The Hydrogen Atom

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Chapter 1

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Notes on the exact derivation of the n energy levels of the hydrogen atom in three dimensions.

1.1 Exact energy levels

The time independent Schrödinger equation

$$\hat{H}\Psi\left(r,\theta,\phi\right) = E\Psi\left(r,\theta,\phi\right) \tag{1.1}$$

$$\hat{H} = \hat{T} + V \qquad \hat{T} = -\frac{\hbar^2}{2\mu}\nabla^2 \qquad V = \frac{1}{4\pi\varepsilon_0}\frac{Qq}{|\vec{r}-\vec{R}|} \tag{1.2}$$

where $\vec{R}$ is the location of the atomic nucleus, $\vec{r}$ is the location of the electron, Q is the charge of the nucleus, q is the charge of the electron. To reduce the two body problem to a one body problem we have also introduced the reduced mass of the hydrogen atom

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_p} \tag{1.3}$$

where m_e is the electron mass and m_p is the mass of a proton [1].

In three dimensional, sperical co-ordinateds $\nabla^2 f$ is defined as

$$\nabla^2 f = \frac{1}{r}\frac{\partial^2}{\partial r^2}\left(rf\right) + \frac{1}{r^2 sin\left(\theta\right)}\frac{\partial}{\partial\theta}\left(sin\left(\theta\right)\frac{\partial}{\partial\theta}f\right) + \frac{1}{r^2 sin\left(\theta\right)}\frac{\partial^2}{\partial\phi^2}f \tag{1.4}$$

with θ defined as the polar coordinate $(0 < \theta < \pi)$ and ϕ is the azimuthal coordinate $(0 < \phi < 2\pi)$.

We would like $\Psi\left(r,\theta,\phi\right)$ to be of the form

$$\Psi\left(r,\theta,\phi\right) = R\left(r\right)Y\left(\theta,\phi\right) \tag{1.5}$$

Equation (1.1) can now be evaluated with equation (1.5) and with separation of variables, the radial component can be written as

$$\frac{\partial^2}{\partial r^2}R + \frac{2}{r}\frac{\partial}{\partial r}R + \left(\frac{2\mu}{\hbar^2}\left(E - \frac{Qq}{4\pi\epsilon_0 r}\right) - \frac{l\left(l+1\right)}{r^2}\right)R = 0 \tag{1.6}$$

which is not directly solvable (the details of this evaluation can be found in the appendix section 2.1). However, at large values of r, the $1/r$ terms will tend to zero, and that the electron density should also tend to zero so that we require a decaying solution of the form

$$R_\infty = e^{-\frac{r}{a}} \tag{1.7}$$

which when used in equation (1.6) produces

$$\frac{\hbar^2}{2\mu a^2} - \left(\frac{\hbar^2}{\mu a} + \frac{Qq}{4\pi\epsilon_0}\right)\frac{1}{r} - \frac{\hbar^2 l\left(l+1\right)}{2\mu r^2} = E \tag{1.8}$$

with the previous requirement of $1/r \to 0$

$$E_1 = -\frac{\hbar^2}{2\mu a^2} \tag{1.9}$$

and from the prefactor of the $1/r$ terms we can determine that

$$a = -\frac{\hbar^2 4\pi\epsilon_0}{Qq\mu} \tag{1.10}$$

and we finaly have the ground state energy

$$E_1 = -\frac{Q^2 q^2 \mu}{32\hbar^2\pi^2\epsilon_0^2} \approx -13.598547375016173 eV \tag{1.11}$$

The full quantised energy (that requires derivation) is

$$E_n = -\frac{1}{n^2}\frac{Q^2 q^2 \mu}{32\hbar^2\pi^2\epsilon_0^2} \tag{1.12}$$

and the next four energy levels are

$$E_2 = -3.399636843754043 eV \tag{1.13}$$

$$E_3 = -1.51094970833513 eV \tag{1.14}$$

$$E_4 = -0.8499092109385108 eV \tag{1.15}$$

$$E_5 = -0.5439418950006469 eV \tag{1.16}$$

Chapter 2

Appendix

2.1 Evaluating the Hydrogen atom PDEs

Using equation (1.1) with the definitions in (1.2) and the separable wave function in equation (1.5) we can start to evaluate the Schrödinger equation

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}(rRY)+\frac{1}{r^2 sin(\theta)}\frac{\partial}{\partial\theta}\left(sin(\theta)\frac{\partial}{\partial\theta}RY\right)+\frac{1}{r^2 sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}RY+\frac{2\mu}{\hbar^2}\left(E-\frac{Qq}{4\pi\varepsilon_0 r}\right)RY=0 \tag{2.1}$$

The radial and angular terms can then be grouped by multiplying through by r^2 and dividing by RY to produce

$$\frac{r}{R}\frac{\partial^2}{\partial r^2}(rR)+\frac{1}{Y sin(\theta)}\frac{\partial}{\partial\theta}\left(sin(\theta)\frac{\partial}{\partial\theta}Y\right)+\frac{1}{Y sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}Y+\frac{2\mu r^2}{\hbar^2}\left(E-\frac{Qq}{4\pi\varepsilon_0 r}\right)=0 \tag{2.2}$$

Each component can be equated to some constant A

$$\frac{r}{R}\frac{\partial^2}{\partial r^2}(rR)+\frac{2\mu r^2}{\hbar^2}\left(E-\frac{Qq}{4\pi\varepsilon_0 r}\right)-A=0 \tag{2.3}$$

$$\frac{1}{Y sin(\theta)}\frac{\partial}{\partial\theta}\left(sin(\theta)\frac{\partial}{\partial\theta}Y\right)+\frac{1}{Y sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}Y+A=0 \tag{2.4}$$

We can then serparate the θ and ϕ conponents by requiring $Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$

$$\Phi sin(\theta)\frac{\partial}{\partial\theta}\left(sin(\theta)\frac{\partial}{\partial\theta}\Theta\right)+\Theta\frac{\partial^2}{\partial\phi^2}\Phi+A\Theta\Phi sin^2(\theta)=0 \tag{2.5}$$

and we have the two equations

$$\frac{\partial^2}{\partial\phi^2}\Phi+B\Phi=0 \tag{2.6}$$

$$\frac{sin(\theta)}{\Theta}\frac{\partial}{\partial\theta}\left(sin(\theta)\frac{\partial}{\partial\theta}\Theta\right)+A sin^2(\theta)-B=0 \tag{2.7}$$

We can then solve equation (2.6) to find B, equation (2.7) to find A and equation (2.3) to find the energy E. Equation (2.6) has the solution

$$\Phi(\phi) = c_1 e^{im\phi} + c_2 e^{-im\phi} \tag{2.8}$$

with $B = m^2$ where m must be an integer number to prevent the value of the azimuth wave function being different for $\phi = 0$ and $\phi = 2\pi$.

For the θ dependence, equation (2.7) requires a bit more manipulation; we should first introduce a few more definitions

$$\Theta(\theta) = P(cos(\theta)) \qquad x = cos(\theta) \qquad \frac{\partial}{\partial\theta} = \frac{\partial x}{\partial\theta}\frac{\partial}{\partial x} = -sin(\theta)\frac{\partial}{\partial x} \tag{2.9}$$

We can now write equation (2.7) as

$$-\frac{\partial}{\partial x}\left(sin^2(\theta)\frac{\partial}{\partial x}P\right) + \left(A - \frac{m^2}{sin^2(\theta)}\right)P = 0 \tag{2.10}$$

and with the trigonometric identiy $sin^2(\theta) = 1 - cos(\theta)^2$ we can write

$$\frac{\partial}{\partial x}\left(\left(1-x^2\right)\frac{\partial}{\partial x}P\right) + \left(A - \frac{m^2}{1-x^2}\right)P = 0 \tag{2.11}$$

Evaluating the differental

$$\frac{\partial}{\partial x}\left(\left(1-x^2\right)\frac{\partial}{\partial x}P\right) = \left(1-x^2\right)\frac{\partial^2}{\partial x^2}P - 2x\frac{\partial}{\partial x}P \tag{2.12}$$

results in the partial differential equation

$$\left(1-x^2\right)\frac{\partial^2}{\partial x^2}P - 2x\frac{\partial}{\partial x} + \left(A - \frac{m^2}{1-x^2}\right)P = 0 \tag{2.13}$$

which with $A = l(l+1)$ has the solution of the associated Legendre polynomials [2]

$$P = c_3 P_l^m(x) + c_4 Q_l^m(x) \tag{2.14}$$

where l is an integer.

With the definition of A we can write equation (2.3) as

$$\frac{\partial^2}{\partial r^2}R + \frac{2}{r}\frac{\partial}{\partial r}R + \left(\frac{2\mu}{\hbar^2}\left(E - \frac{Qq}{4\pi\epsilon_0 r}\right) - \frac{l(l+1)}{r^2}\right)R = 0 \tag{2.15}$$

Bibliography

[1] Abramowitz and Stegun 1972; Zwillinger 1997, p. 7

[2] Abramowitz and Stegun 1972; Zwillinger 1997, p. 124