Three-dimensional Square Well Potential

Square Well Potential

A potential that takes 0 at outside the sphere of radius a, and takes a constant value $-V_0(V_0 > 0)$ inside the sphere:

$$V(r) = \begin{cases} -V_0 & : r \leq a \\ 0 & : r > a \end{cases} \tag{1}$$

This is called a square well potential. Although it is an extraordinary case for the potentials and seems quite inconvenient in dealing with the real world, it is extremely practical and convenient in a way. In most books on quantum mechanics, a hydrogen atom is adopted for the examples, with an electron treated inside the coulomb potential $-e^2/(4\pi\varepsilon_0 r)$ that is protracted in sequence, and has divergence in the position of atomic nucleus. The problems concerning with the coulomb potential may be accurately solved in analytical sense, yet there exists many unique aspects as well.

Given the three-dimensional potentials as (1), the time-independent Schrodinger's equation of an electron may be:

$$(-\frac{\hbar^2}{2m}\Delta + V(r))\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \tag{2}$$

This is the problem involving the spherical symmetry potential, in which the section depending on the anglular part of wavefunction $\psi(\boldsymbol{r})$ is given as spherical function $Y_{\ell m}(\theta, \phi)$, and the entirety may be written in a form of separation of variables:

$$\psi(\boldsymbol{r}) = R_\ell(r)Y_{\ell m}(\theta, \phi) \tag{3}$$

The process of applying the separation of variables to the equation (2) will yield the differential equation that obeys the radial wavefunction $R_\ell(r)$:

$$\frac{1}{r^2}\frac{d}{dr}(r^2\frac{dR_\ell(r)}{dr}) + \{\frac{2m}{\hbar^2}(E - V(r)) - \frac{\ell(\ell+1)}{r^2}\}R_\ell(r) = 0 \tag{4}$$

The last term $-\ell(\ell+1)/r^2$ in the equation above represents the centrifugal force potential, which occurs by having the angular momentum operator to act on the function. For the equation (4), we need to divide in two different situations: the plus and minus of E for the further verification.

Where $E < 0$, the conditions for E should be restricted to $-V_0 < E < 0$. If the wavefunction vanishes from the potential center $(r \to \infty)$, the effect given by the centrifugal force potential and the contribution by the terms in first order differentials can be ignored, thus (4) may be written in approximation:

$$\frac{d^2}{dr^2}R_\ell - \frac{2m}{\hbar^2}|E|R_\ell = 0$$

The behaviors of the wavefunction in a distance may be considered to follow the equation above. To solve the equation:

$$R_\ell \sim \exp(-\sqrt{\frac{2m|E|}{\hbar^2}}r), \quad (r \to \infty) \tag{5a}$$

This shows when the wavefunction steps outside the region of potential, the function exponentially decays. As we observe in later on, we should be aware of the fact that there may be no solution for $E < 0$,while $V_0 > 0$.

In the case where $E > 0$, we can treat the wavefunction in the same way, however, the function does not decay rapidly in the far distance away but rather decays slowly as it oscillates.

$$R_\ell \sim \frac{1}{r}\exp(\pm i\sqrt{\frac{2mE}{\hbar^2}}r) \ : \quad (r \to \infty) \tag{5b}$$

When $E > 0$, the solution takes arbitrary values of E, hence the continuous values for the eigenenergy are allowed (continuous eigenvalue problems).

In rewriting the differential equation (4) with careful observation of the behaviors in wavefunction (6a~d), we can determine a general equation (6):

$$\begin{aligned}
-V_0 < E < 0, \quad r < a: \quad & \alpha = \sqrt{2m(E+V_0)/\hbar^2}, \quad & \rho = \alpha r \quad (6a)\\
-V_0 < E < 0, \quad r > a: \quad & \beta = \sqrt{-2mE/\hbar^2}, \quad & \rho = i\beta r \quad (6b)\\
E > 0, \quad r < a: \quad & k_i = \sqrt{2m(E+V_0)/\hbar^2}, \quad & \rho = k_i r \quad (6c)\\
E > 0, \quad r > a: \quad & k_o = \sqrt{2mE/\hbar^2}, \quad & \rho = k_o r \quad (6d)
\end{aligned}$$

$$\frac{d^2}{d\rho^2}R_\ell + \frac{2}{\rho}\frac{d}{d\rho}R_\ell + \{1 - \frac{\ell(\ell+1)}{\rho^2}\}R_\ell = 0. \tag{6}$$

Here α, β, k_i, k_0 are defined as positive real number. An independent variable ρ remains positive real number except for the case in (6b) where $-V_0 < E < 0, r > a$ the variable takes the pure imaginary number. The differential equation (6) is commonly known to be the differential equations for spherical Bessel function, and which has been very well examined.

Let us now consider the linear ordinary differential equation below:

$$y'' + p(x)y' + q(x)y = 0 \tag{7}$$

In most cases, the differential equations adopted in physics appears to be in the similar forms because the differential equations are written in the second order linear differential equations in dynamical systems as well as in electric circuit. If we can have Taylor expansion of $p(x)$ and $q(x)$ at around $x = x_0$, in other words, if we can obtain the following equations:

$$p(x) = \sum_{n=0}^{\infty} a_n (x - x_0)^n, \quad q(x) = \sum_{n=0}^{\infty} b_n (x - x_0)^n$$

The elementary solutions for both in (7) may be obtained as following:

$$y(x) = \sum_{n=0}^{\infty} c_n (x - x_0)^n$$

Here $x = x_0$ is called a regular point.

Whereas $p(x)$ and $q(x)$ contain the singular points in $x = x_0$, and written at most:

$$(x - x_0)p(x) = \sum_{n=0}^{\infty} a_n (x - x_0)^n, \quad (x - x_0)^2 q(x) = \sum_{n=0}^{\infty} b_n (x - x_0)^n$$

Then $x = x_0$ is called the regular singular point for the differential equations. Moreover, one of the two elementary solutions should be obtained in series in this case.

$$y(x) = \sum_{n=0}^{\infty} c_n (x - x_0)^{s+n}$$

Based on the definition, the differential equations (6) takes $\rho = 0$ as the regular singular point. Now, before we generalize the case, let's consider for the situation where $\ell = 0, \quad E < 0$. We define $R_0(\rho) = u(\rho)/\rho$, and then following can be established:

$$\frac{d^2 u}{d\rho^2} + u = 0 \tag{8a}$$

We easily gain the general solution:

$$R_0(\rho) = A\frac{\sin\rho}{\rho} + B\frac{\cos\rho}{\rho} \tag{8b}$$

Invariables A, B are determined by the boundary conditions, and apparently ρ takes either the positive real number or the pure imaginary number. For the equations corresponding to (6a,b), we can write the followings:

$$R_0(r) = A_i\frac{\sin\alpha r}{\alpha r} + B_i\frac{\cos\alpha r}{\alpha r} \qquad : -V_0 < E < 0, \quad r < a \qquad (9a)$$

$$R_0(r) = A_o\frac{\sin i\beta r}{i\beta r} + B_o\frac{\cos i\beta r}{i\beta r} = A_o\frac{e^{-\beta r} - e^{\beta r}}{-2\beta r} + B_o\frac{e^{-\beta r} + e^{\beta r}}{2i\beta r}$$

$$: -V_0 < E < 0, \quad r > a \qquad (9b)$$

Notice in (9b), variables in trigonometric function become the pure imaginary number and the following relations are used:

$$\sin ix = (e^{i(ix)} - e^{-i(ix)})/2i = (e^{-x} - e^{x})/2i,$$

$$\cos ix = (e^{i(ix)} + e^{-i(ix)})/2 = (e^{-x} + e^{x})/2$$

Now, take a close look at the behaviors of $r = 0$ at extremely close $r \approx 0$. Power expansion the (9a) for $r \approx 0$ in terms of r, then obtain the followings:

$$R_0(r) = A_i(1 - \frac{(\alpha r)^2}{3!} + \frac{(\alpha r)^4}{5!}\cdots) + B_i\frac{1}{\alpha r}(1 - \frac{(\alpha r)^2}{2!} + \frac{(\alpha r)^4}{4!}\cdots)$$

At first sight, this seems to be treated possibly as a solution because there is no terms that has divergence at the vicinity $r = 0$ in terms of the integral $\int R_0(r)^2 r^2 dr$, however, $(1/r)$ takes following against Laplacian:

$$\Delta(\frac{1}{r}) = -4\pi\delta^{(3)}(\boldsymbol{r}) \qquad (10)$$

$\cos\alpha r/\alpha r$ does not satisfy the solutions of Schrodinger's equation at $r = 0$, and therefore, should be discarded. In correspondence to (9a):

$$B_i = 0 \qquad (9a')$$

(9a') is the result gained from boundary condition at $r = 0$. At this point, we examine (10). We apply the Green's theorem of three dimensions:

$$\int_V (u\Delta v - v\Delta u)d^3\boldsymbol{r} = \int_S (u\frac{\partial v}{\partial n} - v\frac{\partial u}{\partial n})dS$$

While we treat $v = 1/r$, $u(\boldsymbol{r})$ of $\partial u/\partial r$ etc. as finite functions at origin vicinity. On the one hand, the left side integrals deals with inside the small sphere with radius a and the origin $r = 0$, on the other hand, the right side integrals deals with the surface of the sphere. Moreover, $\partial u/\partial n$ represents the derivative $\partial u/\partial r$, which directed perpendicularly outward on the surface of a sphere with radius a of the function u. Accordingly, the equation above can be reformed and written as: (given $d\Omega = \sin\theta d\theta d\phi$)

$$\int_{r<a}(u\Delta(\frac{1}{r})-\frac{1}{r}\Delta u)r^2drd\Omega=\int(u\frac{\partial(1/r)}{\partial r}-\frac{1}{r}\frac{\partial u}{\partial r})_{r=a}a^2d\Omega.$$

Here we draw the radius a near to 0, both the left side and the right side second terms turns 0:

$$\lim_{a\to 0}\int_{r<a}u\Delta(\frac{1}{r})r^2drd\Omega=\lim_{a\to 0}\int u(a,\theta,\phi)(-\frac{1}{a^2})a^2d\Omega$$
$$=-\lim_{a\to 0}\int u(a,\theta,\phi)d\Omega=-4\pi u(0)$$

This fact clearly indicates (10).

As we take the next step, now consider the behavior where $r\to\infty$. Where $E<0$, the term $e^{\beta r}/r$ diverges infinitely, hence this is not allowed in the case. So, the boundary condition where $r\to\infty$ for (9b) is determined as:

$$A_o-B_oi=0 \qquad \text{(9b')}$$

To put in order, (9a)~(9b) are reformed and written as following:

$$R_0(r)=A_i\frac{\sin\alpha r}{\alpha r} \quad :-V_0<E<0,\quad r<a \qquad \text{(11a)}$$

$$R_0(r)=C_o\frac{e^{-\beta r}}{\beta r} \quad :-V_0<E<0,\quad r>a \qquad \text{(11b)}$$

So far, we have considered the solutions in the regions of $r>a$ and $r<a$, then investigated the behaviors at $r\cong 0$, also at $r\to\infty$ to find the conditions that can be physically allowed. In the next step, the solutions for each region should be connected on the boundary line $r=a$. Intrinsically, the differential equations contain the second order differentials, thus tacitly requires the continuity of the function $R_0(r)$ and its first order differential coefficient. This is the third boundary condition for $r=a$:

$$R_0(a+0)=R_0(a-0) \qquad \text{(12a)}$$

$$\frac{d}{dr}R_0(a+0)=\frac{d}{dr}R_0(a-0) \qquad \text{(12b)}$$

The two equations above define the relationship between the value A_i/C_o and α,β when $E<0$ the relationship between the value A_i'/C_o' and k_i, k_o when $E>0$. The absolute values for A_i/C_o and A_i'/C_o' are determined by the conditions for normalization and incident waves. If there is the only necessity for determining the energy eigenvalue with no concern for the coefficient such as A_i, we should consider the following equation:

$$[\frac{dR_0}{dr}/R_0]_{r=a+0}=[\frac{dR_0}{dr}/R_0]_{r=a-0} \qquad \text{(13)}$$

Using (11a~b), we can write the following:

$$\alpha \cot \alpha a = -\beta : \quad -V_0 < E < 0 \tag{14a}$$

First, in the case where $-V_0 < E < 0$, let's examine the eigenenergy that depends on (14a). α and β are not considered as independent invariables but rather considered as the following as we can see in (6a~b):

$$\alpha^2 + \beta^2 = 2mV_0/\hbar^2 \tag{15}$$

From (14a) and (15), eliminate β:

$$(\alpha a)^2 \mathrm{cosec}^2 \alpha a = 2mV_0 a^2/\hbar^2 \tag{16}$$

From (14a), assume to be an arbitrary positive integer or 0, and then with $\beta > 0$, the condition can be described as:

$$(n + \frac{1}{2})\pi \le \alpha a < (n+1)\pi \tag{17}$$

With (17), (16) should write over again to have:

$$\alpha a = \sqrt{2mV_0 a^2/\hbar^2} \cos(\alpha a - (n + \frac{1}{2})\pi) \tag{18}$$

Thus, we obtain the following simultaneous equations:

$$\begin{cases} \alpha a = \gamma + (n + \frac{1}{2})\pi \quad (0 \le \gamma < \frac{\pi}{2}) \\ \alpha a = \sqrt{2mV_0 a^2/\hbar^2} \cos \gamma \end{cases} \tag{19}$$

Although, the equations cannot be solved analytically, it is possible to obtain the solutions using graph. In Fig.7.1, shows the two equations drawn by the transverse axis $\gamma (0 < \gamma < \frac{\pi}{2})$ and the vertical axis αa . By reading the values at the intersection α, the values for the eigenenergy should be determined. It is also studied that the numbers of the bound state $(E < 0)$ are invariable in the value V_0.

$$(n - \frac{1}{2})\pi \le \sqrt{2mV_0 a^2/\hbar^2} < (n + \frac{1}{2})\pi \tag{20}$$

There are n intersections that can define the bound state, and we find the n bound states in accordance. As the value $V_0 a^2$ increases and deeper the potentials, the energy for the bound state decreases. When $\sqrt{2mV_0 a^2/\hbar^2} = (n + 1/2)\pi$ there will be a new bound state added at $E = 0$. With the value $V_0 a^2$ too small, there will be no bound states:

$$\sqrt{2mV_0a^2/\hbar^2} < \frac{\pi}{2} \tag{21}$$

----Fig.1-----

Eigenstate of $\ell \neq 0$

Let's study the solution for (6) in terms of ℓ:

$$R_\ell(\rho) = \frac{1}{\sqrt{\rho}}u(\rho) \tag{22}$$

Change the variable then (6) becomes:

$$\frac{d^2u}{d\rho^2} + \frac{1}{\rho}\frac{du}{d\rho} + (1 - \frac{(\ell+\frac{1}{2})^2}{\rho^2})u = 0 \tag{23}$$

In terms of arbitrary number ν:

$$\frac{d^2\omega_\nu}{d\rho^2} + \frac{1}{\rho}\frac{d\omega_\nu}{d\rho} + (1 - \frac{\nu^2}{\rho^2})\omega_\nu = 0 \tag{24}$$

This differential equation (24) is commonly known as Bessel differential equations. There are two elemental solutions, in which one of the two solutions is called Bessel function and that represents the width series near $\rho = 0$.

$$J_\nu(\rho) = (\frac{\rho}{2})^\nu \sum_{n=0}^{\infty} \frac{(-1)^n(\rho/2)^{2n}}{n!\Gamma(\nu+n+1)} \tag{25}$$

$\Gamma(z)$ is the gamma function, and is defined as following when *z* is the integer or half odd integer:

$$\Gamma(n+1) = n!\ , \quad \Gamma(n+\frac{1}{2}) = \frac{(2n)!}{2^{2n}n!}\sqrt{\pi}\ ; \quad (n = 0, 1, 2\cdots)$$

For the other independent solution is given by following with $J_\nu(\rho)$

$$\begin{cases} N_\nu(\rho) = \dfrac{1}{\sin\nu\pi}[\cos\nu\pi J_\nu(\rho) - J_{-\nu}(\rho)], \\ N_n(\rho) = \dfrac{1}{\pi}[\dfrac{\partial J_\nu(\rho)}{\partial\nu} - (-1)^n\dfrac{\partial J_{-\nu}(\rho)}{\partial\nu}]_{\nu=n}, \end{cases} \tag{26}$$

Where $\nu \neq$ integer for the first equation, and $\nu =$ integer n for the second equation. $N_\nu(\rho), N_n(\rho)$ are called the second kind Bessel function or Neumann function. If we use J_ν, N_ν for (22), then the two independent solutions for (6) are written as:

$$R_\ell(\rho) = \begin{cases} \sqrt{\dfrac{\pi}{2\rho}}J_{\ell+\frac{1}{2}}(\rho) = j_\ell(\rho) \\ \sqrt{\dfrac{\pi}{2\rho}}N_{\ell+\frac{1}{2}}(\rho) = n_\ell(\rho) \end{cases} \tag{27}$$

j_ℓ, n_ℓ are called the first kind spherical Bessel function and the second kind spherical Bessel function respectively. The second kind spherical Bessel function is often called spherical Neumann function as well. By using trigonometric function, these functions may be written as:

$$j_\ell(\rho) = (-1)^\ell \rho^\ell \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^\ell \frac{\sin\rho}{\rho}$$
$$n_\ell(\rho) = (-1)^{\ell+1} \rho^\ell \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^\ell \frac{\cos\rho}{\rho} \qquad (28)$$

Now, let's express the behavior of j_ℓ, n_ℓ in the Fig.2 to picture a specific shape for $\ell = 0, 1$:

$$j_0(\rho) = \rho^{-1}\sin\rho, \qquad j_1(\rho) = \rho^{-2}(\sin\rho - \rho\cos\rho),$$

$$n_0(\rho) = -\rho^{-1}\cos\rho, \quad n_1(\rho) = -\rho^{-2}(\cos\rho + \rho\sin\rho).$$

Alternatively, conduct series expansion near $\rho \simeq 0$ to write out from the most essential terms:

$$j_\ell(\rho) \sim \frac{\rho^\ell}{(2\ell+1)!!}, \quad n_\ell(\rho) \sim -\frac{(2\ell-1)!!}{\rho^{\ell+1}} \qquad (29a)$$

When $\rho \to \infty$:

$$j_\ell(\rho) \sim \frac{1}{\rho}\cos\left(\rho - \frac{(\ell+1)\pi}{2}\right), \quad n_\ell(\rho) \sim \frac{1}{\rho}\sin\left(\rho - \frac{(\ell+1)\pi}{2}\right) \qquad (29b)$$

The important point for the spherical Bessel function j_ℓ is, to remain regular at origin, while the spherical Neumann function n_ℓ should have its origin taking the pole of the order of $\ell + 1$, and to have both functions slowly decay as they oscillate. The general solution for the equation (6) can be given by the linear combination of $j_\ell(\rho)$ and $n_\ell(\rho)$.

----Fig.2-----

Where $-V_0 < E < 0, r > a$, the variable turns to become the pure imaginary number in the spherical Bessel functions, and therefore should be carefully examined. Although, we can use the same indication method of (28)~(29b), it is easier to see when we conduct linear combination:

$$h_\ell^{(1)}(\rho) = j_\ell(\rho) + i n_\ell(\rho) \qquad (30a)$$

$$h_\ell^{(2)}(\rho) = j_\ell(\rho) - i n_\ell(\rho) \qquad (30b)$$

These are called the first kind and the second kind Hankel functions. The behaviors of spherical Hankel functions for $|\rho| \approx 0$ and $|\rho| \to \infty$ can be obtained by substituting (29a~b) into (30a~b):

$$h_\ell^{(1)}(\rho) \sim -i\frac{(2\ell-1)!!}{\rho^{\ell+1}}, \quad h_\ell^{(2)}(\rho) \sim i\frac{(2\ell-1)!!}{\rho^{\ell+1}}, \quad (|\rho| \sim 0) \qquad (31a)$$

And:

$$h_\ell^{(1)}(\rho) \sim (-i)^{\ell+1}\frac{e^{i\rho}}{\rho}, \quad h_\ell^{(2)}(\rho) \sim i^{\ell+1}\frac{e^{-i\rho}}{\rho}, \quad (|\rho| \to \infty) \qquad (31b)$$

Given $\rho = i\beta r$ for $r \to \infty$:

$$h_\ell^{(1)}(i\beta r) \sim \frac{(-i)^{\ell+1}}{i\beta}\frac{e^{-\beta r}}{r}, \quad h_\ell^{(2)}(i\beta r) \sim \frac{i^{\ell+1}}{i\beta}\frac{e^{\beta r}}{r} \ : \ (r \to \infty) \quad (31c)$$

$h_\ell^{(2)}(i\beta r)$ diverges infinitely, thus this cannot be accepted as a solution for (6). In the same way, $n_\ell(\rho)$ behaves likewise $\rho^{-(\ell+1)}$ at $|\rho| \approx 0$, and which cannot be accepted as solution for the Schrodinger's equations. We have already investigated for the reason when $\ell = 0$, yet when $\ell \neq 0$, the integrals $\int R_\ell(r)^2 r^2 dr$ diverges at the integrals nearby $r = 0$. The solutions are determined as following:

$$-V_0 < E < 0, \quad r < a : R_\ell(r) = A_i^{(\ell)} j_\ell(\alpha r) \qquad (32a)$$

$$-V_0 < E < 0, \quad r > a : R_\ell(r) = C_o^{(\ell)} h_\ell^{(1)}(i\beta r) \qquad (32b)$$

Now that the boundary conditions are scrutinized to define the forms of solutions for $|\rho| \approx 0$ and $|\rho| \to \infty$ to be (32a)~(32b), we need to obtain the wavefunctions that can smoothly connected at $r = a$, as we did for $\ell = 0$.