Wavefunctions of the Hydrogen Atom and Hydrogen Molecular Ion: Supplementary Document

Introduction

This document contains material, derivations, and related miscellany which has been omitted from the primary report for the case of brevity. Where there exists a related footnote, it will be referenced in this document.

Footnote 1: the Laplacian in Spherical Coordinates

Spherical coordinates to Cartesian coordinates:

$$x = r\cos(\theta)\sin(\phi) \tag{1}$$
$$y = r\sin(\theta)\sin(\phi) \tag{2}$$
$$z = r\cos(\phi) \tag{3}$$

And thus the Laplacian in spherical coordinates is as follows:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{r^2\sin\theta^2}\frac{\partial^2}{\partial\phi^2} \tag{4}$$

Footnote 2: Derivation of Separated Wavefunction Components

The solutions to the equations are shown in the report, however we detail the methods here. We begin with the separated differential equations,

$$\tilde{U}(r) + \eta + \frac{2r}{R}\frac{\partial R}{\partial r} + \frac{r^2}{R}\frac{\partial^2 R}{\partial r^2} = 0 \tag{5}$$
$$\cot\theta\frac{\partial Y}{\partial\theta} + \frac{\partial^2 Y}{\partial\theta^2} + \csc\theta\frac{\partial^2 Y}{\partial\phi^2} - \eta Y = 0 \tag{6}$$
$$\cos\theta\frac{\partial\Theta}{\partial\theta} + \sin\theta\frac{\partial^2\Theta}{\partial\theta^2} + (\nu - \eta\sin\theta)\Theta = 0 \tag{7}$$
$$\nu\Phi + \frac{\partial^2\Phi}{\partial\phi^2} = 0 \tag{8}$$

Where equations 7 and 8 are derived from equation 6 by means of variable separation. First examining equation 6, we notice that if $-\eta = +l(l+1)$, we obtain:

$$\cot\theta\frac{\partial Y}{\partial\theta} + \frac{\partial^2 Y}{\partial\theta^2} + \csc\theta\frac{\partial^2 Y}{\partial\phi^2} + l(l+1)Y = 0 \tag{9}$$

Which is of a form which may be solved if,

$$Y(\theta,\phi) = Y_{l,m}(\theta,\phi) \tag{10}$$

Where,

$$Y_{l,m}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(cos\theta)e^{im\phi} \tag{11}$$

Are the spherical harmonics in l, m.Shown here is the *associated Lengendre Polynomial* $P_l^m(x)$, given as follows:

$$P_l^m(x) = (-1)^m(1-x^2)^{m/2}\frac{d^m P_n(x)}{dx^m} \tag{12}$$

$P_n(x)$ is the *Legendre Polynomial*,

$$P_n(x) = \frac{1}{2^l l!}\frac{d^{(l)}}{dx^{(l)}}(x^2-1)^l \tag{13}$$

And thus we find equation 11 solves the polar and azimuthal components of the wavefunction.
We now consider the radial part in equation 5. This may be changed into a suitable form where we may apply *Laguerre polynomials* to determine a solution. First, we use the fact that $-\eta = +l(l+1)$ is required to solve the spherical harmonics. We may also use the expanded form of the altered potential $\tilde{U}(r) = \frac{2mr^2}{\hbar^2}\left(E + \frac{e^2}{r}\right)$ to transform the radial expression into the form:

$$\frac{-\hbar^2}{2m}\left(\frac{2}{r}\frac{\partial R}{\partial r} + \frac{\partial^2 R}{\partial r^2} - \frac{l(l+1)}{r^2}R\right) - \frac{e^2}{r}R = ER \tag{14}$$

The following substitutions may be made:

$$s = \alpha r \tag{15}$$

$$w(s) = R(s/\alpha) \tag{16}$$

$$\alpha = \sqrt{-\frac{8mE}{\hbar^2}} \tag{17}$$

Equation 14 becomes,

$$\frac{\partial^2 w}{\partial s^2} + \frac{2}{s}\frac{\partial 2}{\partial s} - \frac{l(l+1)}{s^2}w - \frac{1}{4}w + \frac{\chi}{s}w = 0 \tag{18}$$

Where:

$$n = \frac{2me^2}{\alpha\hbar^2} = \frac{e^2}{\hbar}\sqrt{\frac{m}{-2E}} \tag{19}$$

Following with the substitution:

$$w(s) = s^l e^{-s/2}y(s) \tag{20}$$

We obtain:

$$s\frac{\partial^2 y}{\partial s} + [2(l+1) - s]\frac{\partial y}{\partial s} + (n-l-1)y = 0 \tag{21}$$

Where this is of a form which may be solved by the *generalised Laguerre polynomial*, given by the Rodrigues formula:

$$L_n^{\alpha}(x) = \frac{x^{-\alpha}e^x}{n!}\frac{\partial^n}{\partial x^n}\left[x^{n+\alpha}e^{-x}\right] \tag{22}$$

Where, with comparison to equation 21, we have $\alpha, n = 2l+1, n-l-1$ in this case. Thus, subsituting in reverse to determine $R(r)$ gives us:

$$R_{n,l}(r) = e^{-(\alpha r)/2}(\alpha r)^l L_{n-l-1}^{2l+1}(\alpha r) \tag{23}$$

Introducing the Bohr radius,

$$a = \frac{\hbar^2}{me^2} \approx 0.6 \times 10^{-10}m \tag{24}$$

The radial part becomes:

$$R_{n,l}(r) = e^{-r/(na)} \left(\frac{2}{na}r\right)^l L^{2l+1}_{n-l-1}\left(\frac{2}{na}r\right) \tag{25}$$

Which is similar in form to what was seen in the main report. We require that the wavefunction is normalised, by introducing a term A such that:

$$\Psi(r,\theta,\phi) = AR_{n,l}(r)Y_{l,m}(\theta,\phi) \Rightarrow \int |\Psi(r,\theta,\phi)|^2 dV = 1 \tag{26}$$

Physically, this ensures that across all space, there is surely only one electron to be found, and thus the probability is 1. Here, $dV = r^2 sin\phi dr d\theta d\phi$ is the spherical volume element. R may be rewritten as:

$$AR_{n,l}(r) = R_{n,l}(r) = \frac{2^{l+1}}{n^{l+2}}\sqrt{\frac{(n-l-1)!}{2n(n+1)!}} r^l e^{-\frac{r}{n}} L^{2l+1}_{n-l-1}\left(\frac{2r}{n}\right) \tag{27}$$

Where we have set $a = 1$. Thus, the full wavefunction is written as:

$$\Psi(r,\theta,\phi) = \frac{2^{l+1}}{n^{l+2}}\sqrt{\frac{(n-l-1)!}{2n(n+1)!}} r^l e^{-\frac{r}{n}} L^{2l+1}_{n-l-1}\left(\frac{2r}{n}\right)\sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}} P^m_l(cos\theta)e^{im\phi} \tag{28}$$

As required.[1]

Footnote 6: Properties of quantum numbers n, l, m

Footnote 2 introduces the *quantum numbers*: integers which dictate the form of the wavefunction and are a necessity to solve the Schrödinger equation,

$$n = \{1, 2, 3, \dots\} \tag{29}$$
$$l = \{0, 1, \dots, n-1\} \tag{30}$$
$$m = \{-l, -l+1, \dots, l-1, l\} \tag{31}$$

Diagrams of the resulting electron orbitals are shown in *Figure 1* in the report.

Footnote 8: Derivation of Laplacian in prolate spheroidal coordinates

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial x^2} \tag{32}$$

Converted to prolate spheroidal coordinates using [6],

$$\nabla^2 = \frac{1}{h_\lambda h_\mu h_\phi}\left[\frac{\partial}{\partial\lambda}\left(\frac{h_\mu h_\phi}{h_\lambda}\right) + \frac{\partial}{\partial\mu}\left(\frac{h_\lambda h_\phi}{h_\mu}\right) + \frac{\partial}{\partial\phi}\left(\frac{h_\lambda h_\mu}{h_\phi}\right)\right] \tag{33}$$

$$h^2_\lambda = \frac{\partial x}{\partial\lambda}^2 + \frac{\partial y}{\partial\lambda}^2 + \frac{\partial z}{\partial\lambda}^2 \tag{34}$$

$$h^2_\mu = \frac{\partial x}{\partial\mu}^2 + \frac{\partial y}{\partial\mu}^2 + \frac{\partial z}{\partial\mu}^2 \tag{35}$$

$$h^2_\phi = \frac{\partial x}{\partial\phi}^2 + \frac{\partial y}{\partial\phi}^2 + \frac{\partial z}{\partial\phi}^2 \tag{36}$$

[1] This derivation is adapted from (N.H. Asmar, 2005) [2]

The metric coefficients for the prolate spheroidal coordinates are then,

$$h_\lambda = \frac{R}{4}\sqrt{\frac{\lambda^2+\mu^2}{\lambda^2+1}}; h_\mu = \frac{R}{4}\sqrt{\frac{\lambda^2+\mu^2}{1-\mu}}; h_\phi = \frac{R}{4}\sqrt{(\lambda^2+1)(1-\mu^2)} \tag{37}$$

plugging in the metric coefficients gives,

$$\nabla^2 = \frac{16}{R^2}\left(\frac{1}{\lambda^2-\mu^2}\left[\frac{\partial}{\partial\lambda}(\lambda^2-1)\frac{\partial}{\partial\lambda} \quad +\frac{\partial}{\partial\mu}(1-\mu^2)\frac{\partial}{\partial\mu}\right] + \frac{1}{(\lambda^2-1)(a-\mu^2}\frac{\partial^2}{\partial\phi^2}\right) \tag{38}$$

Bibliography

[1] L.D. Landau, L.F. Lifshitz (1958), *Quantum Mechanics (Non-relativistic theory)*, Third Edition

[2] N.H. Asmar (2005), *Partial Differential Equations with Fourier Series and Boundary Value Problems*, Third Edition

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[4] D.R. Bates; et al. (1953), *Wave Functions of the Hydrogen Molecular Ion*

[5] F.A. Matsen (1953), *The United Atom Treatment of* H_2^+

[6] M. Abramowitz; et al. (1964), *Handbook of Mathematical Functions*