Hydrogen in a cavity

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The system of a proton and an electron in an inert and impenetrable spherical cavity is studied by solving Schrödinger equation with the correct boundary conditions. The differential equation of a hydrogen atom in a cavity is derived. The numerical results are obtained with the help of a powerful and efficient few-body method, Gaussian Expansion Method. The results show that the correct implantation of the boundary condition is crucial for the energy spectrum of hydrogen in a small cavity.

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I. INTRODUCTION

The study of confined quantum system is an interesting topic recently [1]. With the advance of technique, a number of confined quantum systems can be constructed. For example, the well known confined quantum systems are quantum wells, quantum wires and quantum dots [2]. The study of the confined quantum system is helpful to understand the various properties of nano-structures [3].

The simplest confined quantum system is that a hydrogen atom confined in a spherical cavity. It was first investigated by Michels et al. about 80 years ago [4], followed by Sommerfeld and Welker [5]. Since then the problems concerning confined atoms have been studied by many authors [6]. Various methods are introduced to solve the problem. Perturbation methods [7], variational methods [8], phase integral method [9], etc. In the previous work, people always assume that the proton in the hydrogen is fixed in the cavity, because of the large mass of proton. This assumption is reasonable in the free space, the two-body problem can be reduced to one-body problem by introducing the center-of-mass motion and relative motion coordinates. The boundary condition is applied to the relative motion coordinates of electron. However, the boundary condition should be applied to proton and electron separately. In this case, the two body Schrödinger equation can no longer be divided into the center-of-mass and relative motion, and the situation becomes more complex. To develop a new method to solve the problem of a hydrogen atom confined in an inert and impenetrable spherical cavity is the goal of the present work. As a preliminary work, the angular momentum is set to 0 and only the first three radial states are constructed.

In the present work, the motion of the proton is taken into account. The boundary condition is applied both to the electron and proton motion. The problem is solved numerically with the help of modified gaussian expansion [10]. The method is explained in the next section. The numerical results are presented in the Sec. III. A brief summary is given in the last section.

II. METHOD

The proton-electron system in an impenetrable spherical cavity with radius $r_0$ is shown in Fig. 1. The non-relativistic Hamiltonian of the system is (in atomic unit)

$$H_{ep} = -\frac{\nabla_1^2}{2} - \frac{1}{m_p} \frac{\nabla_2^2}{2} - \frac{1}{r_{12}} + V(r_1) + V(r_2),$$

where $m_p$ is the mass of proton, $r_{12}$ is the distance between electron and proton. The impenetrable spherical cavity is represented as

$$V(r_i) = \begin{cases} 0 & r_i < r_0 \\ \infty & r_i > r_0 \end{cases}$$

FIG. 1: A hydrogen in a cavity.

The Schrödinger equation to be solved is

$$\left[ -\frac{\nabla_1^2}{2} - \frac{1}{m_p} \frac{\nabla_2^2}{2} - \frac{1}{r_{12}} \right] \Psi_{ep}(r_1, r_2) = E_{ep}\Psi_{ep}(r_1, r_2),$$

for $r_1, r_2 < r_0$
with boundary conditions

\[ \Psi^{\text{ep}}(r_1 \geq r_0, r_2) = \Psi^{\text{ep}}(r_1, r_2 \geq r_0) = 0 \quad (4) \]

Because of the cavity, the spatial translational invariance of the system is violated. To separate the motion of the system into center-of-mass motion and relative motion by introducing the Jacobi coordinates is meaningless. However, to remove the center-of-mass kinetic energy is necessary for studying the hydrogen atom in a cavity. So Hamiltonian of a hydrogen atom in a cavity is modified as:

\[ H^H = -\frac{\nabla_r^2}{2} - \frac{1}{\bar{m}_p} \frac{\nabla_x^2}{2} + \frac{1}{2(1 + \bar{m}_p)} \left( \nabla_r \cdot + \frac{1}{r_{12}} \right) + V(r_1) + V(r_2). \quad (5) \]

The Schrödinger equation for a hydrogen in a cavity is

\[ \Psi^H(r_1, r_2) = E^H \Psi^H(r_1, r_2), \quad \text{for } r_1, r_2 < r_0 \quad (6) \]

The standard procedure to solve the equation for hydrogen in a cavity using independent coordinates \( r_1 \) and \( r_2 \)

Due to the spherical symmetry, the wavefunction of the hydrogen in a cavity \( \Psi^H(r_1, r_2, x) \) can be written as \( \Psi^H(r_1, r_2, x = \cos \theta) \) (see Fig. 1). Using \( r_1, r_2, x \), the Hamiltonian can be written as (for \( r_1, r_2 < r_0 \))

To find the analytic solution of \( \Psi^H(r_1, r_2, x) \) is too difficult to be done. So the numerical method is employed. For the sake of simplicity in this work, only the \( L = 0 \) states are considered. Here the Gaussian expansion method, a powerful method for few-body system with high precision is used [10]. The wavefunction \( \Psi^H(r_1, r_2, x) \) is expanded as

\[ \Psi^H(r_1, r_2, x) = \frac{\sin \frac{\pi r_1}{r_0}}{r_1 r_0} \sum_{n=1}^{n_{\text{max}}} c_n e^{-\nu_n r_{12}^2}. \quad (9) \]

The gaussian size parameters are taken in geometric progression

\[ \nu_n = \frac{1}{b_n^2}, \quad b_n = b_1 a^{n-1}, \quad a = \left( \frac{b_{n_{\text{max}}}}{b_1} \right)^{1/n}. \quad (10) \]

The numerical results are obtained by using GEM and are shown in the columns with head \( H^0 \) of Table II where only the eigen-energies and average distance \( d \) between the electron and the proton of first three radial states, 1S, 2S and 3S are presented. The energies agree with the previous results very well. The agreement shows that GEM is an effective method with high precision for the confined quantum systems.

### III. RESULTS

In order to check the precision of GEM, we first do a calculation of the hydrogen in the cavity with proton fixed at the center of the cavity. In this case, the Hamiltonian is simplified to

\[ H^0 = -\frac{\nabla_r^2}{2} - \frac{1}{r_1} + V(r_1). \quad (11) \]
boundary conditions, the eigen-energies and average distance between the electron and the proton. The energy levels of a hydrogen in a cavity are shown in Fig. 2. Considering the motion of proton and using correct boundary conditions, the eigen-energies and average distance $d$ between the electron and the proton are also shown in Table I. Comparing with the results with $H^0$, there are significant differences, especially for the excited states. For the ground state, our results are a little higher than the previous results. For $r_0 = 0.1$, there is a 1% difference. With the increasing cavity radius, the difference decreases. For the large cavity, $r_0 = 50$, the difference will disappears. The remained small difference comes from the reduced masses of electron is used in our calculation. For the $3S$ state, our results deviate from the previous results rather large for $r_0 \leq 10$. We get a smaller energies, which is unusual, compared with the ground state. Further study is needed.

The energy levels of the system are shown in Fig. 2. We can see that for the small cavity, the boundary condition has larger effects on the hydrogen, the energy difference between $3S$ and $2S$ is bigger that between $2S$ and $1S$ (for $r_0 = 1.0$, $E_{3S} - E_{2S} = 8.634$, $E_{2S} - E_{1S} = 6.3028$), this is the feature of a particle moving in a spherical well. For the larger cavity, the Coulomb potential between electron and proton will become dominant, the energy difference between $3S$ and $2S$ is much smaller that between $2S$ and $1S$ (for
$r_0 = 25, E_{3S} - E_{2S} = 0.07, E_{2S} - E_{1S} = 0.3736$), the feature of a particle moving in a Coulomb potential.

Fig. 3 displays the variation of the average distance with the radius of the cavity. Clearly the cavity has much stronger influence on the excited states, because the excited states spread more.

IV. SUMMARY

By considering the motion of proton and using the correct boundary conditions for electron and proton, the hydrogen in an inert and impenetrable spherical cavity are studied by solving Schrödinger equation. A powerful few-body method, GEM is employed to do a numerical calculation. The results show that for a not too large cavity, our results are different from the previous ones with fixed proton. So the correct mount of boundary conditions is important for the confined quantum systems.

It is worth to mention that the center-of-mass motion of the system is removed before solving Schrödinger equation. Including the center-of-mass motion, solving Schrödinger equation, then separating the center-of-mass motion, is another story because of the violation of the translation invariance.

In the present work, only the first three radial states are considered. To generalized the calculation to other states are straightforward, which is our next work.

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