_1 r_i^2 - a_2 r_i^4]$ for R=3Å, and $\phi(r_i) = exp[ar_i^b - (c/(R - r_i))^d]$ for R=5Å and R=8Å. MC procedure has been employed in two steps. The parameters of JF wave functions and trial energies have been found in VMC and then used in DMC (Fixed Node DMC for fermionic trimer). Some results are presented in the Table and in Figures 1 and 2. The errorbars on these Figures range from 2-10%.

In conclusion, we may say that ^4He forms dimers and trimers within SWNT. Due to the smaller mass of ^{3}He, its dimers and trimers are bound less than ^4He dimers and trimers. Moreover, we have not found bound states of ^3He dimers and trimers for R=3Å. The binding energy depends on radius, and it is the strongest for R=5Å. For this R, the molecules are much smaller than in pure infinite 2D or 3D space. The structure of molecules follows the potential form which depends on the tube radius. For instance, atoms are located along the tube axis for R=3Å, while for larger radii they have more freedom to move perpendicularly to the axis.

Table 1
The helium molecules binding energies (in mK) in SWNT. The subscripts b and f mean that calculation is performed for corresponding bosonic and fermionic wave function.

molecule	R=3Å	R=5Å	R=8Å
(^{3}He)$_2$	?	-422(3)	-4.5(4)
(^{4}He)$_2$	-28(1)	-860(4)	-79(1)
(^{3}He)$_3$	?	-600(30)	-4.6(8)
(^{3}He)$_{3,b}$	?	-995(5)	-7(2)
(^{4}He)$_3$	-121(8)	-2095(12)	-265(5)
(^{4}He)$_{3,f}$	-117(13)	-1640(17)	-90(2)

In the limit of $R \to 0$, one could expect no difference in the binding properties of bosons and fermions. To verify this, we have calculated the trimer energies using bosonic and fermionic wave functions for each isotope. For the tube with R=3Å our results show almost no difference between the energy of $(^4He)_3$ and the energy of the fictitious trimer $(^4He)_{3,f}$, which has the same mass and a spin 1/2.

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