Nonrelativistic Hydrogen Atom

Presenting the Analytical Solution

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Introduction

The hydrogen atom represents the simplest quantum mechanical system with relevance to chemistry. It is the only such system that can be solved analytically.

The Hamiltonian

The hydrogen atom can be pictured as an electron moving in an electrostatic potential V set up by a proton. Since we can think of the proton and the electron orbiting a common center of mass, we can use the reduced mass μ for both particles. The hamiltonian of the system is:

$$\hat{H} = \frac{-\hbar}{2\mu}\nabla^2 + \frac{-Ze^2}{4\pi\epsilon_0 r} \tag{1}$$

Where the first term is the kinetic energy, and the second term is the electron-nuclear attraction. $Z = 1$ here.

Schrodinger Equation in Polar Coordinates

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

We will proceed with the the separation of variables, where we will guess $\Psi = R(r)\gamma(\theta,\phi)$. Plugging this into the Sch.Eq and dividing thru by our guess and multiplying by the factor $\frac{2\mu r^2}{\hbar^2}$, we obtain:

Separation of Variables

Radial part:

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-\frac{2\mu r^2}{\hbar^2}\left(V(r)-E\right)=A_R \tag{3}$$

Angular Part:

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\gamma}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]=A_\gamma \tag{4}$$

From this separation, we see that $A_R + A_\gamma = 0$, in addition, we can further separate the angular portion into a θ equation, and a ϕ equation. As such, we guess $\gamma = \Theta\Phi$

Angular part

$$\left[\frac{1}{\Theta}\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+A_{\gamma}\sin^{2}\theta\right]+\frac{1}{\Phi}\frac{\partial^{2}\Phi}{\partial\phi}=0 \tag{5}$$

We can now set each term equal in magnitude but opposite in sign. They will be equal to a constant $-m^2$ for the Φ term, and m^2 for the Θ term

Angular part continued

As such, for the Φ term, we get:

$$\Phi = \exp\{im\phi\} \tag{6}$$

For continuity of the wavefuntion, we need that $\Phi(2\pi) = \Phi(0)$

$$\begin{aligned} \exp\{i2\pi m\} &= \exp\{0\} \\ \exp\{i2\pi m\} &= 1 \\ m &= \pm 1, 0, \pm 2.... \end{aligned} \tag{7}$$

Angular part cont'd

For the Θ term we will get into Legendre territory:

$$\left[\frac{1}{\Theta}\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)+A_\gamma\sin^2\theta\right]=m^2 \tag{8}$$

Multiply by Θ

$$\left[\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)+A_\gamma\Theta\sin^2\theta\right]=m^2\Theta \tag{9}$$

Rearranging:

$$\left[\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)+\Theta\left(A_\gamma-\frac{m^2}{\sin^2\theta}\right)\right]=0 \tag{10}$$

Angular Part cont'd

We now want to simply the expression further, we can perform a substitution, where we define a function $P(cos\theta)$ and $x = cos\theta$, where $cos(\theta)$ will become our independent variable:

$$\frac{\mathrm{d}}{\mathrm{d}\theta} = \frac{\mathrm{d}x}{\mathrm{d}\theta}\frac{\mathrm{d}}{\mathrm{d}x} \tag{11}$$

$$\frac{\mathrm{d}}{\mathrm{d}\theta} = -\sin\theta\frac{\mathrm{d}}{\mathrm{d}x}$$

So now we get:

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(\sin^2\theta\frac{\mathrm{d}P}{\mathrm{d}x}\right) + P\left(A_\gamma - \frac{m^2}{\sin^2\theta}\right) = 0 \tag{12}$$

using the trig identity $\sin^2\theta + \cos^2\theta = 1$, and remembering that $x = cos\theta$ we further obtain:

$$\frac{\mathrm{d}}{\mathrm{d}x}\left((1-x^2)\frac{\mathrm{d}P}{\mathrm{d}x}\right) + P\left(A_\gamma - \frac{m^2}{1-x^2}\right) = 0 \tag{13}$$

Angular Part cont'd

After chain ruling we get the associated Legendre differential equation:

$$(1-x^2)(\frac{\mathrm{d}^2 P}{\mathrm{d}x^2} - \frac{\mathrm{d}P}{\mathrm{d}x}2x) + P(A_\gamma - \frac{m^2}{1-x^2}) = 0 \tag{14}$$

With solutions:

$$P_l^m = \left(1-x^2\right)^m \left(a_0 \sum_0^\infty \frac{a_{2n}}{a_0} x^{2n} + a_1 \sum_1^\infty \frac{a_{2n+1}}{a_1} x^{2n+1} \right) \tag{15}$$

with coefficients:

$$a_{n+2} = \frac{(n+m)(n+m+1) - A_\gamma}{(n+1)(n+2)} a_n \tag{16}$$

The series converges when $A_\gamma = l(l+1)$, where l is an integer. The solutions to the angular part are a product of Legendre polynomials with the ϕ term. These are the spherical harmonics:

$$\boxed{\gamma(\theta, \phi) = P_l^m(\cos\theta)\exp\{im\phi\}}$$

Back to the Radial part

Remember that only the potential has an r dependence. This tells us that the spherical harmonics do not dependend on the potential. This is to be expected since the potential has spherical symmetry. We can write the radial equation has:

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) - \frac{2\mu r^2}{\hbar^2}\left[V - E\right]R = l(l+1)R \tag{17}$$

Performing the substitution $R = \frac{u}{r}$, multiplying thru by $\frac{\hbar^2}{2\mu r}$, r and rearranging we get the Radial equation:

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2 u}{\mathrm{d}r^2} + (V + \frac{\hbar^2 l(l+1)}{2\mu r^2})u = Eu \tag{18}$$

Importantly, the term $\frac{\hbar^2 l(l+1)}{2\mu r^2}$ is the centrifugal term, it "throws" the electron away from the nucleus.

The Hydrogen atom for Real

The equations we worked with so far are valid for any QM problem in which the potential is spherically symmetric. What classifies it as the hydrogen atom specifically is the form of V. Hence, the radial equation for the H-atom is:

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2 u}{\mathrm{d}r^2} + \left(\frac{-e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2 l(l+1)}{2\mu r^2}\right)u = Eu \tag{19}$$

Asymptotic cases: Part 1-Large r

At large r, the $\frac{1}{r}$ and $\frac{1}{r^2}$ terms go to zero, this leaves us with the differential equation:

$$\frac{\mathrm{d}^2 u}{\mathrm{d}r^2} + \frac{2\mu}{\hbar^2} E u = 0 \tag{20}$$

With solution: $u(r) = A\exp\{kr\} + B\exp\{-kr\}$. But at large r, the $\exp\{kr\}$ term blows up, we set $A = 0$, so at large r, $u(r) = B\exp(-kr)$.

Asymptotic cases: Part 2-Small r

At $r \to 0$, the $\frac{1}{r^2}$ term dominates $\frac{1}{r}$, this leaves us with the differential equation:

$$\frac{\mathrm{d}^2 u}{\mathrm{d}r^2} + \frac{l(l+1)}{r^2} u = 0 \tag{21}$$

With solution: $u(r) = Cr^{-l} + Dr^{l+1}$. But at small r, the r^{-l} term blows up, we set $C = 0$, so at small r, $u(r) = Dr^{l+1}$.

So we can guess that the total radial wavefunction will be of the form $u(r) = A\exp\{-kr\}Dr^{l+1}\nu(r)$, where $\nu(r)$ describes the behavior at intermediate r values.

Solution to the Radial Equation

Taking the second derivative of $u(r)$ as we have guessed it and inserting it into the radial equation, will allow us to solve using the series method for the $\nu(r)$. When we do this, we get that the solutions are associated Laguerre Polynomials, and that the physically realizable solutions are only valid if