VANDERBILT UNIVERSITY, MATH 234 SPRING 14: THE SCHRÖDINGER EQUATION.

Contents

1. Introduction.

Our goal is to investigate solutions to the *Schrödinger equation*,

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2\mu}\Delta\Psi + V\Psi, \tag{1.1}$$

where i is the imaginary number $i^2 = -1$; $\hbar = 1.51 \times 10^{-27}\, erg\, s$ is Planck's constant; μ is a positive constant called the mass; $V = V(t,x) : \mathbb{R}\times\mathbb{R}^3 \to \mathbb{R}$ is called the potential function; and the unknown is the complex-valued function $\Psi = \Psi(t,x) : \mathbb{R}\times\mathbb{R}^3 \to \mathbb{C}$ called the wave-function. The variables t and x represent, respectively, the time and space variables.

The Schrödinger equation describes the dynamics of a particle of mass μ interacting with a potential V, according to the laws of Quantum Mechanics. The physical interpretation of Ψ is as follows. If $U \subseteq \mathbb{R}^3$, then

$$\int_U |\Psi(t,x)|^2 \, dx$$

represents the probability of finding the particle in the region U at a time t. In particular, one must have

$$\int_{\mathbb{R}^3} |\Psi(t,x)|^2 \, dx = 1. \tag{1.2}$$

Notice that, upon multiplying Ψ by a suitable constant, condition (1.2) can always be fulfilled as long as

$$\int_{\mathbb{R}^3} |\Psi(t,x)|^2 \, dx < \infty. \tag{1.3}$$

Our treatment will be based on [FY, T, W], to which the student is referred for more details.

2. Separation of variables for a time-independent potential.

We shall assume that V does not depend on time, i.e., $V(t,x) = V(x)$. We will have to divide several expressions by Ψ. In order to make this sensible, it will be assumed that Ψ does not vanish (or, at least, does not vanish on an open set). Look for solutions of the form

$$\Psi(t,x) = T(t)\psi(x), \tag{2.1}$$

Plugging (2.1) into (1.1) gives

$$i\hbar\frac{T'}{T} = -\frac{\hbar^2}{2\mu}\frac{1}{\psi}\Delta\psi + V,$$

The left-hand side depends only on t, whereas the right-hand side depends only on x. Thus, both sides have to be equal to a constant, which we denote be E. Therefore

$$i\hbar T' = ET, \tag{2.2}$$

and

$$-\frac{\hbar^2}{2\mu}\Delta\psi + V\psi = E\psi. \tag{2.3}$$

Equation (2.2) is easily solved. Its solution is

$$T(t) = e^{-\frac{iE}{\hbar}t}, \tag{2.4}$$

where we ignored an arbitrary constant of integration (such constants will be neglected throughout, as an overall constant of integration can be fixed at the very end via condition (1.2)).

2.1. **The time-independent Schrödinger equation.** We now focus on (2.3), known as the *time-independent Schrödinger equation.* To solve it, we assume further that V is *radially symmetric*, i.e., that $V(x) = V(\sqrt{x_1^2+x_2^2+x_3^2})$ or, in spherical coordinates, that $V = V(r)$. This assumption suffices to treat many physical systems of interest.

Recall the expression for the Laplacian in spherical coordinates,

$$\Delta = \partial_r^2 + \frac{2}{r}\partial_r + \frac{1}{r^2}\Delta_{S^2}, \tag{2.5}$$

where

$$\Delta_{S^2} = \partial_\phi^2 + \frac{\cos\phi}{\sin\phi}\partial_\phi + \frac{1}{\sin^2\phi}\partial_\theta^2 \tag{2.6}$$

is the *Laplacian on the unit sphere*, $r \in [0,\infty)$, $\phi \in [0,\pi)$, and $\theta \in [0, 2\pi)$. From now on we shall work in spherical coordinates.

We suppose that

$$\psi(r,\phi,\theta) = R(r)Y(\phi,\theta). \tag{2.7}$$

Plugging (2.7) into (2.3), and using (2.5),

$$-\frac{\hbar^2}{2\mu}\frac{r^2}{R}\left(R'' + \frac{2}{r}R'\right) + (V-E)r^2 = \frac{\hbar^2}{2\mu}\frac{1}{Y}\Delta_{S^2}Y.$$

Since the left-hand side depends only on r and the right-hand side only on (ϕ,θ), both sides must be equal to a constant, which we denote by $-a$. Thus,

$$-\frac{\hbar^2}{2\mu}\left(R'' + \frac{2}{r}R'\right) + \left(V + \frac{a}{r^2}\right)R = ER, \tag{2.8}$$

and

$$\frac{\hbar^2}{2\mu}\Delta_{S^2}Y = -aY. \tag{2.9}$$

2.2. **The angular equation.** We first investigate (2.9), which, in light of (2.6), becomes

$$\partial_\phi^2 Y + \frac{\cos\phi}{\sin\phi}\partial_\phi Y + \frac{1}{\sin^2\phi}\partial_\theta^2 Y = -\frac{2a\mu}{\hbar^2}Y.$$

Supposing

$$Y(\phi,\theta) = \Phi(\phi)\Theta(\theta), \tag{2.10}$$

one gets

$$-\frac{\Theta''}{\Theta} = \frac{\sin^2\phi}{\Phi}\Phi'' + \frac{\sin\phi\cos\phi}{\Phi}\Phi' + \frac{2a\mu\sin^2\phi}{\hbar^2}. \tag{2.11}$$

Once more, both sides ought to be equal to a constant, which we denote by b. One equation becomes

$$\Theta'' = -b\Theta. \tag{2.12}$$

To solve (2.12), we need to analyze the cases $b > 0$, $b = 0$, and $b < 0$. Notice the following boundary condition: the points with coordinates θ and $\theta + 2\pi$ must be identified as they correspond to the same point in $\mathbb{R}^3$. Thus,

$$\Theta(\theta + 2\pi) = \Theta(\theta). \tag{2.13}$$

We immediately see that the case $b < 0$ does not yield a solution satisfying (2.13); $b = 0$ and (2.13) give $\Theta =$constant; and $b > 0$ along with (2.13) give that Θ is a linear combination of $\cos(\sqrt{b}\theta)$ and $\sin(\sqrt{b}\theta)$. All this cases can be summarized by setting

$$b = m^2,\ m \in \mathbb{Z}, \tag{2.14}$$

and writing

$$\Theta(\theta) = e^{im\theta}. \tag{2.15}$$

Next, we move to the Φ-equation. From (2.11) and (2.14), one has

$$\frac{\sin\phi}{\Phi}\frac{d}{d\phi}\left(\sin\phi\frac{d\Phi}{d\phi}\right) - m^2 = -\lambda\sin^2\phi, \tag{2.16}$$

where

$$\lambda = \frac{2\mu}{\hbar^2}a, \tag{2.17}$$

and we used the product rule to rewrite the terms involving derivatives. In order to solve (2.16), let us make the following change of variables,

$$x = \cos\phi,\ 0 \le \phi \le \pi.$$

(strictly speaking, $\phi \in [0,\pi)$, but it is convenient to include $\phi = \pi$. Notice that this change of variables is well-defined since cos is one-to-one for $0 \le \phi \le \pi$). The chain rule gives

$$\sin\phi\frac{d}{d\phi} = \sin\phi\frac{dx}{d\phi}\frac{d}{dx} = -\sin^2\phi\frac{d}{dx} = (\cos^2\phi - 1)\frac{d}{dx} = (x^2-1)\frac{d}{dx},$$

so that (2.16) becomes

$$\frac{d}{dx}\left((1-x^2)\frac{d\Phi}{dx}\right) + \left(\lambda - \frac{m^2}{1-x^2}\right)\Phi = 0. \tag{2.18}$$

To solve (2.18), we seek for a solution of the form

$$\Phi(x) = (1-x^2)^{\frac{|m|}{2}} \frac{d^{|m|}P(x)}{dx^{|m|}}, \tag{2.19}$$

where P solves

$$(1-x^2)\frac{d^2P}{dx^2} - 2x\frac{dP}{dx} + \lambda P = 0. \tag{2.20}$$

To see that this works, differentiate (2.20) $|m|$ times, obtaining

$$(1-x^2)\frac{d^{|m|+2}P}{dx^{|m|+2}} - 2(|m|+1)x\frac{d^{|m|+1}P}{dx^{|m|+1}} + (\lambda - |m|(|m|+1))\frac{d^{|m|}P}{dx^{|m|}} = 0. \tag{2.21}$$

Students are encouraged to verify (2.21) (compute the first few derivatives to see that a pattern as (2.21) emerges). On the other hand, let $\widetilde{\Phi}$ be defined by

$$\Phi(x) = (1-x^2)^{\frac{|m|}{2}}\widetilde{\Phi}(x) \tag{2.22}$$

and plug this into (2.18). Computing the derivative terms,

$$\begin{aligned}
\frac{d}{dx}\left((1-x^2)\frac{d}{dx}\left((1-x^2)^{\frac{|m|}{2}}\widetilde{\Phi}\right)\right) &= \frac{d}{dx}\left(\frac{|m|}{2}(-2x)(1-x^2)^{\frac{|m|}{2}}\widetilde{\Phi} + (1-x^2)^{\frac{|m|}{2}+1}\frac{d\widetilde{\Phi}}{dx}\right)\\
&= (1-x^2)^{\frac{|m|}{2}+1}\frac{d^2\widetilde{\Phi}}{dx^2} + (1-x^2)^{\frac{|m|}{2}}\frac{d\Phi}{dx}\left(\left(\frac{|m|}{2}+1\right)(-2x) + \frac{|m|}{2}(-2x)\right)\\
&+ \frac{|m|}{2}\left((-2x)\frac{|m|}{2}(1-x^2)^{\frac{|m|}{2}-1}(-2x) - 2(1-x^2)^{\frac{|m|}{2}}\right)\widetilde{\Phi}\\
&= (1-x^2)^{\frac{|m|}{2}+1}\frac{d^2\widetilde{\Phi}}{dx^2} - 2x(1-x^2)^{\frac{|m|}{2}}(|m|+1)\frac{d\widetilde{\Phi}}{dx} + \frac{|m|}{2}(1-x^2)^{\frac{|m|}{2}}\left(\frac{2|m|x^2}{1-x^2} - 2\right)\widetilde{\Phi}\\
&= (1-x^2)^{\frac{|m|}{2}}\left((1-x^2)\frac{d^2\widetilde{\Phi}}{dx^2} - 2x(|m|+1)\frac{d\widetilde{\Phi}}{dx} + |m|\left(\frac{|m|x^2}{1-x^2} - 1\right)\widetilde{\Phi}\right).
\end{aligned}$$

By (2.18), this has to equal

$$-\left(\lambda - \frac{m^2}{1-x^2}\right)\Phi = \left(\lambda - \frac{m^2}{1-x^2}\right)(1-x^2)^{\frac{|m|}{2}}\widetilde{\Phi}(x),$$

what gives, after canceling $(1-x^2)^{\frac{|m|}{2}}$,

$$(1-x^2)\frac{d^2\widetilde{\Phi}}{dx^2} - 2x(|m|+1)\frac{d\widetilde{\Phi}}{dx} + \lambda\widetilde{\Phi} + \left(\frac{|m|^2x^2}{1-x^2} - |m| - \frac{|m|^2}{1-x^2}\right)\widetilde{\Phi} = 0.$$

But

$$\frac{|m|^2x^2}{1-x^2} - |m| - \frac{|m|^2}{1-x^2} = \frac{|m|(|m|+1)x^2 - |m|(|m|+1)}{1-x^2} = -|m|(|m|+1),$$

and therefore

$$(1-x^2)\frac{d^2\widetilde{\Phi}}{dx^2} - 2x(|m|+1)\frac{d\widetilde{\Phi}}{dx} + (\lambda - |m|(|m|+1))\widetilde{\Phi} = 0. \tag{2.23}$$

Comparing (2.23) with (2.21), we see that if P solves (2.20), then (2.22) solves (2.18), as claimed.

Therefore, it suffices to solve (2.20). We seek a power series solution of the form

$$P(x) = \sum_{k=0}^{\infty} a_k x^k. \tag{2.24}$$

Plugging (2.24) into (2.20) gives

$$(1 - x^2) \sum_{k=0}^{\infty} k(k-1) a_k x^{k-2} - 2x \sum_{k=0}^{\infty} k a_k x^{k-1} + \lambda \sum_{k=0}^{\infty} a_k x^k = 0,$$

or yet, after rearranging some terms,

$$\sum_{k=0}^{\infty} \left((k+2)(k+1) a_{k+2} - (k(k+1) - \lambda) a_k \right) x^k = 0,$$

which implies the following recurrence relation,

$$a_{k+2} = \frac{k(k+1) - \lambda}{(k+1)(k+2)} a_k,\ k = 0, 1, 2, \dots. \tag{2.25}$$

(2.25) determines all coefficients a_k except a_0 and a_1, which remain arbitrary (this is consistent with the fact that we are solving a second order ODE). Furthermore, a_0 determines all even coefficients, giving rise to an even power series, while while a_1 determines all odd coefficients, giving rise to an odd power series. This two power series, even and odd, are two linearly independent solutions of (2.20).

Next, we investigate the convergence of (2.24). Since it suffices to investigate the convergence of the even and odd expansions separately, as these are two linearly independent solutions, the ratio between two consecutive terms in the expansion is obtained from (2.25), yielding

$$\lim_{k \to \infty} \left| \frac{a_{k+2} x^{x+2}}{a_k x^k} \right| = |x|^2,$$

and thus (2.24) converges for $|x| < 1$ by the ratio test. We need to investigate the case $|x| = 1$, in particular $x = 1$ (which corresponds to $\phi = 0$). Plugging $x = 1$ into (2.24) gives

$$P(1) = \sum_{k=0}^{\infty} a_k. \tag{2.26}$$

From (2.25) we have

$$a_{k+2} = \frac{k^2 + O(k)}{k^2 + O(k)} a_k = \frac{k^2 + O(k)}{k^2 + O(k)} \frac{k^2 + O(k)}{k^2 + O(k)} a_{k-2} = \cdots = \begin{cases} \frac{k^{k+2} + O(k^{k+1})}{k^{k+2} + O(k^{k+1})} a_0, & k \text{ even}, \\ \frac{k^{k+1} + O(k^k)}{k^{k+1} + O(k^k)} a_1, & k \text{ odd}. \end{cases}$$

It follows that

$$\lim_{k \to \infty} a_k \neq 0,$$

and therefore (2.26) diverges by the divergence test, *unless* (2.24) is in fact a *finite sum*; i.e., *unless* $a_k = 0$ *for all* k *greater than a certain* ℓ. Hence, we must have, form some non-negative integer ℓ,

$$a_{\ell+2} = 0 = \frac{\ell(\ell+1) - \lambda}{(\ell+1)(\ell+2)} a_\ell,$$

which implies

$$\lambda = \ell(\ell+1), \tag{2.27}$$

provided that $a_\ell \neq 0$. (2.27) determines λ, and hence the separation constant a in view of (2.17). The conclusion is that there is a family $\{P_\ell\}$ of solutions to (2.20) parametrized by $\ell = 0, 1, 2, \dots$. After conveniently choosing a_0 and a_1 to obtain integer coefficients, the first few P's are

$$P_0(x) = 1,\ P_1(x) = x,\ P_2(x) = 1 - 3x^2,\ P_3(x) = 3x - 5x^3.$$

Since P_ℓ is a polynomial of degree ℓ, from (2.19) it follows that $\Phi = 0$ for $|m| > \ell$. Thus, the values of m are restricted to $|m| \leq \ell$, i.e., the allowed m-values depend on ℓ and satisfy

$$m \in \big\{ -\ell, -\ell+1, \dots, -1, 0, 1, \dots, \ell-1, \ell \big\}. \tag{2.28}$$

We write $m = m_\ell$ when we want to stress this dependence of m on ℓ. One obtains a family of solutions $\{\Phi_{\ell m_\ell}\}$ to (2.18) parametrized by ℓ and m_ℓ, where $\ell = 0, 1, 2, \dots$ and m_ℓ satisfies (2.28). The first few Φ's are

$$\Phi_{00}(x) = 1,$$

$$\Phi_{10}(x) = x,\ \Phi_{1,\pm 1}(x) = (1-x^2)^{\frac{1}{2}},$$

$$\Phi_{20}(x) = 1 - 3x^2,\ \Phi_{2\pm 1}(x) = (1-x^2)^{\frac{1}{2}} x,\ \Phi_{2\pm 2}(x) = 1 - x^2,$$

$$\Phi_{30}(x) = 3x - 5x^3,\ \Phi_{3\pm 1}(x) = (1-x^2)^{\frac{3}{2}}(1-5x^2),\ \Phi_{3\pm 2}(x) = (1-x^2)x,\ \Phi_{3\pm 3}(1-x^2)^{\frac{3}{2}}.$$

Finally, it is necessary to rewrite our solutions in terms of the ϕ variable. Denoting $F_{\ell m_\ell} = \widetilde{\Phi}_{\ell m_\ell}$, and using $1 - x^2 = \sin^2\phi$,

$$\Phi_{\ell m_\ell}(\phi) = \sin^{|m_\ell|} F_{\ell m_\ell}(\cos\phi),\ \ell = 0, 1, 2, \dots,\ |m_\ell| \leq \ell. \tag{2.29}$$

Combining (2.10), (2.15), and (2.29) gives

$$Y_{\ell m_\ell}(\phi, \theta) = e^{i m_\ell \theta} \sin^{|m_\ell|} \phi F_{\ell m_\ell}(\cos\phi),\ \ell = 0, 1, 2, \dots,\ |m_\ell| \leq \ell. \tag{2.30}$$

Notice that, in view of (2.9) and (2.17), Y_{ℓ, m_ℓ} solves

$$\Delta_{S^2} Y_{\ell m_\ell} = -\ell(\ell+1) Y_{\ell m_\ell}.$$

We finish this section with some terminology. Equation (2.20) is known as Legendre equation, and its solutions P_ℓ are known as Legendre polynomials. The functions $F_{\ell m_\ell}$ are known as associated Legendre functions. The functions $Y_{\ell m_\ell}$ are called spherical harmonics. Legendre functions and spherical harmonics have many important applications in Physics. The interested reader is referred to [B] for details.

2.3. **The radial equation.** We now turn our attention to equation (2.8). Using (2.17) and (2.27), equation (2.8) can be written as

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2}\left(E - V(r) \right) R = \ell(\ell+1)\frac{R}{r^2}. \tag{2.31}$$

It is important to stress that the results of section 2.2 are general, i.e., they apply to separation of variables to any radially symmetric potential $V = V(r)$. To solve (2.31), on the other hand, we need to specify the function $V(r)$. We shall assume that V is the potential describing the electromagnetic interaction of an electron with a proton. This covers the important case when one is solving the Schrödinger equation describing the evolution of an electron on a hydrogen atom. In this situation, V takes the form

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}, \tag{2.32}$$

where Z is the nuclear charge (for example, $Z = 1$ for the hydrogen and $Z = 2$ for an ionized helium atom), $-e$ is the electron charge, where $e = 1.6 \times 10^{-19}\, C$, and ε_0 is the vacuum permitivity whose values is $\varepsilon_0 = 8.85 \times 10^{-12}\, F/m$ (farads per meters). In order to investigate solutions to (2.31) with V given by (2.32), one needs more information about the separation constant E.

We claim that E must be real and negative. To see this, multiply equation (2.31) by $r^2 R^*$, where R^* is the complex conjugate of R, and integrate from 0 to ∞:

$$\int_0^\infty R^* \frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) dr - \frac{2\mu}{\hbar^2}\int_0^\infty V|R|^2 r^2\, dr - \ell(\ell+1)\int_0^\infty |R|^2\, dr = -\frac{2\mu}{\hbar^2}E\int_0^\infty |R|^2 r^2\, dr, \quad (2.33)$$

where we used that $|R|^2 = R^* R$. Integrating by parts the first term,

$$\int_0^\infty R^* \frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) dr = -\int_0^\infty \frac{dR^*}{dr}\frac{dR}{dr} r^2\, dr + R^* r^2 \frac{dR}{dr}\Big|_0^\infty = -\int_0^\infty \frac{dR^*}{dr}\frac{dR}{dr} r^2\, dr \quad (2.34)$$

where it has been assumed that R^* and $\frac{dR}{dr}$ vanish sufficiently fast at ∞. Writing

$$R = R_R + iR_C,$$

where R_R and R_C are real-valued, it comes

$$\frac{dR^*}{dr}\frac{dR}{dr} = (\frac{dR_R}{dr} - i\frac{dR_C}{dr})(\frac{dR_R}{dr} + i\frac{dR_C}{dr}) = \left(\frac{dR_R}{dr}\right)^2 + \left(\frac{dR_C}{dr}\right)^2,$$

and we conclude that $\frac{dR^*}{dr}\frac{dR}{dr}$ is real-valued. But from (2.33) and (2.34) we have

$$E = \frac{\int_0^\infty \frac{dR^*}{dr}\frac{dR}{dr} r^2\, dr + \frac{2\mu}{\hbar^2}\int_0^\infty V|R|^2 r^2\, dr + \ell(\ell+1)\int_0^\infty |R|^2\, dr}{\frac{2\mu}{\hbar^2}\int_0^\infty |R|^2 r^2\, dr}. \quad (2.35)$$

Therefore, since all terms on the right-hand side are real, we conclude that E is real as well. Students should notice that (2.35) gives an explicit expression for E in terms of (the integral of) R and other data of the problem (although we shall derive a much more explicit expression for E, see below).

Now that we know that E is real, let us show that it is negative[1]. Let us investigate the behavior of (2.31) for large values of r, i.e., $r \gg 1$. Then we can neglect the terms that contain $\frac{1}{r}$ and (2.31) gives, after expanding the terms in $\frac{d}{dr}$,

$$\frac{d^2 R}{dr^2} \approx -\frac{2\mu E}{\hbar^2} R. \quad (2.36)$$

But for $r \gg 1$ we also have the approximation

$$r\frac{d^2 R}{dr^2} + \frac{dR}{dr} \approx r\frac{d^2 R}{dr^2},$$

so that

$$\frac{d^2(rR)}{dr^2} = r\frac{d^2 R}{dr^2} + 2\frac{dR}{dr} \approx r\frac{d^2 R}{dr^2}. \quad (2.37)$$

Hence, multiplying (2.36) by r and using (2.37),

$$\frac{d^2(rR)}{dr^2} \approx -\frac{2\mu E}{\hbar^2}(rR).$$

This approximate equation can be easily solved, producing

$$rR \approx e^{\pm\frac{\sqrt{-2\mu E}}{\hbar} r}.$$

If $E \geq 0$, then R is a complex function which satisfies

$$|rR| \approx 1 \text{ for } r \gg 1.$$

[1] It is possible to obtain $E < 0$ by a more delicate analysis of (2.35), but here we employ a simpler argument.

Then the integral

$$\int_{\mathbb{R}^3} |\Psi(t,x)|^2 \, dx = \left(\int_0^{2\pi} \int_0^{\pi} |Y(\phi,\theta)|^2 \sin\phi \, d\phi d\theta \right) \left(\int_0^{\infty} |R(r)|^2 r^2 \, dr \right)$$

diverges since $|R(r)|^2 r^2 \approx 1$ for large r. Consequently, condition (1.3) fails, and this does not produce a physically sensible solution.

In light of the above arguments, we assume, once and for all, that $E < 0$. In this case, we can define the real constants

$$\beta^2 = -\frac{2\mu E}{\hbar^2}, \tag{2.38}$$

and

$$\gamma = \frac{\mu Z e^2}{4\pi\varepsilon_0 \hbar^2 \beta}, \tag{2.39}$$

and make the real change of variables

$$\varrho = 2\beta r.$$

With these definitions, equation (2.31), with V given by (2.32), becomes

$$\frac{1}{\varrho^2}\frac{d}{d\varrho}\left(\varrho^2 \frac{dR}{d\varrho}\right) + \left(-\frac{1}{4} - \frac{\ell(\ell+1)}{\varrho^2} + \frac{\gamma}{\varrho}\right) R = 0. \tag{2.40}$$

Equation (2.40) will be solved using a power series expansion, but direct application of the method does not work. To see this, try plugging

$$R(\varrho) = \sum_{k=0}^{\infty} a_k \varrho^k$$

into (2.40), obtaining

$$\sum_{k=0}^{\infty} k(k+1) a_k \varrho^{k-2} - \frac{1}{4}\sum_{k=0}^{\infty} a_k \varrho^k - \ell(\ell+1)\sum_{k=0}^{\infty} a_k \varrho^{k-2} + \gamma \sum_{k=0}^{\infty} a_k \varrho^{k-1} = 0.$$

This can be rewritten as

$$-\ell(\ell+1) a_0 \varrho^{-2} + \left((2 - \ell(\ell+1)) a_1 + \gamma a_0\right) \varrho^{-1}$$
$$+ \sum_{k=0}^{\infty} \left(\left((k+3)(k+2) - \ell(\ell+1)\right) a_{k+2} + \gamma a_{k+1} - \frac{1}{4} a_k \right) \varrho^k = 0. \tag{2.41}$$

Vanishing of each term order by order implies that $a_0 = 0$, then $a_1 = 0$, and subsequently $a_k = 0$ for any k, so $R = 0$. We need, therefore, to try a different approach.

We shall focus on the behavior of (2.40) when $\varrho \gg 1$, in which case the equation simplifies to

$$\frac{1}{\varrho^2}\frac{d}{d\varrho}\left(\varrho^2 \frac{dR}{d\varrho}\right) \approx \frac{R}{4}. \tag{2.42}$$

This (approximate) equation can be solved as follows. Look for a solution of the form $e^{A\varrho}$. Plugging into the equation we find $A = -\frac{1}{2}$, i.e., $e^{-\frac{\varrho}{2}}$ is a (approximate) solution of (2.42). This suggests[2]

[2] The reader may remember that when one solves second order ODEs with constant coefficients, sometimes we have to multiply a solution by a suitable power of the variable in order to produce a particular solution or a second linearly independent solution. What it is being done here resembles that: we have some information about solutions, i.e., that $e^{-\frac{\varrho}{2}}$ solves the equation (in an approximate sense) for large values of ϱ. Thus, we try multiplying by $e^{-\frac{\varrho}{2}}$ to construct the full, exact solution.

looking for solutions of (2.40) in the form

$$R(\varrho) = e^{-\frac{\varrho}{2}} G(\varrho). \tag{2.43}$$

Plugging (2.43) into (2.40) gives an equation for G,

$$\frac{d^2G}{d\varrho^2} + \left(\frac{2}{\varrho} - 1\right)\frac{\partial G}{\partial \varrho} + \left(\frac{\gamma - 1}{\varrho} - \frac{\ell(\ell+1)}{\varrho^2}\right) G = 0. \tag{2.44}$$

We seek a solution of the form

$$G(\varrho) = \varrho^s \sum_{k=0}^{\infty} a_k \varrho^k = \sum_{k=0}^{\infty} a_k \varrho^{k+s}, \tag{2.45}$$

where s is to be determined. The term ϱ^s has been included due to the $\frac{1}{\varrho}$ terms in the equation, as these may lead to singular terms that do not fit into a general recurrence relation, as it occurred in (2.41). Notice that the traditional procedure is included in this approach by simply setting $s = 0$.

Plugging (2.45) into (2.44) gives, after some algebra,

$$\begin{aligned} &(s(s+1) - \ell(\ell+1))\, a_0 \varrho^{s-2} \\ &+ \sum_{k=0}^{\infty} \Big(((s+k+1)(s+k+2) - \ell(\ell+1))a_{k+1} - (s+k+1-\gamma)a_k \Big) \varrho^{s+k-1} = 0. \end{aligned} \tag{2.46}$$

The vanishing of the term in ϱ^{s-2} requires

$$s(s+1) - \ell(\ell+1) = 0,$$

which has roots $s = \ell$ and $s = -(\ell+1)$. This latter root is rejected on the basis that it does not yield a finite solution when $\varrho \to 0^+$, i.e., $G(\varrho)$ blows up at the origin when $s = -(\ell+1)$ (recall that ℓ is non-negative).

Using $s = \ell$, one finds from (2.46) the following recurrence relation,

$$a_{k+1} = \frac{k + \ell + 1 - \gamma}{(k+\ell+1)(k+\ell+2) - \ell(\ell+1)} a_k. \tag{2.47}$$

From (2.47) and the ratio test, we see at once that (2.45), with $s = \ell$, converges for all values of ϱ.

In order for (2.45) to be an acceptable solution, we also must verify (1.3). From (2.47), it follows that

$$a_{k+1} = \frac{k + \cdots}{k^2 + \cdots} a_k = \frac{1 + \cdots}{k + \cdots} a_k,$$

and

$$a_k = \frac{k - 1 + \cdots}{(k-1)^2 + \cdots} a_{k-1} = \frac{1 + \cdots}{(k-1) + \cdots} a_{k-1},$$

so that

$$\begin{aligned} a_{k+1} &= \frac{1 + \cdots}{k + \cdots} a_k = \frac{1 + \cdots}{k + \cdots}\frac{1 + \cdots}{(k-1) + \cdots} a_{k-1} \\ &= \frac{1 + \cdots}{k(k-1) + \cdots} a_{k-1}. \end{aligned}$$

Continuing this way,

$$a_{k+1} = \frac{1 + \cdots}{k(k-1)(k-2)\cdots(k-j) + \cdots} a_{k-j}.$$

Remembering that

$$e^{\varrho} = \sum_{k=0}^{\infty} \frac{1}{k!} \varrho^k,$$

we see that $G(\varrho)$ is asymptotic to $\varrho^s e^{\varrho}$, i.e., its series expansion behaves very much like the series of $\varrho^\ell e^{\varrho}$ (recall that $s = \ell$):

$$G(\varrho) \sim \varrho^\ell e^{\varrho},$$

which implies, upon recalling (2.43),

$$R(\varrho) = e^{-\frac{\varrho}{2}} G(\varrho) \sim e^{-\frac{\varrho}{2}} \varrho^\ell e^{\varrho} = \varrho^\ell e^{\frac{\varrho}{2}},$$

which diverges when $\varrho \to \infty$. As a consequence, (1.3) is not satisfied. This will be the case, *unless* the series (2.45) terminates, i.e., unless $a_k = 0$ for all k greater than a certain n. From (2.47), this means

$$k + \ell + 1 - \gamma = 0,$$

i.e.,

$$\gamma = k + \ell + 1.$$

In particular, γ has to be an integer,

$$\gamma = n,\ n = \ell + 1, \ell + 2, \dots.$$

With this, the series terminates at the $(n - (\ell + 1))^{\text{th}}$ term, and G is a polynomial of degree $n - 1$. Recalling (2.38) and (2.39), we have found the possible values for the separation constant $E = E_n$, namely,

$$E_n = -\frac{\mu Z^2 e^4}{2(4\pi\varepsilon_0)^2 \hbar^2 n^2},\ n = 1, 2, 3, \dots \tag{2.48}$$

We write $R_{n\ell}$ to indicate that R is parametrized by the integers n and ℓ, with $n = \ell, \ell + 1, \dots$. We can now write, for each n, the corresponding $R_{n\ell}$ by using (2.47) to find the polynomial $G = G_{n\ell}$, and then $R_{n\ell}$ via (2.43). Unwrapping all our definitions,

$$R_{n\ell}(r) = e^{-\frac{Zr}{na_0}} \left(\frac{Zr}{a_0} \right)^\ell G_{n\ell} \left(\frac{Zr}{a_0} \right),$$

where

$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{\mu e^2}.$$

In light of (2.7), we see that ψ is also parametrized by n, ℓ, and m_ℓ. Instead of thinking of n varying according to $n = \ell, \ell + 1, \dots$, we can equivalently think of ℓ as constrained by $\ell = 0, 1, \dots, n - 1$, for each given $n = 1, 2, \dots$, what is more convenient in order to organize the parameters n, ℓ, m_ℓ. We obtain, therefore, a family of solutions to (2.3),

$$\psi_{n\ell m_\ell} = R_{n\ell} Y_{\ell m_\ell}, \tag{2.49}$$

where

$$\begin{aligned} &n = 1, 2, 3, \dots, \\ &\ell = 0, 1, 2, \dots, n - 1, \\ &m_\ell = -\ell, -\ell + 1, \dots, 0, \dots, \ell - 1, \ell. \end{aligned} \tag{2.50}$$

Our final solution is then given, in view of (2.1) and (2.4), by

$$\Psi(t,x) = A_{n\ell m_\ell} e^{-\frac{iE_n}{\hbar}t}\psi_{n\ell m_\ell},$$

where n, ℓ, and m_ℓ satisfy (2.50), E_n and $\psi_{n\ell m_\ell}$ are given by (2.48) and (2.49), respectively, and $A_{n\ell m_\ell}$ is a constant (depending on n, ℓ, and m_ℓ) that ensures (1.2), i.e., $A_{n\ell m_\ell}$ is given by

$$A_{n\ell m_\ell} = \left(\int_{\mathbb{R}^3} |\psi_{n\ell m_\ell}|^2\right)^{-\frac{1}{2}}.$$

The term $e^{-\frac{iE_n}{\hbar}t}$ does not contribute to $|\Psi|^2$ (since $(e^{-\frac{iE_n}{\hbar}t})^*(e^{-\frac{iE_n}{\hbar}t}) = (e^{+\frac{iE_n}{\hbar}t})(e^{-\frac{iE_n}{\hbar}t}) = 1$). It is customary to absorb the constant $A_{n\ell m_\ell}$ into $\psi_{n\ell m_\ell}$, in which case

$$\int_{\mathbb{R}^3} |\psi_{n\ell m_\ell}|^2 = 1.$$

Or course, (1.2) is automatically satisfied in this case.

3. Final comments.

We close with some remarks about the physical meaning of the problem we just described. Readers are referred to [W] for a more thorough physical discussion. Below, we list some the first few $\psi_{n\ell m_\ell}$.

n	ℓ	m_ℓ	$\psi_{n\ell m_\ell}$
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$
2	0	0	$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(2-\frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$
2	1	0	$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\frac{Zr}{a_0}e^{-\frac{Zr}{2a_0}}\cos\phi$
2	1	$\pm$ 1	$\psi_{21\pm1} = \frac{1}{8\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\frac{Zr}{a_0}e^{-\frac{Zr}{2a_0}}\sin\phi e^{\pm i\theta}$
3	0	0	$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(27-18\frac{Zr}{a_0}+2\frac{Z^2r^2}{z_0^2}\right) e^{-\frac{Zr}{3a_0}}$
3	1	0	$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(6-\frac{Zr}{a_0}\right)\frac{Zr}{a_0}e^{-\frac{Zr}{3a_0}}\cos\phi$
3	1	$\pm$ 1	$\psi_{31\pm1} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(6-\frac{Zr}{a_0}\right)\frac{Zr}{a_0}e^{-\frac{Zr}{3a_0}}\cos\phi e^{\pm i\theta}$
3	2	0	$\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\frac{Z^2r^2}{a_0^2}e^{-\frac{Zr}{3a_0}}(3\cos^2\phi-1)$
3	2	$\pm$ 1	$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\frac{Z^2r^2}{a_0^2}e^{-\frac{Zr}{3a_0}}\sin\phi\cos\phi e^{\pm i\theta}$
3	2	$\pm$ 2	$\psi_{32\pm2} = \frac{1}{262\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\frac{Z^2r^2}{a_0^2}e^{-\frac{Zr}{3a_0}}\sin^2\phi e^{\pm 2i\theta}$

It is possible to show that the constants E_n, $\ell(\ell+1)$, and m_ℓ have important physical interpretation: E_n corresponds to the electron energy, $\ell(\ell+1)$ to the magnitude of its orbital angular momentum, and m_ℓ to the projection of the orbital angular momentum onto the z-axis. The reader should notice that these quantities cannot be arbitrary, being allowed to take values only on a countable set of multiples of integers. This is a distinctive feature of Quantum Mechanics (we say that the energy and orbital angular momentum are "quantized"). The indices n, ℓ, and m_ℓ are called *quantum numbers*.

One-electron atoms with $\ell = 0, 1, 2, 3$ are labeled s, p, d, f. In hydrogen and hydrogen-like atoms, this letter is preceded by a number giving the energy level n. Thus, the lowest energy state of the hydrogen atom is $1s$; the next to the lowest are $2s$ and $2p$; the next $3s, 3p, 3d$ and so on. These are the so-called "orbitals" that the student is likely to have learned in Chemistry. Remembering that $|\Psi|^2$ is a probability density, what these orbitals represent are "clouds of probability," highlighting the regions of three-dimensional space where it is more likely to find the electron.

We finish mentioning that in a more detailed treatment of the problem, μ is not exactly the mass of the particle being described, but rather the reduced mass of the system. This is because, strictly speaking, the electron does not orbit the proton, but both orbit the center of mass of the system electron–proton. This is very much like the situation of the Earth orbiting the Sun: both bodies move due to their reciprocal gravitational attraction, although the Sun, begin much more massive, barely feels the pull caused by Earth's gravitational field, and that is why one usually thinks of the Earth orbiting an standing-still Sun. A similar situation occurs for the proton and the electron. We remark, however, that the calculations we presented apply, with no change, to this more accurate situation: we only have to change the value of μ to be the reduced mass.

References

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