Appendix BB

Solution of the Schrödinger Equation in Spherical Coordinates

SEPARATION OF THE SCHRÖDINGER EQUATION

The Schrödinger equation for an electron with mass m moving about a nucleus with mass M and charge eZ can be written

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(\mathbf{r}) - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}\psi(\mathbf{r}) = E\psi(\mathbf{r}), \tag{BB.1}$$

where the reduced mass μ is defined by the equation

$$\mu = \frac{mM}{m+M}. \tag{BB.2}$$

Using the expression for the Laplacian operator in spherical coordinates given in Appendix AA, the Scrödinger equation can be written

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}\psi = E\psi. \tag{BB.3}$$

The above equation can be solved by the method of separation of variables by writing the wave function as a product of a functions of the radial and angular coordinates

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi).$$

Substituting the product function into Eq. (BB.3) and dividing by $-\hbar^2/2\mu r^2$ times the product function, we obtain

$$\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \frac{2\mu r^2}{\hbar^2}\left[E + \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}\right] = -\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]. \tag{BB.4}$$

Since the left-hand side of the above equation depends only on r and the right-hand side depends both on θ and ϕ, both sides must be equal to a constant that we call λ. The resulting radial equation can be written

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \left[\frac{2\mu}{\hbar^2}\left(E + \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}\right) - \frac{\lambda}{r^2}\right]R = 0, \tag{BB.5}$$

and the angular equation is

$$-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} = \lambda Y. \tag{BB.6}$$

Using Eq. (AA.10), we may identify the second of these two last equations as the eigenvalue equation of the angular momentum operator $\mathbf{l}^2$ with eigenvalue $\hbar^2\lambda$. We shall use a purely algebraic line of argument in Appendix CC to show that the eigenvalues of the orbital angular momentum operator $\mathbf{l}^2$ are $\hbar^2\, l(l+1)$, where l is the angular momentum quantum number. We may thus identify the separation constant λ as being $l(l+1)$ and write the radial equation

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right)+\left[\frac{2\mu}{\hbar^2}\left(E+\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}\right)-\frac{l(l+1)}{r^2}\right]R=0, \tag{BB.7}$$

We consider now more fully the radial equation. Evaluating the derivatives of the first term in the equation, we obtain

$$\frac{\mathrm{d}^2R}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}R}{\mathrm{d}r}+\left[\frac{2\mu}{\hbar^2}\left(E+\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}\right)-\frac{l(l+1)}{r^2}\right]R=0. \tag{BB.8}$$

The above equation can be simplified by introducing the change of variables

$$\rho=\alpha r, \tag{BB.9}$$

where α is a constant yet to be specified. The equation defining the change of variables can be written

$$r=\alpha^{-1}\rho. \tag{BB.10}$$

The derivatives of the radial function R can then be expressed in terms of the new variable ρ by using the chain rule. We have

$$\frac{\mathrm{d}R}{\mathrm{d}r}=\frac{\mathrm{d}\rho}{\mathrm{d}r}\frac{\mathrm{d}R}{\mathrm{d}\rho}=\alpha\frac{\mathrm{d}R}{\mathrm{d}\rho}. \tag{BB.11}$$

Similarly, the second derivative can be written

$$\frac{\mathrm{d}^2R}{\mathrm{d}r^2}=\alpha^2\frac{\mathrm{d}^2R}{\mathrm{d}\rho^2}. \tag{BB.12}$$

Substituting Eqs. (BB.10)-(BB.12) into Eq. (BB.13) and dividing the resulting equation by α^2, we obtain

$$\frac{\mathrm{d}^2R}{\mathrm{d}\rho^2}+\frac{2}{\rho}\frac{\mathrm{d}R}{\mathrm{d}\rho}+\left[\left(\frac{2\mu Ze^2}{\hbar^2 4\pi\epsilon_0\alpha}\right)\frac{1}{\rho}+\frac{2\mu E}{\hbar^2\alpha^2}-\frac{l(l+1)}{\rho^2}\right]R=0. \tag{BB.13}$$

To simplify this last equation, we now make the following choice of α

$$\alpha^2=\frac{8\mu|E|}{\hbar^2}, \tag{BB.14}$$

and we define a new parameter ν by the equation

$$\nu=\frac{2\mu Ze^2}{\hbar^2 4\pi\epsilon_0\alpha}, \tag{BB.15}$$

The radial equation then becomes

$$\frac{\mathrm{d}^2R}{\mathrm{d}\rho^2}+\frac{2}{\rho}\frac{\mathrm{d}R}{\mathrm{d}\rho}+\left[\frac{\nu}{\rho}-\frac{1}{4}-\frac{l(l+1)}{\rho^2}\right]R=0, \tag{BB.16}$$

where the new variable ρ is related to the radial distance r by Eq. (BB.9).

In this appendix we shall solve the radial equation (BB.7) using the power series method. We first note that the first two terms in the equation and the last term depend upon the -2 power of ρ, while the third term in the equation depends upon the -1 power of ρ and the forth term depends upon the 0 power. Since the equation depends upon more than two powers of ρ, it cannot be solved directly by the power series method. To overcome this difficulty, we examine the behavior of the equation for large values of r for which the fourth term in the equation dominates over the third and last terms. The function $\mathrm{e}^{-\rho/2}$, which is everywhere finite, is a solution of the radial equation for large r. This suggests we look for an exact solution of Eq. (BB.16) of the form

$$R(\rho)=F(\rho)\mathrm{e}^{-\rho/2}, \tag{BB.17}$$

where $F(\rho)$ is a function of ρ. We shall substitute this representation of $R(\rho)$ into Eq. (BB.7) and in this way derive an equation for $F(\rho)$. Using Eq. (BB.17), the first and second derivatives of $R(\rho)$ can be written

$$\begin{aligned}\frac{\mathrm{d}R}{\mathrm{d}\rho}&=-\frac{1}{2}\mathrm{e}^{-\rho/2}F+\mathrm{e}^{-\rho/2}\frac{\mathrm{d}F}{\mathrm{d}\rho},\\ \frac{\mathrm{d}^2R}{\mathrm{d}\rho^2}&=\frac{1}{4}\mathrm{e}^{-\rho/2}F-\mathrm{e}^{-\rho/2}\frac{\mathrm{d}F}{\mathrm{d}\rho}+\mathrm{e}^{-\rho/2}\frac{\mathrm{d}^2F}{\mathrm{d}\rho^2}.\end{aligned} \tag{BB.18}$$

Substituting Eqs. (BB.17) and (BB.18) into Eq. (BB.16) leads to the equation

$$\frac{d^2F}{d\rho^2} + \left(\frac{2}{\rho} - 1\right)\frac{dF}{d\rho} + \left[\frac{\nu - 1}{\rho} - \frac{l(l+1)}{\rho^2}\right]F = 0. \tag{BB.19}$$

We note that the first, second, and last terms of the new radial equation depend upon the -2 power of ρ, while the remaining two terms in the equation depend upon the -1 power of ρ. Since Eq. (BB.7) only involves two powers of ρ, it is amendable to a power series solution.

We now look for a solution for $F(\rho)$ of the form

$$F(\rho) = \rho^s L(\rho), \tag{BB.20}$$

where the function $L(\rho)$ can be expressed as a power series

$$L(\rho) = \sum_{k=0}^{\infty} a_k \, \rho^k. \tag{BB.21}$$

We shall suppose that the coefficient a_0 in the expansion of $L(\rho)$ is not equal to zero and that the function ρ^s gives the dependence of the function $F(\rho)$ near the origin. The requirement that $F(\rho)$ be finite can be satisfied if s has integer values equal or greater than zero. Substituting Eq. (BB.20) into Eq. (BB.19) gives the following equation for L

$$\rho^2 \frac{d^2L}{d\rho^2} + \rho\,[2(s+1) - \rho]\,\frac{dL}{d\rho} + [\rho(\nu - s - 1) + s(s+1) - l(l+1)]\,L = 0.$$

Substituting $\rho = 0$ in the above equation, leads to the condition

$$s(s+1) - l(l+1) = 0.$$

This quadratic equation has two roots: $s = l$ and $s = -(l+1)$. Only the root $s = l$ is consistent with the boundary condition that the radial function $R(\rho)$ be finite for $\rho = 0$. The equation for L then becomes

$$\rho \frac{d^2L}{d\rho^2} + [2(l+1) - \rho]\,\frac{dL}{d\rho} + (\nu - l - 1))\,L = 0. \tag{BB.22}$$

Notice that the first and second terms of the above equation depend upon the -1 power of ρ, while the remaining terms in the equation depend upon the 0 power of ρ.

To obtains a power seres solution of Eq. (BB.22), we take the first two derivatives of Eq. (BB.21) to obtain

$$\frac{dL}{d\rho} = \sum_{k=1}^{\infty} k a_k \, \rho^{k-1},$$

$$\frac{d^2F}{d\rho^2} = \sum_{k=2}^{\infty} k(k-1) a_k \, \rho^{k-2}.$$

We substitute these expressions for $L(\rho)$ and its derivatives into Eq. (BB.22) to obtain

$$\sum_{k=2}^{\infty} k(k-1) a_k \, \rho^{k-1} + 2(l+1)\sum_{k=1}^{\infty} k a_k \rho^{k-1} - \sum_{k=1}^{\infty} k a_k \, \rho^k + (\nu - l - 1)\sum_{k=0}^{\infty} a_k \, \rho^k = 0.$$

Notice that the first and second summations involve ρ^{k-1}, while the third and forth sums involve ρ^k. Because of the factor $k - 1$ in the first sum, the first summation can be extended to $k = 1$ and because of the factor k in the third sum, the third summation can be extended to $k = 0$, and the equation may be written

$$\sum_{k=1}^{\infty}[k(k-1)+2k(l+1)]a_k\rho^{k-1}-\sum_{k=1}^{\infty}[k-(\nu-l-1)]a_k\,\rho^k=0.$$

The first summation in the above equation has the variable ρ is raised to the power $k-1$, while in the second summation has ρ raised to the power k. In order to bring these different contribution together so that they contain terms corresponding to the same power of ρ, we make the following substitution in the first summation

$$k=k'+1, \tag{BB.23}$$

and we simplify the terms within the two summations to obtain

$$\sum_{k'=0}^{\infty}(k'+1)(k'+2l+2)a_{k'+1}\,\rho^{k'}-\sum_{k=0}^{\infty}(k-\nu+l+1)a_k\,\rho^k=0.$$

As with a change of variables for a problem involving integrals, the lower limit of the first summation is obtained by substituting the value $k=1$ into Eq. (BB.23) defining the change of variables. We now replace the dummy variable k' with k in the first summation and draw all of the terms together within a single summation to obtain

$$\sum_{k=0}^{\infty}\left[(k+1)(k+2l+2)a_{k+1}-(k-\nu+l+1)a_k\right]\rho^k=0.$$

This equation can hold for all values of y only if the coefficient of every power of ρ is equal to zero. This leads to the following *recursion formula*

$$a_{k+1}=\frac{k+l+1-\nu}{(k+1)(k+2l+1)}\,a_k. \tag{BB.24}$$

The recursion formula gives $a_1, a_2, a_3, \ldots$ in terms of a_0. We may thus regard $L(\rho)$ to be defined in terms of the two constant a_0. We must examine, however, the behavior of $L(\rho)$ as y approaches infinity. Since the behavior of $H(y)$ for large values of y will depend upon the terms far out in the power series, we consider the recursion formula (BB.24) for large values of k. This gives

$$\frac{a_{k+1}}{a_k}\rightarrow\frac{k}{k^2}=\frac{1}{k}.$$

We now compare this result with the Taylor series expansion of the function e^{ρ}

$$e^{\rho}=1+\rho+\frac{1}{2!}\rho^2+\cdots+\frac{1}{k!}\rho^k+\frac{1}{(k+1)!}\rho^{k+1}+\cdots.$$

The ratio of the coefficients of this series for large values of k is

$$\frac{1/(k+1)!}{1/k!}=\frac{k!}{(k+1)!}=\frac{1}{k+1}\rightarrow\frac{1}{k}.$$

The ratio of successive terms for these two series is the same for large values of k. This means that the power series representation of $L(\rho)$ has the same dependence upon ρ for large values of ρ as the function e^{ρ}. Recall now that the radial function $R(\rho)$ is related to $F(\rho)$ by Eq. (BB.17), and $F(\rho)$ is related to $L(\rho)$ by Eq. (BB.20) with $s=l$. Setting $L(\rho)=e^{\rho}$ leads to the following behavior of the radial function for large ρ

$$R(\rho)=e^{-\rho/2}\rho^l e^{\rho}=\rho^l e^{\rho/2}\quad\text{as } y\rightarrow\infty.$$

The radial function we have obtained from the series expansion thus becomes infinite as $y\rightarrow\infty$, which is unacceptable. There is only one way of avoiding this consequence and that is to terminate the infinite series. The series can be terminated by letting ν be equal to an integer n, such that

$$\nu=n=n'+l+1. \tag{BB.25}$$

The recursion formula (BB.24) then implies that the coefficient a_{n+1} is equal to zero, and the function $L(\rho)$ will be a polynomial of degree n. Equations (BB.17) and (BB.20) with $s=l$ then implies that the radial function $R(\rho)$ is equal to a polynomial times the function $e^{-\rho/2}$, which means that R approaches zero as $\rho\rightarrow\infty$. Setting $\nu=n$ and solving Eqs. (BB.14) and (BB.15) for the energy, we obtain

$$|E| = \frac{\mu Z^2 e^4}{2(4\pi\epsilon_0)^2\hbar^2}\,\frac{1}{n^2}.$$

The energy of the nth bound state of a hydrogen-like ion with nuclear charge Ze is

$$E_n = -\frac{\mu Z^2 e^4}{2(4\pi\epsilon_0)^2\hbar^2}\,\frac{1}{n^2}. \tag{BB.26}$$

Using the reduced mass μ for the electron mass takes into account the fact that the finite mass of the nucleus. For the hydrogen atom with $Z = 1$ and with the reduced mass μ equal to m, Eq. (BB.26) reduces the expression for energy E_n for the hydrogen atom in Chapter 1.

The polynomials $L(\rho)$ may be identified as *associated Languere polynomials* L_q^p which satisfy the equation

$$\rho\frac{d^2L_q^p}{d\rho^2} + \left[p + 1 - \rho\right]\frac{dL_q^p}{d\rho} + (q - p)\,L_q^p = 0. \tag{BB.27}$$

Equating the coefficients in Eqs. (BB.22) and (BB.27), we see that $p = 2l + 1$ and $q = n + l$. The appropriate polynomials are given by the equation

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1}(-1)^{k+1}\frac{[(n+l)!]^2\rho^k}{(n-l-1-k)!(2l+1+k)!k!}. \tag{BB.28}$$

The normalized radial wave functions for a hydrogen-like ion can be written

$$R_{nl}(r) = -A_{nl}e^{-\rho/2}\rho^l L_{n+l}^{2l+1}(\rho) \tag{BB.29}$$

with the normalization coefficients given by the equation

$$A_{nl} = \left\{\left(\frac{2Z}{na_0}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}, \tag{BB.30}$$

where

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \quad \text{and} \quad \rho = \frac{2Z}{na_0}r.$$

The first three radial functions, which can be found using Eqs. (BB.28) and (BB.29), are

$$R_{10}(r) = \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} 2e^{-Zr/a_0},$$

$$R_{20}(r) = \left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(2 - \frac{Zr}{a_0}\right)e^{-Zr/2a_0},$$

$$R_{21}(r) = \left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\frac{Zr}{a_0\sqrt{3}}\,e^{-Zr/2a_0}.$$