Full Solution for the Hydrogen Atom Wavefunctions

Ethan Huecker

Dec 2022

Preface: In these notes I explicitly solve for the radial and angular wavefunctions of the hydrogen atom. Useful sources used were [1, 2].

---

1 Introduction

The Schrödinger equation for the hydrogen atom has the form

$$\hat{H}_{\text{atom}} |\psi\rangle = E |\psi\rangle \iff \left(-\frac{\hbar^2 \nabla^2}{2\mu} + V(r)\right)\psi = E\psi \tag{1}$$

assuming that the momentum operator has the form $p = -i\hbar\nabla$ on position eigenstates. Note also that $\mu = m_e m_p/(m_e + m_p)$ is the reduced mass of the H-atom system ... so I am working in the center of mass frame. Due to the spherical symmetry, it will be advantageous to use the Laplacian in spherical coordinates,

$$\begin{aligned} \nabla^2 &= \frac{1}{r^2}\partial_r\left(r^2\partial_r\right) + \frac{1}{r^2\sin\theta}\partial_\theta\left(\sin\theta\partial_\theta\right) + \frac{1}{r^2\sin^2\theta}\partial_\phi^2 \\ &= \partial_r^2 + \frac{2}{r}\partial_r - \frac{L^2}{\hbar^2 r^2}, \end{aligned} \tag{2}$$

where I used the fact that the angular component involves the angular momentum operator L. Using this form of the Laplacian in (1), I find

$$\frac{1}{r^2}\partial_r\left(r^2\partial_r\right)\psi + \frac{1}{r^2\sin\theta}\partial_\theta\left(\sin\theta\partial_\theta\right)\psi + \frac{1}{r^2\sin^2\theta}\partial_\phi^2\psi - \frac{2\mu}{\hbar^2}\left(V(r) - E\right)\psi = 0 \tag{3}$$

after some trivial algebra. I will assume this equation is separable into a radial and angular part, $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$, giving

$$Y(\theta,\phi)\frac{1}{r^2}\partial_r\left(r^2\partial_r\right)R(r) + \frac{R(r)}{r^2\sin\theta}\partial_\theta\left(\sin\theta\partial_\theta\right)Y(\theta,\phi) + \frac{R(r)}{r^2\sin^2\theta}\partial_\phi^2 Y(\theta,\phi) - \frac{2\mu}{\hbar^2}\left(V(r) - E\right)R(r)Y(\theta,\phi) = 0. \tag{4}$$

Dividing this equation by $R(r)Y(\theta,\phi)$ and multiplying by r^2 gives

$$\begin{aligned} &\left\{\frac{1}{R(r)}\partial_r\left(r^2\partial_r\right)R(r) - \frac{2\mu r^2}{\hbar^2}\left(V(r) - E\right)\right\} \\ &\qquad + \left\{\frac{1}{Y(\theta,\phi)\sin\theta}\partial_\theta\left(\sin\theta\partial_\theta\right)Y(\theta,\phi) + \frac{1}{Y(\theta,\phi)\sin^2\theta}\partial_\phi^2 Y(\theta,\phi)\right\} = 0, \end{aligned} \tag{5}$$

where I introduced brackets to highlight the successful radial/angular separation. Both of the bracketed factors must add to zero, so they only differ by some constant. To save some algebra, I will use some insight and assume the constant is $l(l+1)$, where l is the angular-momentum quantum number. Therefore, the radial and angular equations are

$$\begin{aligned} \frac{1}{R(r)}\partial_r\left(r^2\partial_r\right)R(r) - \frac{2\mu r^2}{\hbar^2}\left(V(r) - E\right) &= l(l+1), \\ \frac{1}{Y(\theta,\phi)\sin\theta}\partial_\theta\left(\sin\theta\partial_\theta\right)Y(\theta,\phi) + \frac{1}{Y(\theta,\phi)\sin^2\theta}\partial_\phi^2 Y(\theta,\phi) &= -l(l+1), \end{aligned} \tag{6}$$

respectively.

2 Angular Equation

I will assume the angular component is also separable ... $Y(\theta,\phi)=P(\theta)g(\phi)$. This gives, after some simple algebra,

$$\left\{\frac{\sin\theta}{P(\theta)}\partial_\theta\left(\sin\theta\partial_\theta\right)P(\theta)+l(l+1)\sin^2\theta\right\}+\left\{\frac{1}{g(\phi)}\partial_\phi^2 g(\phi)\right\}=0, \tag{7}$$

where I collected like variables into brackets. As before, each bracketed factor must differ by some constant, which from insight I will define as the square of the magnetic-moment quantum number m^2. It follows that

$$\begin{aligned}\frac{\sin\theta}{P(\theta)}\partial_\theta\left(\sin\theta\partial_\theta\right)P(\theta)+l(l+1)\sin^2\theta=m^2,\\ \frac{1}{g(\phi)}\partial_\phi^2 g(\phi)=-m^2,\end{aligned} \tag{8}$$

are the two equations determining the angular component of the wavefunction. The above azimuthal equation is trivial:

$$\partial_\phi^2 g(\phi)=-m^2 g(\phi)\implies g(\phi)=e^{im\phi}, \tag{9}$$

and is purely a phase.

For the above polar equation, I will first multiply by $P(\theta)$, then expand the first term:

$$\sin^2\theta\partial_\theta^2 P(\theta)+\sin\theta\cos\theta\partial_\theta P(\theta)+l(l+1)\sin^2\theta P(\theta)-m^2P(\theta)=0. \tag{10}$$

Next, I will make the substitution $x=\cos\theta$. The derivatives must change,

$$\partial_\theta=-\sin\theta\frac{d}{dx}, \qquad \text{or} \qquad \sin\theta\partial_\theta=-\left(1-x^2\right)\frac{d}{dx}, \tag{11}$$

as well as

$$\partial_\theta^2=-\partial_\theta\left(-\sin\theta\frac{d}{dx}\right)=\left(1-x^2\right)\frac{d^2}{dx^2}-x\frac{d}{dx}. \tag{12}$$

Therefore, the polar equation (8) becomes

$$\left(1-x^2\right)\left[\left(1-x^2\right)\frac{d^2P(x)}{dx^2}-x\frac{dP(x)}{dx}\right]-x\left(1-x^2\right)\frac{dP(x)}{dx}+l(l+1)\left(1-x^2\right)P(x)-m^2P(x)=0, \tag{13}$$

which can be divided by $\left(1-x^2\right)$ to give

$$\left(1-x^2\right)\frac{d^2P(x)}{dx^2}-2x\frac{dP(x)}{dx}+l(l+1)P(x)-\frac{m^2}{1-x^2}P(x)=0. \tag{14}$$

This is the exact form of the associated Legendre equation, with solutions known as ”associated Legendre polynomials”. These (orthogonal) polynomials can be generated from the following relation,

$$P_l^m(x)=\left(1-x^2\right)^{m/2}\frac{d^m}{dx^m}P_l(x), \qquad \text{if} \qquad P_l(x)=\frac{(-1)^l}{2^l l!}\frac{d^l}{dx^l}\left(1-x^2\right)^l, \tag{15}$$

where $l\in\mathbb{Z}$, and $0\leq m\leq l$. It will be necessary to define the polynomials on the range $-l\leq m\leq l$, and for that it is simple to show

$$P_l^{-m}(x)=(-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(x). \tag{16}$$

It will also be helpful to note the orthogonality property

$$\int_{-1}^{1}dx\ P_k^m(x)P_l^m(x)=\frac{2(l+m)!}{(2l+1)(l-m)!}\delta_{k,l}, \tag{17}$$

which is difficult to derive; see Appendix A for details!

Now, I can use (9) and (14) to write the full angular wavefunction as

$$Y_l^m(\theta,\phi) = N P_l^m(\cos\theta) e^{im\phi}, \tag{18}$$

after re-substituting $x = \cos\theta$, and multiplying by some normalization constant N. What is this normalization constant? Well,

$$\begin{aligned}
\int d\Omega \left(Y_{l'}^{m'}(\theta,\phi)\right)^* Y_l^m(\theta,\phi) &= \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \ \left(Y_{l'}^{m'}(\theta,\phi)\right)^* Y_l^m(\theta,\phi) \\
&= |N|^2 \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \ P_{l'}^{m'}(\cos\theta) P_l^m(\cos\theta) e^{i(m-m')\phi} \\
&= 2\pi |N|^2 \delta_{m,m'} \int_0^{\pi} d\theta \ P_{l'}^{m}(\cos\theta) P_l^m(\cos\theta) \\
&= \frac{4\pi(l+m)!}{(2l+1)(l-m)!} |N|^2 \delta_{m,m'} \delta_{l,l'} \\
&= \delta_{m,m'} \delta_{l,l'}.
\end{aligned} \tag{19}$$

$$|N| = \left(\frac{(2l+1)(l-m)!}{4\pi(l+m)!}\right)^{1/2} \implies \boxed{Y_l^m(\theta,\phi) = \left(\frac{(2l+1)(l-m)!}{4\pi(l+m)!}\right)^{1/2} P_l^m(\cos\theta) e^{im\phi}} \tag{20}$$

This is the final form of the angular wavefunctions (spherical harmonics).[1] Since $m \geq 0$ by definition, the negative $m < 0$ wavefunctions are given by

$$Y_l^{-m}(\theta,\phi) = (-1)^m \left(Y_l^m(\theta,\phi)\right)^*. \tag{21}$$

[1] If you took a chemistry course, you already know what these look like.

3 Radial Equation

I will assume the usual Coulomb potential $V(r) = -e^2/r$. Then, (6) can be written as

$$\partial_r \left(r^2 \partial_r\right) R(r) + \Big[\frac{2\mu e^2 r}{\hbar^2} + \frac{2\mu E r^2}{\hbar^2} - l(l+1)\Big] R(r) = 0, \tag{22}$$

after multiplying by $R(r)$ and distributing some constants. The trick is to make the substitution $u(r) = rR(r)$, which changes the derivatives via

$$\partial_r R(r) = \partial_r \left(\frac{u(r)}{r}\right) = \frac{1}{r}\partial_r u(r) - \frac{u(r)}{r^2}, \tag{23}$$

as well as

$$\partial_r^2 R(r) = \partial_r \left(\frac{1}{r}\partial_r u(r)\right) - \partial_r \left(\frac{u(r)}{r^2}\right) = -\frac{2}{r^2}\partial_r u(r) + \frac{1}{r}\partial_r^2 u(r) + \frac{2u(r)}{r^3}, \tag{24}$$

which forces the first term in the radial equation to change as follows:

$$\begin{aligned}\partial_r \left(r^2 \partial_r\right) R(r) = r^2 \partial_r^2 R(r) + 2r\partial_r R(r) &= -2\partial_r u(r) + r\partial_r^2 u(r) + \frac{2u(r)}{r} + 2\partial_r u(r) - \frac{2u(r)}{r} \\ &= r\partial_r^2 u(r).\end{aligned} \tag{25}$$

Therefore, (22) can be written as

$$\partial_r^2 u(r) + \Big[\frac{2\mu e^2}{\hbar^2 r} + \frac{2\mu E}{\hbar^2} - \frac{l(l+1)}{r^2}\Big] u(r) = 0, \tag{26}$$

where I divided both sides by r^2. Now, I will make two definitions:

$$a_0 = \frac{\hbar^2}{\mu e^2} \approx 0.529 \ , \qquad \left(\frac{\epsilon}{2}\right)^2 = -\frac{2\mu E}{\hbar^2}, \tag{27}$$

where a_0 is the Bohr radius of the H-atom. Then, (26) becomes

$$\partial_r^2 u(r) + \Big[\frac{2}{a_0 r} - \left(\frac{\epsilon}{2}\right)^2 - \frac{l(l+1)}{r^2}\Big] u(r) = 0. \tag{28}$$

Next, I will make the substitution $x = r\epsilon$. The derivatives then change as $\partial_r = \epsilon \frac{d}{dx}$ and $\partial_r^2 = \epsilon^2 \frac{d^2}{dx^2}$, resulting in

$$\frac{d^2 u(x)}{dx^2} + \Big[\frac{2}{a_0 \epsilon x} - \frac{1}{4} - \frac{l(l+1)}{x^2}\Big] u(x) = 0, \tag{29}$$

after dividing by a factor of ϵ^2. Why did I do this? Well, note that the associated Laguerre equation has the form

$$\frac{d^2 y_j^k}{dx^2} + \Big[\frac{2j+k+1}{2x} - \frac{1}{4} - \frac{k^2-1}{4x^2}\Big] y_j^k = 0, \tag{30}$$

with a general solution

$$y_j^k(x) = e^{-x/2} x^{(k+1)/2} L_j^k(x), \tag{31}$$

assuming $L_j^k(x)$ are the associated Laguerre polynomials

$$L_j^k(x) = (-1)^k \frac{d^k}{dx^k} L_{j+k}(x), \qquad \text{if} \qquad L_{j+k}(x) = e^x \frac{d^{j+k}}{dx^{j+k}} \left(e^{-x} x^{j+k}\right), \tag{32}$$

Therefore, comparing (31) to (32) gives the correspondence

$$\frac{2j+k+1}{2} = \frac{2}{a_0 \epsilon}, \qquad l(l+1) = \frac{k^2-1}{4} \implies k = 2l+1, \tag{33}$$

and if I define the principal quantum number $n = j + l + 1$,

$$\frac{2j + k + 1}{2} = \frac{2}{a_0 \epsilon} \implies \epsilon = \frac{2}{a_0 n}, \tag{34}$$

after some trivial algebra. Therefore, the r.h.s of (27) implies

$$E = \frac{-\hbar^2}{2\mu}\left(\frac{\epsilon}{2}\right)^2 = \frac{-\hbar^2}{2\mu}\left(\frac{1}{a_0 n}\right)^2 \implies \boxed{E_n = -\frac{\hbar^2}{2\mu a_0^2 n} \approx -\frac{13.6 \text{ eV}}{n}} \tag{35}$$

and the energies are quantized in units of the Rydberg constant $R = \hbar^2/2\mu a_0^2 \approx 13.6$ eV. Therefore, substituting everything into (31) gives

$$u_j^k(r) = e^{-r/a_0 n}\left(\frac{2r}{a_0 n}\right)^{l+1} L_{n-l-1}^{2l+1}\left(\frac{2r}{a_0 n}\right), \tag{36}$$

or after going back to $R(r)$,

$$\boxed{R_j^k(r) = \left(\frac{2}{a_0 n}\right)^{3/2}\left(\frac{(n-l-1)!}{2n\left((n+1)!\right)^3}\right)^{1/2} e^{-r/a_0 n}\left(\frac{2r}{a_0 n}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{a_0 n}\right)} \tag{37}$$

where I added a coefficient for normalization. This is the final form for the radial equation.

A Orthogonality of the Associated Legendre Polynomials

Here, my goal is to determine the orthogonality of the associated Legendre polynomials

$$\begin{aligned} P_l^m(x) &= \left(1-x^2\right)^{m/2} \frac{d^m P_l(x)}{dx^m} \\ &= \frac{1}{2^l l!} \left(1-x^2\right)^{m/2} \frac{d^{l+m}}{dx^{l+m}} \left(x^2-1\right)^l . \end{aligned} \tag{38}$$

Knowing their orthogonality is great, as they are closely related to the spherical harmonics present in the wavefunction of the hydrogen atom. Here, we have

$$\begin{aligned} \int_{-1}^{1} P_p^m P_q^m \, dx &= \frac{1}{2^p p!} \frac{1}{2^q q!} \int_{-1}^{1} \left(1-x^2\right)^m \frac{d^{p+m}}{dx^{p+m}} \left(x^2-1\right)^p \frac{d^{q+m}}{dx^{q+m}} \left(x^2-1\right)^q \\ &:= \frac{(-1)^m}{2^{p+q} p! q!} \int_{-1}^{1} f^m \frac{d^{p+m} f^p}{dx^{p+m}} \frac{d^{q+m} f^q}{dx^{q+m}} \, dx, \end{aligned} \tag{39}$$

under the definition $f(x) = x^2 - 1$, which saves some space. Note that the domain of $P_l^m(x)$ is $[-1, 1]$, and is the reason for the integration bounds.

For reasons that will become apparent, I will do integration by parts $q+m$ times. Are the partially integrated terms zero or nonzero? Well, they are

$$\begin{aligned} &\frac{d^{q+m-1} f^q}{dx^{q+m-1}} f^m \frac{d^{p+m} f^p}{dx^{p+m}} \bigg|_{-1}^{1} - \frac{d^{q+m-2} f^q}{dx^{q+m-2}} \frac{d^1}{dx^1} \left(f^m \frac{d^{p+m} f^p}{dx^{p+m}} \right) \bigg|_{-1}^{1} \\ &\qquad + \frac{d^{q+m-3} f^q}{dx^{q+m-3}} \frac{d^2}{dx^2} \left(f^m \frac{d^{p+m} f^p}{dx^{p+m}} \right) \bigg|_{-1}^{1} + \cdots + f^q \frac{d^{q+m-1}}{dx^{q+m-1}} \left(f^m \frac{d^{p+m} f^p}{dx^{p+m}} \right) \bigg|_{-1}^{1}. \end{aligned} \tag{40}$$

The first and last terms are zero because they are proportional to f^m, which vanishes at the end points, so the question is whether the pure derivative terms are zero. Note that for m integrations by parts, the derivative term with the parentheses will be proportional to f^1, and will be zero. Similarly, all iterations $< m$ will have higher order powers of f, and will vanish. After this point, for iterations $> m$ the derivative term with parentheses will be nonzero, but note that the left-most derivative term will then be zero, as (for example $m+1$),

$$\frac{d^{q-1} f^q}{dx^{q-1}} \frac{d^m}{dx^m} \left(f^m \frac{d^{p+m} f^p}{dx^{p+m}} \right) \bigg|_{-1}^{1}, \tag{41}$$

which is proportional to f^1 and is indeed zero. All other iterations $> m$ give higher order powers of $f(x)$, and must be zero as well!

Therefore, I find that each partially integrated term is zero up to $q+m$ integrations by parts, so (39) can be recast as

$$\int_{-1}^{1} P_p^m P_q^m \, dx = \frac{(-1)^m (-1)^{q+m}}{2^{p+q} p! q!} \int_{-1}^{1} f^q \frac{d^{q+m}}{dx^{q+m}} \left(f^m \frac{d^{p+m} f^p}{dx^{p+m}} \right) dx. \tag{42}$$

Now let's inspect the remaining derivative term, looking at purely the leading order[2]

$$\begin{aligned} \frac{d^{q+m}}{dx^{q+m}} \left(f^m \frac{d^{p+m} f^p}{dx^{p+m}} \right) &\sim \frac{d^{q+m}}{dx^{q+m}} \left(x^{2m} \frac{d^{p+m} x^{2p}}{dx^{p+m}} \right) \\ &\sim \frac{d^{q+m}}{dx^{q+m}} \left(x^{2m} x^{p-m} \right) \\ &\sim \frac{d^{q+m}}{dx^{q+m}} \left(x^{p+m} \right) = \begin{cases} 0 & q > p \\ \text{const.} & q = p \end{cases} \end{aligned} \tag{43}$$

Note the orthogonality condition is invariant under $q \leftrightarrow p$, so this statement is valid for $q < p$ as well. Clearly then the associated Legendre polynomials are only non-zero for $q = p$, and they are orthogonal. □

[2] All lower orders vanish from the derivative.

The question now is what the overlap (42) is when $q = p$. Let's build up the integrand piece-by-piece, noting that

$$\frac{d^j x^i}{dx^j} = \frac{\Gamma(1+i)}{\Gamma(1-j+i)} x^{i-j}, \tag{44}$$

which is quite non-intuitive. Here,

$$\begin{aligned}
f^q \frac{d^{q+m}}{dx^{q+m}}\left(f^m \frac{d^{p+m} f^p}{dx^{p+m}}\right) &= \left(x^2-1\right)^q \frac{d^{q+m}}{dx^{q+m}}\left(\left(x^2-1\right)^m \frac{d^{p+m}}{dx^{p+m}}\left(x^2-1\right)^p\right) \\
&\sim \frac{\Gamma(1+2p)}{\Gamma(1-(p+m)+2p)}\left(x^2-1\right)^q \frac{d^{q+m}}{dx^{q+m}}\left(\left(x^2-1\right)^m x^{2p-(p+m)}\right) \\
&\sim \frac{(2p)!}{(p-m)!}\left(x^2-1\right)^q \frac{d^{q+m}}{dx^{q+m}}\left(x^{p+m}\right) \\
&\xrightarrow{q=p} \frac{(2p)!}{(p-m)!}\left(x^2-1\right)^p \frac{d^{p+m}}{dx^{p+m}}\left(x^{p+m}\right) \\
&= \frac{(2p)!}{(p-m)!}\frac{\Gamma(1+p+m)}{\Gamma(1)}\left(x^2-1\right)^p \\
&= (2p)!\frac{(p+m)!}{(p-m)!}\left(x^2-1\right)^p
\end{aligned} \tag{45}$$

where I used the fact that only the highest terms will survive in the end, and I dropped all else early. Therefore, the orthogonality (42) can be written as

$$\begin{aligned}
\int_{-1}^{1} P_p^m P_q^m \, dx &= \frac{(-1)^{2m+p}}{2^{2p}(p!)^2}(2p)!\frac{(p+m)!}{(p-m)!}\delta_{p,q}\int_{-1}^{1}\left(x^2-1\right)^p \, dx \\
&= \frac{(2p)!}{2^{2p}(p!)^2}\frac{(p+m)!}{(p-m)!}\delta_{p,q}\int_{-1}^{1}\left(1-x^2\right)^p \, dx \\
&\xrightarrow{x=\sin\theta} \frac{(2p)!}{2^{2p}(p!)^2}\frac{(p+m)!}{(p-m)!}\delta_{p,q}\int_{-\pi/2}^{\pi/2}\cos^{2p+1}\theta \, d\theta \\
&= \frac{(2p)!}{2^{2p}(p!)^2}\frac{(p+m)!}{(p-m)!}\delta_{p,q}\left[2\int_{0}^{\pi/2}\cos^{2p+1}\theta \, d\theta\right],
\end{aligned} \tag{46}$$

where I used the fact that the integrand is even in the three equivalence to change the bounds. Why did I put the integral in brackets? Well, looking at the definition of the Beta function tells me that the term in brackets is simply $B(\frac{1}{2}, p+1)$. So,

$$\begin{aligned}
\int_{-1}^{1} P_p^m P_q^m \, dx = \frac{(2p)!}{2^{2p}(p!)^2}\frac{(p+m)!}{(p-m)!}\delta_{p,q}B\left(\frac{1}{2}, p+1\right) &= \frac{(2p)!}{2^{2p}(p!)^2}\frac{(p+m)!}{(p-m)!}\delta_{p,q}\frac{\Gamma(1/2)\Gamma(p+1)}{\Gamma(p+1/2+1)} \\
&= \frac{(2p)!}{2^{2p}(p!)^2}\frac{(p+m)!}{(p-m)!}\delta_{p,q}\frac{p!\sqrt{\pi}}{(p+1/2)\Gamma(p+1/2)} \\
&\xrightarrow{(10.08)} \frac{(2p)!}{2^{2p}(p!)^2}\frac{(p+m)!}{(p-m)!}\delta_{p,q}\frac{p!\sqrt{\pi}}{(p+1/2)}\frac{2^{2p}p!}{\sqrt{\pi}(2p)!} \\
&= \frac{(p+m)!}{(p+1/2)(p-m)!}\delta_{p,q}
\end{aligned} \tag{47}$$

$$\therefore \boxed{\int_{-1}^{1} P_p^m P_q^m \, dx = \frac{2(p+m)!}{(2p+1)(p-m)!}\delta_{p,q}} \tag{48}$$

References

[1] J. J. Sakurai and Jim Napolitano. *Modern Quantum Mechanics*. Cambridge University Press, Cambridge, UK, 2 edition, 2017.

[2] John S. Townsend. *A Modern Approach to Quantum Mechanics*. University Science Books, Sausalito, CA, 2 edition, 2012.