On the Size of Quantum Dots with Bound Hydrogenic Impurity States

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Some particular bound state energies of an electron, under Coulomb potential field, confined in a two-dimensional circle and a three-dimensional sphere are analytically derived. The derivation shows that the electron cannot be bound in a negative energy state when the circle (or sphere) is smaller than a certain critical size. The critical size dependency on the strength of Coulomb potential and the angular momentum of the electron is also analytically derived. This system mimics quantum dots. Therefore the derivation provides new information on a minimum critical size of quantum dots with hydrogenic impurity.

Key Words: Coulomb potential, Quantum dots, Confluent hypergeometric functions

Introduction

When electrons are confined on a scale comparable to their de Broglie wavelength, their motion is restricted in space. This confinement is found in nanostructures, for example, quantum dots. Quantum dots are found to have quantized energy levels so that they are sometimes called artificial atoms. A lot of experimental and theoretical investigations on the characteristics of quantum dots have been reported.[1-9] The frequently found or manufactured three-dimensional quantum dots are spherical, for example, CdSe nanoparticles. Here electrons are confined within a finite sphere. Two-dimensional quantum dots appear in interface, for example, in the vicinity of junctions between insulators and semiconductors, or between a vacuum and liquid helium. In this case, electrons are confined to a thin layer at the interface. The two-dimensional circular quantum dots also have been frequently investigated.[10-18]

Quantum dots are small materials containing a tiny droplet of free electrons. Strictly speaking, these electrons interact with each other. However many-electron quantum dots can be approximated as one-electron quantum dots. For example, in a hole-electron system, an extra electron (under the influence of Coulomb potential by the hole) moves rather freely from the interaction with other electrons. This kind of quantum dot is so called a hydrogenic impurity system and it can be treated as one-electron system.[19,20]

In this work, the quantized energy levels of hydrogenic impurity state – an electron confined within a finite space where Coulomb potential is present – are theoretically investigated. Both two-dimensional circular confinement (circle) and three-dimensional spherical confinement (sphere) are investigated. It is a textbook knowledge that the energy levels can be exactly obtained when the electron is not confined. But the finite confinement system cannot be solved exactly. This confinement system has both positive and negative bound states. The emphasis is given on the negative bound states because not only the negative bound states can be spontaneously formed from a free electron but also the exact energy for a particular negative bound state (with a particular size of confinement) can be obtained in an analytical manner.

Solving the relevant differential equation, one obtains not only the state energies but also the relationship between the confinement size and the energy.[19]

In the next section the two-dimensional confined system is defined and solved. The mathematical procedure of obtaining the negative bound state energies and confinement size is explicitly presented. In order to gather the information that will be utilized to understand the critical size of quantum dots, the interpretation on the mathematical expressions is also provided. In the following section the three-dimensional confined system is solved. The mathematical technique to solve this system is identical with that of the two-dimensional system. The chemical information learned from this mathematical labor is also presented. Finally several comments on the size of quantum dots with a hydrogenic impurity are provided in the conclusion section.

Solution of a Two-dimensional Confined System

In our model study, a two-dimensional quantum dot is a circle and a hydrogenic impurity is assumed to be an electron moving within the circle under the influence of Coulomb potential. From a theoretical point of view, it is the so-called circle billiard with Coulomb potential in.[21,22]

For the circle of radius r_0, the radial Schrödinger equation for an electron of mass μ, with an angular momentum quantum number m, is[21-23]

$$\left[-\frac{\hbar^2}{2\mu}\left\{ \frac{d^2}{dr^2} + \frac{m^2 - 1/4}{r^2} \right\} + V(r) \right] \Psi_{n,m}(r) = E_{n,m}\Psi_{n,m}(r) \quad (0 < r < r_0)$$

$$(1)$$

where the Coulomb potential $V(r) = -\dfrac{A}{r}$ existing only, within the circle. The positive number A is a parameter for potential strength. n is a radial quantum number (or a number of radial nodes in wave function $\Psi_{n,m}(r)$) for the state with energy $E_{n,m}$. Of course, n is 0, 1, 2, … and m is 0, ±1, ±2, … Since the electron is confined within the circle of radius r_0, the boundary condition is that the wave function must be zero at r_0, i.e., $\Psi_{n,m}(r_0) = 0$.

A brief idea of solving Eq. (1) for negative bound states has

been reported[19] and we adopt the same mathematical technique. Let

$$\rho = \nu r \ \text{and} \ \nu = \sqrt{\frac{8\mu}{\hbar^2}(-E_{n,l})} \ . \tag{2}$$

ν is a real number because the energy $E_{n,m}$ is negative for negative bound states. With substitution of $\Psi_{n,m}(r) = \rho^{|m|+\frac{1}{2}}e^{-\rho/2}U(\rho)$, Eq. (1) can be rewritten as

$$\rho\frac{d^2U(\rho)}{d\rho^2} + (c-\rho)\frac{dU(\rho)}{d\rho} - aU(\rho) = 0 \tag{3}$$

where

$$c = 2|m| + 1 \tag{4}$$

and

$$a = \left(\frac{2\mu}{\hbar^2}\right)^{1/2}\frac{A}{2\sqrt{-E_{n,m}}} + |m| + \frac{1}{2} \ . \tag{5}$$

Eq. (3) is the well-known confluent hypergeometric equation[24] and the solution is the confluent hypergeometric function (or Kummer's function), i.e.,

$$U(\rho) = {}_1F_1(a,c;\rho) = 1 + \frac{a}{c}\rho + \frac{a(a+1)}{c(c+1)}\frac{\rho^2}{2!} + \dots \tag{6}$$

The ground ($n = 0$) negative bound state with an angular momentum m, i.e., $(0, m)$ state, appears when $a = -1$. The boundary condition ($\Psi_{0,m}(r_0) = 0$) dictates that

$$U(\rho_0) = 1 + \frac{a}{c}\rho_0 = 0 \tag{7}$$

where $\rho_0(=\nu r_0) = -\frac{c}{a} = c = 2|m| + 1$. $\tag{8}$

Therefore the ground state wave function is

$$\Psi_{0,m}(r) = \rho^{|m|+1/2}e^{-\rho/2}\left(1 - \frac{1}{c}\rho\right) \ . \tag{9}$$

Obviously it has no nodes so that the radial quantum number is zero, i.e., $n = 0$, as expected.

One can obtain the ground state energy, using Eq. (5),

$$E_{0,m} = -\frac{\mu A^2}{2\hbar^2}\frac{1}{\left(|m|+\frac{3}{2}\right)^2} \ . \tag{10}$$

Of course, $E_{0,m} = E_{0,-m}$. The radius of circle for the $(0, m)$ state is, using Eqs. (2), (8) and (10),

$$r_0 = \frac{\hbar^2}{2\mu A}\left(|m|+\frac{3}{2}\right)(2|m|+1) \ . \tag{11}$$

The energy in Eq. (10) is the exact (analytically derived) ground state energy when a particle is confined within a circle of radius given in Eq. (11).

Now let us consider the first excited state ($n = 1$, i.e., $(1, m)$ state) that has one radial node in wave function. The first

excited negative bound state appears when $a = -2$. The boun-boundary condition ($\Psi_{0,m}(r_0) = 0$) dictates that

$$U(\rho_0) = 1 + \frac{a}{c}\rho_0 + \frac{a(a+1)}{c(c+1)}\frac{\rho_0^2}{2!} = 0 \ . \tag{12}$$

By solving the quadratic equation (12) one obtains

$$\rho_0 = c + 1 - \sqrt{c+1} = 2|m| + 2 - \sqrt{2|m|+2} \tag{13}$$

or $\rho_0 = c + 1 + \sqrt{c+1} = 2|m| + 2 + \sqrt{2|m|+2} \ . \tag{14}$

The solution (13) is the position where the wave function is zero, i.e., a node. The second solution (14) is the edge (or boundary) of the circle where the boundary condition is satisfied.

Therefore the first excited state wave function is

$$\Psi_{1,m}(r) = \rho^{|m|+\frac{1}{2}}e^{-\rho/2}\left(1 - \frac{1}{c}\rho + \frac{1}{c(c+1)}\rho^2\right) \ . \tag{15}$$

One can obtain the state energy using Eq. (5) with $a = -2$,

$$E_{1,m} = E_{1,-m} = -\frac{\mu A^2}{2\hbar^2}\frac{1}{\left(|m|+\frac{5}{2}\right)^2} \ . \tag{16}$$

The radius of circle for the $(1, m)$ state is, using Eqs. (2), (14) and (16),

$$r_0 = \frac{\hbar^2}{2\mu A}\left(|m|+\frac{5}{2}\right)\left(2|m|+2+\sqrt{2|m|+2}\right) \ . \tag{17}$$

The energy in Eq. (16) is the exact first excited state energy when an electron is confined within a circle of radius given in Eq. (17).

From the above derivation, one observes the followings:

1) When the angular momentum of electron $|m|$ increases, the ground state energy $(0, m)$ decreases (approximately $E_{0,m} \propto |m|^{-2}$) but the radius of circle increases (approximately $r_0 \propto |m|^2$) as shown in Eqs. (10) and (11).

2) As the strength of the Coulomb potential (A) increases, the ground state energy decreases (more negative, i.e., $E_{0,m} \propto -A^2$) and the radius of circle also decreases ($r_0 \propto A^{-1}$). See Eqs. (10) and (11).

3) Comparing Eq. (11) with Eq. (17), one finds that the radius for the first excited state with negative energy is larger than that for the ground state with negative energy. It indicates that the first excited bound state with negative energy does not exist when the radius of circle is smaller than the radius given in Eq. (17). Therefore the first excited state of the electron in the circle with the radius given in Eq. (10) must have a positive energy, which is proved by numerical calcul-ations.[19,20] There must be a minimum critical size of circle to hold at least one negative bound state in it. The smallest circle that can have the ground bound state with negative energy is the one having the radius given in Eq. (11), i.e., the minimum critical size of circle. The radius in Eq. (17) is the minimum

critical size of circle having the first excited state with negative energy.

4) From Eqs. (10) and (16), one immediately notices that $E_{1,m} = E_{0,m+1}$, i.e., the states $(1, m)$ and $(0, m+1)$ are isoenergetic when m is positive. Generally, $E_{1,|m|} = E_{0,|m|+1}$. But the radius of circle for the $(1, m)$ state (see Eq. (17)) is larger than that of the $(0, m+1)$ state $\left(r_0 = \frac{\hbar^2}{2\mu A}\left(|m|+\frac{5}{2}\right)(2|m|+3)\right)$ derived from Eq. (11)). It in dicates that not only the energy but also the wave function affects the size of circle.

5) When the radius of circle is infinity, Eq. (1) can be solved exactly for all states.[23] The energy for (n, m) state is

$$E_{n,m} = -\frac{\mu A^2}{2\hbar^2}\frac{1}{\left(n+|m|+\frac{1}{2}\right)^2}$$. Comparing it with Eqs. (10) and

(16), one finds that the ground state energy $(n = 0)$ in the circle with radius of Eq. (11) is identical with the first excited $(n = 1)$ state energy in the infinite circle. The first excited state energy $(n = 1)$ in the circle with radius of Eq. (17) is identical with the second excited $(n = 2)$ state energy in the infinite circle. Although the physical application of this finding is not immediate, we would like to note that it must be related to supersymmetry nature of the system.[25-29] See also the previous paragraph 4.

Hydrogenic Impurity States in a Three-dimensional Quantum Dot

A three-dimensional quantum dot is a sphere and a hydrogenic impurity is assumed to be an electron moving within the sphere under the influence of Coulomb potential. This system is identical with a hydrogen atom with a finite size, i.e., the electron moves under the influence of proton within a confinement.

For the sphere of radius r_0, the radial Schrödinger equation for an electron of mass μ, with an angular momentum quantum number l $(= 0, 1, 2, \ldots)$ is

$$\left[-\frac{\hbar^2}{2\mu}\left\{\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}\right\}-\frac{A}{r}\right]\Psi_{n,l}(r) = E_{n,l}\Psi_{n,l}(r)\,(0 < r < r_0) \quad (18)$$

with the boundary condition of $\Psi_{n,l}(r_0) = 0$. Eq. (18) is the same as the two-dimensional Schrödinger equation Eq. (1). The only difference is the centrifugal term $\frac{m^2-1/4}{r^2}$ in Eq. (1) is replaced with $\frac{l(l+1)}{r^2}$ in Eq. (18). The angular momentum associated with m is, of course, a projected component of the angular momentum with l. Needless to say, the same mathematical technique employed in solving Eq. (1) can be applied to solving Eq. (18).

Let $\rho = \nu r$ and $\nu = \sqrt{\frac{8\mu}{\hbar^2}(-E_{n,l})}$ (19)

With substitution of $\Psi_{n,l}(r) = \rho^{l+1}e^{-\rho/2}U(\rho)$, Eq. (18) becomes the confluent hypergeometric equation as

$$\rho\frac{d^2U(\rho)}{d\rho^2} + (c-\rho)\frac{dU(\rho)}{d\rho} - aU(\rho) = 0 \quad (20)$$

where

$$c = 2l + 2 \quad (21)$$

$$a = \left(\frac{2\mu}{\hbar^2}\right)^{1/2}\frac{A}{2\sqrt{-E_{n,l}}} + l + 1 \quad (22)$$

Again $U(\rho)$ is the confluent hypergeometric function.

The ground bound state with negative energy appears when $a = -1$. Using the boundary condition $(\Psi_{0,l}(r_0) = 0)$, one obtains

$$\rho_0(= \nu r_0) = -\frac{c}{a} = c = 2l + 2 \quad . \quad (23)$$

and the ground state wave function,

$$\Psi_{0,l}(r) = \rho^{l+1}e^{-\rho/2}\left(1-\frac{1}{c}\rho\right) . \quad (24)$$

The ground state energy is

$$E_{0,l} = -\frac{\mu A^2}{2\hbar^2}\frac{1}{(1+2)^2} \quad . \quad (25)$$

The radius of circle is

$$r_0 = \frac{\hbar^2}{2\mu A}(l+2)(2l+2) . \quad (26)$$

The first excited bound state with negative energy appears when $a = -2$. Using the same algebraic manipulation in the previous section, one obtains the first excited state wave function with $n = 1$,

$$\Psi_{1,l}(r) = \rho^{l+1}e^{-\rho/2}\left(1-\frac{1}{c}\rho+\frac{1}{c(c+1)}\rho^2\right) , \quad (27)$$

the first excited state energy

$$E_{1,l} = -\frac{\mu A^2}{2\hbar^2}\frac{1}{(l+3)^2} , \quad (28)$$

and the radius of sphere

$$r_0 = \frac{\hbar^2}{2\mu A}(l+3)\left(2l+3+\sqrt{2l+3}\right) . \quad (29)$$

The observations learned from the two-dimensional work are all valid for this three-dimensional quantum dot. We summarize physical meanings related to the size of three-dimensional quantum dots.

1) A quantum dot with bound hydrogenic impurity states with negative energy must be larger than a certain critical size. The minimum critical size of quantum dot with the ground bound state $(0, l)$ and the first excited bound state $(1, l)$ is given in Eq. (26) and Eq. (29), respectively. The critical size with the first excited state is larger than that with the ground state. One should note that, in this study, the critical size is meaningful only when the hydrogenic impurity state is a negative

Table 1. The minimum critical size of three-dimensional quantum dots with bound hydrogenic impurity states with negative energy (For notations, see the text)

impurity state	1s	2s	2p	3p	3d	4d
critical size (nm)	0.1058	0.3756	0.3175	0.7658	0.6350	1.276

energy state.

2) The critical size decreases as the Coulomb potential strength increases, i.e., $r_0 \propto A^{-1}$. When the Coulomb potential becomes stronger, the impurity is more tightly bound so that the size of quantum dot becomes smaller.

3) The critical size is also related to the angular momentum that the hydrogenic impurity has. As shown in Eqs. (26) and (29), the critical size of quantum dots increases as the angular momentum increases, i.e., approximately $r_0 \propto l^2$.

4) The minimum critical size of quantum dots with the hydrogenic impurity of the same energy is not necessarily the same. It is influenced by the wave function as well as the energy.

In Table 1, the minimum critical size of three-dimensional quantum dots with bound hydrogenic impurity states with negative energy is presented. In this example, an electron within quantum dot moves under Coulomb potential field, $V(r) = -\dfrac{e^2}{r}$ (e is the unit charge). It simulates a situation where hole ($+e$) is created and an electron ($-e$) moves under the influence of the hole charge. When $n = 0$ and $l = 0$, using the notation of artificial atoms, the impurity state is denoted as 1s. (The well-known principal quantum number N is defined as $N = n + l + 1$. Therefore $N = 1$ for the case of $n = 0$ and $l = 0$.) 2s for $n = 1$ and $l = 0$, 2p for $n = 0$ and $l = 1$, 3p for $n = 1$ and $l = 1$, 3d for $n = 0$ and $l = 2$, and 4d for $n = 1$ and $l = 2$ are used. From the Table one sees that the minimum critical size of quantum dot in 1s is smaller than that in 2p and the critical size in 2p is smaller than that in 3d though the three states have the same n=0. That is, the larger l is, the larger becomes the critical size. The critical size of quantum dot in 2s (i.e., $n = 1$, $l = 0$ so that $n + l = 1$) is larger than that in 2p (i.e., $n = 0$, $l = 1$ so that $n + l = 1$) though the two states are isoenergetic. The same trend is found between 3p and 3d. One finds that the critical size becomes larger when the wave function has many nodes.

Conclusions

A confined Coulomb potential system, i.e., an electron moving under the influence of Coulomb potential within a finite circle or sphere, is theoretically investigated. The system cannot be exactly solved. But for a particular confinement size, it can be solved for a particular negative bound state exactly and analytically. The analytical solution provides a physical insight into the system.

The model system mimics quantum dots so that this theoretical derivation yields the information on the size of quantum dots that have a hydrogenic impurity. It is found that there should be a minimum critical size of quantum dots to hold bound hydrogenic impurity states with negative energy. This model study implies that a hydrogenic impurity state of quantum dot smaller than a certain critical size does not exist when the quantum dot is formed from a free electron with zero kinetic energy. (Of course when electrons have nonzero kinetic energy, impurity states having positive energy can be obtained.) The critical size of quantum dots in the negative ground bound state is smaller than that in the negative excited state. When the Coulomb potential becomes stronger, the impurity is more tightly bound so that the size of quantum dot becomes smaller. The critical size increases as the angular momentum increases. Importantly the critical size of quantum dots depends on the wave function as well as the energy. The analytical findings on the size of quantum dots are all verified by a test calculation.

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