Energy Levels Of Hydrogen Atom Using Ladder Operators

Ava Khamseh
Supervisor: Dr. Brian Pendleton

The University of Edinburgh
August 2011

Acknowledgement

I would like to thank my Direction of Studies, Dr. Brian Pendleton for his supervision, support and encouragement.

Abstract

The aim of this paper is to first use the Schrödinger wavefunction methods and then the ladder operator methods in order to study the energy levels of both the quantum Simple Harmonic Oscillator (SHO) and the Hydrogen atom.

Introduction

Starting from the Simple Harmonic Oscillator[1] we first work through the solution of the bound-state wavefunctions for the harmonic oscillator in order to obtain the energy eigenvalues, $E = (n + \frac{1}{2})\hbar\omega$, energy eigenfunctions and the Hermite polynomials by solving differential equations. Then, we will use algebraic ladder operator methods in order to find the energy eigenvalues which should result in the same answer.
In the second section the aim is to find the the energy levels of the Hydrogen atom[1] using the two methods[2] explored in the previous section. However, this difference between the SHO and the Hydrogen atom is that in the case of the latter we need to consider "three dimensional" space. Finally the results of both methods will be compared in the end.

1 The Harmonic Oscillator

1.1 Differential Equations Method

For the SHO the Hamiltonian is of the form

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}kx^2 \tag{1.1}$$

So the time independent Schrödinger equation 1.1 becomes

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x) \tag{1.2}$$

Now, introducing the frequency of the oscillator

$$\omega = \sqrt{\frac{k}{m}} \tag{1.3}$$

writing

$$\varepsilon = \frac{2E}{\hbar\omega} \tag{1.4}$$

and substituting for k and E into equation 1.2 we get

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+\frac{1}{2}\omega^2 mx^2\psi(x) = \frac{\varepsilon\hbar\omega}{2}\psi\left(x\right) \;\Rightarrow\; \frac{d^2\psi(x)}{dx^2}+\frac{\omega m}{\hbar}\left[\varepsilon - \frac{\omega m}{\hbar}x^2\right]\psi\left(x\right) = 0 \tag{1.5}$$

Changing variables to

$$y = \sqrt{\frac{m\omega}{\hbar}} \tag{1.6}$$

equation 1.5 can then be written as

$$\frac{d^2\psi}{dy^2} + \left(\varepsilon - y^2\right)\psi = 0 \tag{1.7}$$

As $y^2 \to \infty$, ε becomes negligible in comparison with y^2 and we can rewrite equation 1.7 as

$$\frac{d^2\psi_0(y)}{dy^2} - y^2\psi_0(y) = 0 \tag{1.8}$$

Now if we multiply the equation by $2\frac{d\psi_0}{dy}$ and use the chain rule we get

$$\frac{d}{dy}\left(\frac{d\psi_0}{dy}\right)^2 - y^2\frac{d}{dy}\left(\psi_0^2\right) = 0 \;\Rightarrow\; \frac{d}{dy}\left[\left(\frac{d\psi_0(x)}{dy}\right)^2 - y^2\psi_0^2\right] = -2y\psi_0^2 \tag{1.9}$$

In order to make this equation simpler, we assume that the term on the right side of the equation can be neglected. However, we will check later that this assumption is correct. So we have

$$\frac{d}{dy}\left[\left(\frac{d\psi_0(x)}{dy}\right)^2 - y^2\psi_0^2\right] = 0 \tag{1.10}$$

Integrating both side of the above equation with respect to (y) and rearranging,

$$\frac{d\psi_0(x)}{dy} = (C + y^2\psi_0^2)^{1/2} \tag{1.11}$$

Both ψ_0 and $\frac{d\psi_0}{dy}$ must vanish at infinity, so $C = 0$ so

$$\frac{d\psi_0(x)}{dy} = \pm y\psi_0 \tag{1.12}$$

and the acceptable solution, which vanishes at infinity is

$$\psi_0(y) = e^{-y^2/2} \tag{1.13}$$

If we now observe the term $\frac{d}{dy}(y^2\psi_0^2)$ which appears in equation 1.9,

$$\frac{d}{dy}(y^2\psi_0^2) = \frac{d}{dy}(y^2e^{-y^2}) \simeq -2y^3e^{-y^2} + 2ye^{-y^2} \tag{1.14}$$

it can be said that $2y\psi_0^2 = 2ye^{-y^2}$ is indeed negligible compared with $-2y^3e^{-y^2}$ for large y so the assumption made above is correct.
Hence, we can make an ansatz that the general solution for $\psi(y)$ takes the form

$$\psi(y) = h(y)e^{-y^2/2} \tag{1.15}$$

NB Note that this is a general solution for $\psi(y)$ not $\psi_0(y)$ which is only defined for large y.

It is important to mention that the solution is exact for the ground state where $h\,(y) = 1$ (see equation 1.17, for $m = 0$, $h\,(y) = a_0 = 1$)
We insert this back into equation 1.7 and devide both sides by $e^{y^2/2}$ to get

$$\frac{d^2h(y)}{dy^2} - 2y\frac{dh(y)}{dy} + (\varepsilon - 1)h(y) = 0 \tag{1.16}$$

Now that we have considered the behavior at infinity, we should observe the behavior near $y = 0$ by starting from the power series expansion

$$h(y) = \sum_{m=0}^{\infty} a_m y^m \tag{1.17}$$

which when substituted into equation 1.16, rearranged and devided by y^m results in the recursion relation

$$(m+1)(m+2)a_{m+2} = (2m - \varepsilon + 1)a_m \tag{1.18}$$

For large m , ie $m > N$ where N is a large number, we have

$$m^2 a_m \simeq 2m a_m \;\Rightarrow\; a_{m+2} \simeq \frac{2}{m}a_m \tag{1.19}$$

which implies that the general solution to $h(y)$ is

$h(y)$ = (solution for $m < N$) + (solution for $m \geq N$)

so $h(y)$ = (a polynomial in y)

$$+a_N\left[y^N + \frac{2}{N}y^{N+2} + \frac{2^2}{N(N+2)}y^{N+4} + \frac{2^3}{N(N+2)(N+4)}y^{N+6} + \dots\right] \tag{1.20}$$

where the first term just comes from the power series expansion and last terms is derived as follows

1. $m = N \Rightarrow a_N y^N$
2. According to equation 1.19 , $a_{N+2} = \frac{2}{N}a_N \;\Rightarrow\; \frac{2}{N}a_N y^{N+2}$
3. Applying 1.19 again, $a_{N+4} = \frac{2}{N+2}a_{N+2} = \frac{2}{N+2}(\frac{2}{N}a_N) = \frac{2^2}{N(N+2)}a_N \;\Rightarrow\; \frac{2^2}{N(N+2)}y^{N+4}$

and so on. Note that, for simplicity, we have only considered the even solution.

The second term in equation 1.20 can, for reasons that will soon become clear, be written in the following form

$$a_N y^2\left[y^{N-2} + \frac{1}{\frac{N}{2}}y^N + \frac{1}{\left(\frac{N}{2}\right)\left(\frac{N}{2}+1\right)}y^{N+2} + \dots\right]$$

$$= a_N y^2 \frac{\left(\frac{N}{2}-1\right)!}{\left(\frac{N}{2}-1\right)!}\left[\left(y^2\right)^{\frac{N}{2}-1} + \frac{1}{\frac{N}{2}}(y^2)^{\frac{N}{2}} + \frac{1}{\left(\frac{N}{2}\right)\left(\frac{N}{2}+1\right)}(y^2)^{\frac{N}{2}+1} + \dots\right]$$

$$= a_N y^2 \left(\frac{N}{2}-1\right)! \left[\frac{\left(y^2\right)^{\frac{N}{2}-1}}{(\frac{N}{2}-1)!} + \frac{(y^2)^{\frac{N}{2}}}{(\frac{N}{2})!} + \frac{(y^2)^{\frac{N}{2}+1}}{(\frac{N}{2}+1)!}\right] \tag{1.21}$$

We introduce k such that $N = 2k$ so the equation above takes the form

$$y^2(k-1)! \left[\frac{\left(y^2\right)^{k-1}}{(k-1)!} + \frac{\left(y^2\right)^{k}}{k!} + \frac{\left(y^2\right)^{k+1}}{(k+1)!} + \dots\right]$$

$$= y^2(k-1)! \left[e^{y^2} - \left[1 + y^2 + \frac{\left(y^2\right)^2}{2!} + \dots \frac{\left(y^2\right)^{k-2}}{(k-2)!}\right]\right] \tag{1.22}$$

Where we have made use of the Taylor series for the exponential function $e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$

In other words, equation 1.22 can be interpreted as ($h(y)$ = a polynomail + a constant $\times$ $y^2 e^{y^2}$).

When this is substituted back into equation 1.15 ,

$$\psi(y) = (a\,polynomial \times e^{-y^2/2}) + (a\,constant \times y^2 e^{y^2/2}) \tag{1.23}$$

which does not vanish at infinity so it is not an acceptable solution. Therefore, the recursion relation 1.18 must terminate for some n, ie,

$$2n - \varepsilon + 1 = 0 \;\Rightarrow\; \varepsilon = 2n + 1 \tag{1.24}$$

If we know go back to the definition of ε on page 3 , $E = \frac{\varepsilon \hbar \omega}{2}$,

$$E = \hbar\omega(n + \frac{1}{2})\,;\; n = 0, 1, 2, \dots \tag{1.25}$$

which is the energy eigenvalue for the Simple Harmonic Oscillator.

The polynomials $h(y)$ (apart from the nomalisation constants) are known as the Hermite polynomials $H_n(y)$ and some of their important properties are stated below,

$$\frac{d^2 H_n(y)}{dy} - 2y\frac{dH_n(y)}{dy} + 2nH_n(y) = 0 \tag{1.26}$$

and the recursion relations

$$H_{n+1} - 2yH_n + 2nH_{n-1} = 0 \tag{1.27}$$

$$H_{n+1} + \frac{dH_n}{dy} - 2yH_n = 0 \tag{1.28}$$

Both of the above relations can be proved by induction and it is left as an exercise for the reader.

The first few polynomials are listed below:

$$H_0\,(y) = 1$$

$$H_1\,(y) = 2y$$

$$H_2(y) = 4y^2 - 2$$

$$H_3(y) = 8y^3 - 12y$$

1.2 Operator Methods

The Hamiltonian for the SHO is of the form

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \tag{1.29}$$

where the operators for momentum and position are $\hat{p} = -i\hbar\frac{\partial}{\partial x}$ and $\hat{x} = x$ respectively.
Note that both of these operators are Hermitian, ie, they have real eigenvalues.

It is useful to prove that these operators are hermitian:
For any linear operator $\hat{O}$, the hermitian conjugate $\hat{O}^\dagger$ is defined by

$$\int_{-\infty}^{\infty} dx\psi^*(x)\,\hat{O}\psi(x) = \int_{-\infty}^{\infty} dx\left(\hat{O}^\dagger\psi(x)\right)^*\psi(x) \tag{1.30}$$

In other words,

$$\langle\psi|O|\psi\rangle = \langle\hat{O}^\dagger\psi|\psi\rangle \tag{1.31}$$

Hence, for the momentum operator $\hat{p}$ we have

$$\int_{-\infty}^{\infty} dx\psi^*(x)\,\hat{p}\psi(x) = \int_{-\infty}^{\infty} dx\psi^*\left(-i\hbar\frac{d}{dx}\right)\psi = -i\hbar\int_{-\infty}^{\infty} dx\psi^*\frac{d\psi}{dx}$$

Using integration by parts

$$= -i\hbar\left\{[(\psi^*\psi)]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} dx\left(\frac{d\psi^*}{dx}\right)\psi\right\} = i\hbar\int_{-\infty}^{\infty} dx\left(\frac{d\psi^*}{dx}\right)\psi$$

andassuming that ψ and ψ^* vanish at $\pm\infty$,

$$= \int_{-\infty}^{\infty} dx\left(-i\hbar\frac{d\psi}{dx}\right)^*\psi = \int_{-\infty}^{\infty} dx\,(\hat{p}\psi(x))^*\,\psi(x) \tag{1.32}$$

Therefore, $\hat{p} = \hat{p}^\dagger = -i\hbar\frac{d}{dx}$ as required.
The same argument holds for x.
The commutation relation between the two operators is

$$[\hat{p}, \hat{x}] = \hat{p}\hat{x} - \hat{x}\hat{p} = -i\hbar \tag{1.33}$$

One might think that the Hamiltonian (1.29) can be written in the form

$$\hat{H} = \omega\left(\sqrt{\frac{m\omega}{2}}\hat{x} - i\frac{\hat{p}}{\sqrt{2m\omega}}\right)\left(\sqrt{\frac{m\omega}{2}}\hat{x} + i\frac{\hat{p}}{\sqrt{2m\omega}}\right) \tag{1.34}$$

However, since $\hat{p}$ and $\hat{x}$ do not commute, equation 1.34 is not correct.

In fact,

$$\omega\left(\sqrt{\frac{m\omega}{2}}\hat{x}-i\frac{\hat{p}}{\sqrt{2m\omega}}\right)\left(\sqrt{\frac{m\omega}{2}}\hat{x}+i\frac{\hat{p}}{\sqrt{2m\omega}}\right)=\frac{m\omega^2}{2}\hat{x}^2+\frac{i\omega}{2}\hat{x}\hat{p}-\frac{i\omega}{2}\hat{p}\hat{x}+\frac{\hat{p}^2}{2m}$$
$$=\frac{m\omega^2}{2}\hat{x}^2+\frac{\hat{p}^2}{2m}-\frac{i\omega}{2}(\hat{p}\hat{x}-\hat{x}\hat{p})=\frac{m\omega^2}{2}\hat{x}^2+\frac{\hat{p}^2}{2m}-\frac{i\omega}{2}(-i\hbar)$$
$$=\hat{H}-\frac{1}{2}\hbar\omega \tag{1.35}$$

Now, we introduce the operators $\hat{A}$ and $\hat{A}^\dagger$ such that

$$\hat{A}=\sqrt{\frac{m\omega}{2\hbar}}\hat{x}+i\frac{\hat{p}}{\sqrt{2m\omega\hbar}} \tag{1.36}$$

$$\hat{A}^\dagger=\sqrt{\frac{m\omega}{2\hbar}}\hat{x}+i\frac{\hat{p}}{\sqrt{2m\omega\hbar}} \tag{1.37}$$

where the factor of $\sqrt{\frac{1}{\hbar}}$ is introduced in order to make the operators dimensionless.
Note that since $\hat{x}$ and $\hat{p}$ are both Hermitian, $\hat{A}^\dagger$ is the Hermitian conjugate of $\hat{A}$.
Since $\hat{x}$ commutes with itself, and so does $\hat{p}$, in order to obtain the relation $\left[A, A^\dagger\right]$ we only need to consider

$$\left[\hat{A},\hat{A}^\dagger\right]=\left[\sqrt{\frac{m\omega}{2\hbar}}\hat{x},-i\frac{\hat{p}}{\sqrt{2m\omega\hbar}}\right]+\left[i\frac{\hat{p}}{\sqrt{2m\omega\hbar}},\sqrt{\frac{m\omega}{2\hbar}}\hat{x}\right]=-\frac{i}{2\hbar}\left[\hat{x},\hat{p}\right]+\frac{i}{2\hbar}\left[\hat{p},\hat{x}\right]=1 \tag{1.38}$$

Equation 1.35 implies that

$$\hat{H}=\hbar\omega\left(\hat{A}^\dagger\hat{A}+\frac{1}{2}\right) \tag{1.39}$$

We also have

$$\left[\hat{H},\hat{A}\right]=\hbar\omega\left[\hat{A}^\dagger\hat{A},\hat{A}\right]=\hbar\omega\left[\hat{A}^\dagger\hat{A}-\hat{A}\hat{A}^\dagger\right]\hat{A}=-\hbar\omega\hat{A} \tag{1.40}$$

$$\left[\hat{H},\hat{A}^\dagger\right]=\hbar\omega\left[\hat{A}^\dagger\hat{A},\hat{A}^\dagger\right]=\hbar\omega\hat{A}^\dagger\left[\hat{A}\hat{A}^\dagger-\hat{A}^\dagger\hat{A}\right]=\hbar\omega\hat{A}^\dagger \tag{1.41}$$

The eigenvalue equation for the Hamiltonian is

$$\hat{H}|E\rangle=E|E\rangle \tag{1.42}$$

Now, let us consider the state $\hat{A}|E\rangle$.
Using the commutation relation 1.40

$$\hat{H}\hat{A}|E\rangle=\hat{A}\hat{H}|E\rangle-\hbar\omega\hat{A}|E\rangle=(E-\hbar\omega)\hat{A}|E\rangle \tag{1.43}$$

Therefore, it can be said that $\hat{A}|E\rangle$ is also an eigenstate of $\hat{H}$ but with the energy lowered by $\hbar\omega$. Each time we apply $\hat{A}$ again, the energy will be lowered by $\hbar\omega$ but there is a point where this process must terminate since the expectation

value of $\hat{H}$ is positive. The state of lowest energy is called the **ground state** and is denoted by $|0\rangle$.
So for the ground state

$$\hat{A}|0\rangle = 0 \tag{1.44}$$

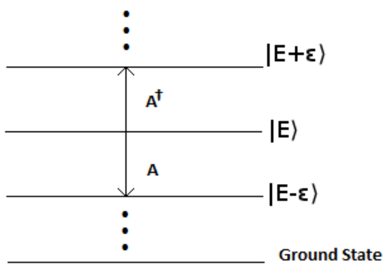
where the energy cannot be lowered any more. Using equation 1.39 the energy of the ground state is

$$\hat{H}|0\rangle = \hbar\omega\left(\hat{A}^{\dagger}\hat{A} + \frac{1}{2}\right)|0\rangle = \frac{1}{2}\hbar\omega|0\rangle \tag{1.45}$$

Let us now consider the energy for the state $\hat{A}^{\dagger}|0\rangle$,

$$\hat{H}\hat{A}^{\dagger}|0\rangle = \left(\hat{A}^{\dagger}\hat{H} + \hbar\omega\hat{A}^{\dagger}\right)|0\rangle = \hbar\omega\left(\frac{1}{2} + 1\right)\hat{A}^{\dagger}|0\rangle \tag{1.46}$$

This time the energy is $\hbar\omega$ more than that of the ground state. When $\hat{A}^{\dagger}$ is applied again, the energy will increase by a further $\hbar\omega$, ie two units of energy above the ground state, and so on.
In this context, $\hat{A}^{\dagger}$ and $\hat{A}$ are known as the **ladder operators**. The figure below [1] indicates the raising and lowering operators where $\varepsilon = \hbar\omega$.



Hence it can be concluded that

$$E = \left(n + \frac{1}{2}\right)\hbar\omega \tag{1.47}$$

which is exactly the same as the enegy eigenvalue (equation 1.25) derived in the previous section using the differential equations method. So we have derived the energy levels for the SHO using two different methods.

2 The Hydrogen atom

2.1 Differential equations method

We start from the 3-D Schrödinger equation

$$\hat{H}\psi(\mathbf{r}) = \left(\frac{\hat{\mathbf{p}}^2}{2\mu} + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{2.1}$$

where $\hat{\mathbf{p}}^2 = \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2$ and $\hat{\mathbf{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z) = \left(-i\hbar\frac{\partial}{\partial x}, -i\hbar\frac{\partial}{\partial y}, -i\hbar\frac{\partial}{\partial z}\right)$ and μ is the reduced mass[1] and the Schrödinger equation is written as a partial differential equation

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi\left(x,y,z\right) + V\left(x,y,z,\right)\psi\left(x,y,z\right) = E\psi\left(x,y,z\right) \tag{2.2}$$

With $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$
In spherical polar coordinates[3] this becomes[2]

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right) \tag{2.3}$$

which can be written in the form[3]

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\mathbf{L^2}}{\hbar^2 r^2} \tag{2.4}$$

where $\mathbf{L}$ is the orbital angular momentum.
We will only consider the case of a **central potential** so that the potential $V = V(r)$ only depends on the distance from the origin. So the Schrödinger equation becomes

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)\psi\left(\mathbf{r}\right) + \frac{\mathbf{L}^2}{2\mu r^2}\psi\left(\mathbf{r}\right) + V\left(\mathbf{r}\right)\psi\left(\mathbf{r}\right) = E\psi\left(\mathbf{r}\right) \tag{2.5}$$

The wavefunction $\psi\left(\mathbf{r}\right)$ can be split into radial and angular components

$$\psi\left(\mathbf{r}\right) = R_{nl}(r)Y_{lm}(\theta,\varphi) \tag{2.6}$$

which is then substituted back into equation 2.5 to get

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{l\left(l+1\right)}{r^2}\right)R_{nl}\left(r\right) + V\left(r\right)R_{nl}\left(r\right) = E_{nl}R_{nl}\left(r\right) \tag{2.7}$$

Note: we have used the fact that $Y_{lm}(\theta,\varphi)$ are eigenfunctions of $\mathbf{L}^2$ with eigenvalue $\hbar^2 l\left(l+1\right)$. [4]

For the case of Hydrogen atom we have the attractive Coulomb potential in SI units

$$V\left(r\right) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \tag{2.8}$$

so the Schrödinger equation 2.7 becomes

[1]For a two-body system we need to consider the reduced mass $\mu = \frac{m_e M}{m_e+M}$ where m_e is the mass of the electron and M is the mass of the proton.
[2]These are all fully derived in "Mathematics for Physics 4: Fields" lecture notes. Alternatively refer to Suppliment 7-B of the "Quantum Physics" (Ref [1]) on www.wiley.com/college/gasiorowicz
[3]Refere to equation (7B-9) of the Suppliment.
[4]Refer to Chapter 7 of "Quantum Physics" by S.Gasiorowicz.

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}+\frac{2\mu}{\hbar^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}-\frac{\hbar^2 l\,(l+1)}{2\mu r^2}\right)\right]R\,(r)=0 \tag{2.9}$$

We only consider the solutions with $E<0$, ie the bound states. To make the above equation simpler, let us define the dimensionless parameters ρ and λ such that

$$\rho=\sqrt{\frac{8\mu\mid E\mid}{\hbar^2}}r \tag{2.10}$$

and

$$\lambda=\frac{Ze^2}{4\pi\varepsilon_0\hbar}\sqrt{\frac{\mu}{2\mid E\mid}}=Z\alpha\sqrt{\frac{\mu c^2}{2\mid E\mid}} \tag{2.11}$$

with $\alpha=\frac{e^2}{4\pi\varepsilon_0\hbar c}=1/137$. Now, equation 2.9 takes the form

$$\frac{d^2R\,(\rho)}{d\rho^2}+\frac{2}{\rho}\frac{dR\,(\rho)}{d\rho}-\frac{l\,(l+1)}{\rho^2}R\,(\rho)+\left(\frac{\lambda}{\rho}-\frac{1}{4}\right)R\,(\rho)=0 \tag{2.12}$$

In order to solve this we will first consider the behavior for large ρ , ie

$$\frac{d^2R}{d\rho^2}-\frac{1}{4}R=0 \tag{2.13}$$

the acceptable solution that behaves properly at infinity, ie goes to zero, is

$$R\approx e^{-\rho/2} \tag{2.14}$$

therefore, for all ρ , we make an ansatz for the general solution to be of the form

$$R\,(\rho)=e^{-\rho/2}G\,(\rho) \tag{2.15}$$

for some function $G\,(\rho)$. Substituting back into equation 2.12 we get

$$\frac{d^2G}{d\rho^2}-\left(1-\frac{2}{\rho}\right)\frac{dG}{d\rho}+\left[\frac{\lambda-1}{\rho}-\frac{l\,(l+1)}{\rho^2}\right]G=0 \tag{2.16}$$

In order to be able so solve this, first consider very small ρ , so the equation becomes

$$\frac{d^2G}{d\rho^2}+\frac{2}{\rho}\frac{dG}{d\rho}-\frac{l\,(l+1)}{\rho^2}G\cong 0 \tag{2.17}$$

By observing the equation one can conclude that $G\,(\rho)\propto\rho^l$. So the general solution will be of the form

$$G\,(\rho)=\rho^l H\,(\rho) \tag{2.18}$$

therfore

$$\frac{d^2H}{d\rho^2}+\left(\frac{2l+2}{\rho}-1\right)\frac{dH}{d\rho}+\frac{\lambda-l-1}{\rho}H=0 \tag{2.19}$$

which is implied by substituting equation 2.18 into 2.16 .
In order to solve this differential equation, we use the same method used in part 1 of section1, ie the power series expansion

$$H(\rho) = \sum_{k=0}^{\infty} a_k \rho^k \tag{2.20}$$

which can be substituted into 2.19 and rearranged to yield

$$\sum_{k=0}^{\infty} a_k \left[k(k-1)\rho^{k-2} + k\left(\frac{2l+2}{\rho} - 1\right)\rho^{k-1} + (\lambda - l - 1)\rho^{k-1} \right] = 0$$

$$\Rightarrow \sum_{k=0}^{\infty} \rho^{k-1} \left[(k+1)(k+2l+2)a_{k+1} + (\lambda - l - 1)a_k \right] = 0 \tag{2.21}$$

So the coefficient of ρ^{k-1} must be zero which implies the recursion relation below

$$\frac{a_{k+1}}{a_k} = \frac{k+l+1-\lambda}{(k+2l+2)(k+1)} \tag{2.22}$$

Again, the general solution of $H(\rho)=$ (solution for $k < N$) $+$ (solution for $k > N$) where N is a large number.
For small k, ie $k < N$, we have a polynomial in ρ . However for large $k > N$ the above relation can be written as

$$\frac{a_{k+1}}{a_k} \to \frac{k}{k^2} = \frac{1}{k} \tag{2.23}$$

It can easily be shown that for very large k

$$a_{k+1} = \frac{1}{k!} \tag{2.24}$$

Hence $H(\rho) =$ (a polynomial in ρ) $+$ e^{ρ} which is not acceptable since $R(\rho)$ will have the term $\rho^l e^{-\rho/2} \times e^{\rho}$ which means that $R(\rho)$ will grow as $e^{\rho/2}$ which does not vanish at infinity. So the recursion relation 2.22 must terminate, ie

$$k + l + 1 - \lambda = 0$$

It can be said that for a given l there exists an integer k , denoted by n_r , such that

$$\lambda = n_r + l + 1 \tag{2.25}$$

In fact, the principal quantum number n is defined as

$$n = n_r + l + 1 \tag{2.26}$$

From $\lambda = n$ and equation 2.11,

$$E = -\frac{1}{2}\mu c^2 \frac{(Z\alpha)^2}{n^2} \tag{2.27}$$

Also, since $n_r \geq 0$, one can conclude that n is an integer and $n \geq l + 1$.
The energy can also be written in the following form using 2.11 and substituing for α and λ,

$$E = -\left(\frac{Z}{4\pi\varepsilon_0}\right)^2 \times \frac{\mu e^4}{2n^2\hbar^2} \tag{2.28}$$

For the case of Hydrogen, $Z = 1$.

2.2 Operator Method

Finally, we use operator methods to derive the Bohr levels of the hydrogen atom. This is an extension and generalisation of the techniques used in part 2 of section 1.

The Hamiltonian can be written as

$$\hat{H} = \frac{p_r^2}{2\mu} + \frac{\mathbf{L}^2}{2\mu r^2} - \frac{e^2}{r} \tag{2.29}$$

where

$$p_r = -i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) \tag{2.30}$$

and the potential is in cgs units.
It can be checked that this is the same as the Hamiltonian used in section 2.1 (compare with equations 2.4 and 2.5) , in fact

$$p_r^2\left[\psi\left(x\right)\right] = p_r\left[p_r\left(\psi\right)\right] = -i\hbar p_r\left[\frac{\partial\psi}{\partial r} + \frac{\psi}{r}\right] = \left(-i\hbar\right)^2\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)\left[\frac{\partial\psi}{\partial r} + \frac{\psi}{r}\right]$$

$$= -\hbar^2\left(\frac{\partial\psi^2}{\partial r^2} + \frac{\partial}{\partial r}\left(\frac{\psi}{r}\right) + \frac{1}{r}\frac{\partial\psi}{\partial r} + \frac{\psi}{r^2}\right) = -\hbar^2\left(\frac{\partial\psi^2}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r}\right) \tag{2.31}$$

and the potential $V = -\frac{e^2}{r}$. The only difference is that the potential in the previouse section was taken to be $V = -\frac{Ze^2}{4\pi\varepsilon_0 r}$ which is different by a factor of $\frac{1}{4\pi\varepsilon_0}$ (for hydrogen Z=1). This is merely due to use of different units.
As it can be seen, the Hamiltonian is only written in a different way.

The operators, $\hat{H}$, $\mathbf{L}^2$ and L_z (the component of angular momentum in the z-direciton) satisfy the eigenvalue equations

$$H|E,\ell,m\rangle = E|E,\ell,m\rangle \tag{2.32}$$

$$\mathbf{L}^2|E,\ell,m\rangle = \hbar^2\ell\left(\ell+1\right)|E,\ell,m\rangle \tag{2.33}$$

$$L_z|E,\ell,m\rangle = \hbar m|E,\ell,m\rangle \tag{2.34}$$

where ℓ takes non-negative integer values and $m = -\ell, -\ell+1, \ldots, 0, 1, \ldots, \ell$. The states $|E,\ell,m\rangle$ are in the domain of definition of operators $\hat{H}$, $\mathbf{L}^2$ and L_z. It can be observed that these operators commute.
Equations 2.32 and 2.33 imply that

$$H|E,\ell,m\rangle = H_\ell|E,\ell,m\rangle = E|E,\ell,m\rangle \tag{2.35}$$

where

$$H_\ell = \frac{p_r^2}{2\mu} + \frac{\hbar^2\ell\left(\ell+1\right)}{2\mu r^2} - \frac{e^2}{r} \tag{2.36}$$

Now, we **define** the operator D_ℓ such that

$$D_\ell = p_r - i\left(\frac{(\ell+1)\hbar}{r} - \frac{\mu e^2}{(\ell+1)\hbar}\right) \tag{2.37}$$

Then we define the adjoint of D_ℓ, $D_\ell^\dagger$, extending equations 1.30 and 1.31 to 3-D space. In other words, we integrate over $d^3\mathbf{x}$ by considering arbitrary functions $f(\mathbf{x})$, $g(\mathbf{x})$ such that $rf(\mathbf{x})$ and $rg(\mathbf{x})$ vanish for both $r \to \infty$ and $r \to 0_+$. So the aim is to find $D_\ell^\dagger$ such that

$$\langle g|D_\ell|f\rangle = \langle D_\ell^\dagger g|f\rangle \tag{2.38}$$

The right hand side is

$$\int g^* D_\ell f \; d\mathbf{x}^3$$

For simplicity, we assume that f and g are functions of r only, ie, they do not depend on θ and ϕ. It is left to the reader to prove the results for the general case, $f(\mathbf{x})$ and $g(\mathbf{x})$.
Using polar coordinates

$$= \int_0^\pi \int_0^{2\pi} \int_0^\infty g^*(r)\, D_\ell f(r) \;\; r^2 \sin\theta \; dr\, d\theta\, d\phi$$

$$= 4\pi \int_0^\infty g^* \left[p_r - i\left(\frac{(\ell+1)\hbar}{r} - \frac{\mu e^2}{(\ell+1)\hbar}\right)\right] f(r) \;\; r^2 \; dr$$

this can be broken into two steps:

1. We find $p_r^\dagger$,

$$\langle g|p_r|f\rangle = 4\pi \int_0^\infty g^* \left[-i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)\right] f\, r^2\, dr = 4\pi\,(-i\hbar)\left[\int_0^\infty g^* \frac{\partial f}{\partial r} r^2\, dr + \int_0^\infty g^* f\, r\, dr\right]$$

then we integrate by parts to get

$$= (-i\hbar)\, 4\pi \left\{\left[g^* r^2 f\right]_0^\infty - \int_0^\infty \frac{\partial g}{\partial r} r^2 f\, dr - 2\int_0^\infty r g^* f + \int_0^\infty g^* f\, r\, dr\right\}$$

the first term goes is zero by applying boundary conditions, so

$$= (i\hbar)\, 4\pi \left[\int_0^\infty \frac{\partial g^*}{\partial r} r^2 f\, dr + \int_0^\infty g^* f\, r\, dr\right] = \int_0^\pi \int_0^{2\pi} \int_0^\infty \left(i\hbar \frac{\partial g^*}{\partial r} + i\hbar \frac{g^*}{r}\right) f\, r^2 \sin\theta \; dr\, d\theta\, d\phi$$

$$= \int_0^\pi \int_0^{2\pi} \int_0^\infty \left[-i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) g\right]^* f\, r^2 \sin\theta \; dr\, d\theta\, d\phi = \langle p_r g|f\rangle$$

Hence, p_r is hermitian

$$\langle \mathrm{g}|p_r|\mathrm{f}\rangle = \langle p_r g|f\rangle \Longrightarrow p_r = p_r^\dagger \tag{2.39}$$

2. Using the same method it can be shown that $\frac{1}{r}$ is also hermitian.

Therefore, (1) and (2) imply that

$$D^\dagger = p_r + i\left(\frac{(\ell+1)\hbar}{r} - \frac{\mu e^2}{(\ell+1)\hbar}\right) \tag{2.40}$$

Before we proceed, it would be useful to prove the following relations:

- $p_r^2 = -\hbar^2 \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} \right)$ (already shown above, see equation 2.31)

- $[p_r\,,\, r] = -i\hbar$

  Proof: Take some function $f(r)$, then
  $[p_r\,,\, r](f) = -i\hbar \left\{ \left(\frac{\partial}{\partial r} + \frac{1}{r} \right) [r\, f] - r\, \left[\left(\frac{\partial}{\partial r} + \frac{1}{r} \right)\, f \right] \right\} = -i\hbar \left(r\frac{\partial f}{\partial r} + f + f - r\frac{\partial f}{\partial r} - f \right) = -i\hbar\, (f)$

- $\left[p_r\,,\, \frac{1}{r}\right] = \frac{i\hbar}{r^2}$

  Proof:
  $\left[p_r\,,\, \frac{1}{r}\right](f) = -i\hbar \left\{ \left(\frac{\partial}{\partial r} + \frac{1}{r} \right) \left[\frac{f}{r} \right] - \frac{1}{r} \left[\frac{\partial f}{\partial r} + \frac{f}{r} \right] \right\} = -i\hbar \left[\frac{1}{r}\frac{\partial f}{\partial r} - \frac{f}{r^2} + \frac{f}{r^2} - \frac{1}{r}\frac{\partial f}{\partial r} - \frac{f}{r^2} \right] = \frac{i\hbar}{r^2}\,(f)$

- $\left[p_r\,,\, \frac{1}{r^2}\right] = \frac{2i\hbar}{r^3}$

  Proof:
  $\left[p_r\,,\, \frac{1}{r^2}\right](f) = -i\hbar \left\{ \left(\frac{\partial}{\partial r} + \frac{1}{r} \right) \left[\frac{f}{r^2} \right] - \frac{1}{r^2} \left[\frac{\partial f}{\partial r} + \frac{f}{r} \right] \right\} = -i\hbar \left[\frac{1}{r^2}\frac{\partial f}{\partial r} - \frac{2f}{r^3} + \frac{f}{r^3} - \frac{1}{r^2}\frac{\partial f}{\partial r} + \frac{f}{r^3} \right] = \frac{2i\hbar}{r^3}\,(f)$

- $\left[p_r^2\,,\, \frac{1}{r}\right] = \frac{2\hbar}{r^2}\left(ip_r - \frac{\hbar}{r} \right)$

  Proof:
  $\left[p_r^2\,,\, \frac{1}{r}\right](f) = -\hbar^2 \left\{ \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} \right) \left[\frac{f}{r} \right] - \frac{1}{r} \left[\frac{\partial^2 f}{\partial r^2} + \frac{2}{r}\frac{\partial f}{\partial r} \right] \right\}$
  $-\hbar^2 \left(\frac{1}{r}\frac{\partial^2 f}{\partial r^2} - \frac{2}{r^2}\frac{\partial f}{\partial r} + \frac{2f}{r^3} + \frac{2}{r^2}\frac{\partial f}{\partial r} - \frac{2f}{r^3} - \frac{1}{r}\frac{\partial^2 f}{\partial r^2} - \frac{2}{r^2}\frac{\partial f}{\partial r} \right) = \frac{2\hbar^2}{r^2}\frac{\partial}{\partial r}(f) = \frac{2\hbar}{r^2}\left(ip_r - \frac{\hbar}{r} \right)(f)$

Using what we have, the following four relations can be established

$$\boxed{H_{\ell+1} D_\ell^\dagger = D_\ell^\dagger H_\ell \qquad (2.41)}$$

Proof:

$$D_\ell^\dagger H_\ell = \left[D_\ell^\dagger\,,\, H_\ell \right] + H_\ell D_\ell^\dagger = \frac{\hbar^2 \ell\,(\ell+1)}{2\mu} \left[p_r\,,\, \frac{1}{r^2} \right] - e^2 \left[p_r\,,\, \frac{1}{r} \right] + \frac{i\,(\ell+1)\,\hbar}{2\mu} \left[\frac{1}{r}\,,\, p_r^2 \right] + H_\ell D_\ell^\dagger$$

$$= \frac{\hbar^2 \ell\,(\ell+1)}{2\mu} \left[\frac{2i\hbar}{r^3} \right] - e^2 \left[\frac{i\hbar}{r^2} \right] + \frac{i\,(\ell+1)\,\hbar}{2\mu} \times \frac{2\hbar}{r^2} \left(\frac{\hbar}{r} - ip_r \right) + H_\ell D_\ell^\dagger$$

$$= H_\ell D_\ell^\dagger + \frac{\hbar^2\,(\ell+1)}{\mu r^2} \left(\frac{i\hbar\ell}{r} - \frac{i\mu e^2}{(\ell+1)\,\hbar} + \frac{i\hbar}{r} + p_r \right) = \left[H_\ell + \frac{2\hbar^2\,(\ell+1)}{2\mu r^2} \right] D_\ell^\dagger = H_{\ell+1} D_\ell^\dagger$$

$$\boxed{H_\ell D_\ell = D_\ell H_{\ell+1} \qquad (2.42)}$$

Proof: Using the above results, we have

$$\left(D_\ell^\dagger H_\ell\right)^\dagger = \left(H_{\ell+1} D_\ell^\dagger\right)^\dagger \implies H_\ell^\dagger D_\ell = D_\ell H_{\ell+1}^\dagger$$

but the Hamiltonian is hermitian, ie $H = H^\dagger$, so

$$H_\ell D_\ell = D_\ell H_{\ell+1}$$

$$\boxed{D_\ell D_\ell^\dagger = 2\mu\left(H_\ell + \frac{\mu e^4}{2\left(\ell+1\right)^2\hbar^2}\right) \qquad (2.43)}$$

Proof: Starting from the definition of D_ℓ and $D_\ell^\dagger$ and applying them on an arbitrary function $f\left(r\right)$ we have

$$D_\ell\left(D_\ell^\dagger\left[f\left(r\right)\right]\right)$$

$$= \left\{-i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) - i\left(\frac{\left(\ell+1\right)\hbar}{r} - \frac{\mu e^2}{\left(\ell+1\right)\hbar}\right)\right\}\left[-i\hbar\left(\frac{\partial f}{\partial r} + \frac{f}{r}\right) + i\left(\frac{\left(\ell+1\right)\hbar}{r}f - \frac{\mu e^2}{\left(\ell+1\right)\hbar}f\right)\right]$$

$$= -\hbar^2\left(\frac{\partial^2 f}{\partial r^2} + \frac{2}{r}\frac{\partial f}{\partial r}\right) + \hbar\left(\frac{\left(\ell+1\right)\hbar}{r}\frac{\partial f}{\partial r} - \frac{\mu e^2}{\left(\ell+1\right)\hbar}\frac{\partial f}{\partial r} - \frac{\mu e^2 f}{\left(\ell+1\right)\hbar r}\right)$$

$$-\hbar\left(\frac{\left(\ell+1\right)\hbar}{r} - \frac{\mu e^2}{\left(\ell+1\right)\hbar}\right)\left(\frac{\partial f}{\partial r} + \frac{f}{r}\right) + \left(\frac{\left(\ell+1\right)\hbar}{r} - \frac{\mu e^2}{\left(\ell+1\right)\hbar}\right)^2\left[f\right]$$

$$\implies D_\ell D_\ell^\dagger = p_r^2 - \frac{\hbar^2\left(\ell+1\right)}{r^2} + \left(\frac{\left(\ell+1\right)\hbar}{r} - \frac{\mu e^2}{\left(\ell+1\right)\hbar}\right)^2$$

$$= 2\mu\left(\frac{p_r^2}{2\mu} + \frac{\left(\ell+1\right)^2\hbar^2}{2\mu r^2} - \frac{\hbar^2\left(\ell+1\right)}{2\mu r^2} - \frac{e^2}{r} + \frac{\mu e^4}{2\left(\ell+1\right)^2\hbar^2}\right) = 2\mu\left(H_\ell + \frac{\mu e^4}{2\left(\ell+1\right)^2\hbar^2}\right)$$

$$\boxed{D_\ell^\dagger D_\ell = 2\mu\left(H_{\ell+1} + \frac{\mu e^4}{2\left(\ell+1\right)^2\hbar^2}\right) \qquad (2.44)}$$

Proof: Using 2.43

$$D_\ell D_\ell^\dagger\left(D_\ell\right) = 2\mu\left(H_\ell + \frac{\mu e^4}{2\left(\ell+1\right)^2\hbar^2}\right)\left(D_\ell\right) = 2\mu\left(H_\ell D_\ell + \frac{\mu e^4}{2\left(\ell+1\right)^2\hbar^2}D_\ell\right)$$

But 2.42 implies that

$$\Rightarrow\ D_\ell D_\ell^\dagger D_\ell = 2\mu\left(D_\ell H_{\ell+1} + \frac{\mu e^4}{2\left(\ell+1\right)^2\hbar^2}D_\ell\right)$$

$$\Rightarrow\ D_\ell\left(D_\ell^\dagger D_\ell\right) = D_\ell\left[2\mu\left(H_{\ell+1} + \frac{\mu e^4}{2\left(\ell+1\right)^2\hbar^2}\right)\right]$$

$$\Rightarrow\ \left(D_\ell^\dagger D_\ell\right) = 2\mu\left(H_{\ell+1} + \frac{\mu e^4}{2\left(\ell+1\right)^2\hbar^2}\right)$$

Therefore, we have

$$\langle E,\ell,m|D_\ell D_\ell^\dagger|E,\ell,m\rangle = 2\mu\left(E+\frac{\mu e^4}{2\left(\ell+1\right)^2\hbar^2}\right)\langle E,\ell,m|E,\ell,m\rangle = 2\mu\left(E+\frac{\mu e^4}{2\left(\ell+1\right)^2\hbar^2}\right) \tag{2.45}$$

which is always positive since

$$\langle E,\ell,m|D_\ell D_\ell^\dagger|E,\ell,m\rangle = \parallel D_\ell^\dagger|E,\ell,m\rangle \parallel^2 \geq 0 \tag{2.46}$$

and the length of the vector is always positive.
In other words

$$E \geq -\frac{\mu e^4}{2\left(\ell+1\right)^2\hbar^2} \tag{2.47}$$

The minimum possible value for the energy is when$\ell = 0$, ie

$$E = -\frac{\mu e^4}{2\hbar^2} \tag{2.48}$$

for ℓ larger than this, the positivity is violated.
However, we will show that this is also an eigenvalue of the Hamiltonian $\hat{H}$.
Using equations 2.35 and 2.41 , we have in general,

$$H_{\ell+1}\left(D_\ell^\dagger|E,\ell,m\rangle\right) = D_\ell^\dagger\left(H_\ell|E,\ell,m\rangle\right) = E\left(D_\ell^\dagger|E,\ell,m\rangle\right) \tag{2.49}$$

which implies that $D_\ell^\dagger|E,\ell,m\rangle$ is an eigenstate of $H_{\ell+1}$ with the same enegry E, so

$$D_\ell^\dagger|E,\ell,m\rangle = c_\ell^\dagger|E,\ell+1,m\rangle \tag{2.50}$$

we can write

$$c^\dagger = i\left[2\mu\left(E+\frac{\mu e^4}{2\left(\ell+1\right)^2\hbar^2}\right)\right]^{1/2} \tag{2.51}$$

where the factor i is chosen for convenience.
It can be said that $D_{\ell+1}^\dagger D_\ell^\dagger|E,\ell,m\rangle$ is an eigenstate of $H_{\ell+2}$ and so on. However, due to the positivity of $D_\ell D_\ell^\dagger$, the sequence must terminate for some $\ell = \ell_{max}$ for $\underline{E} \leq E < 0$. Hence, for $E + \frac{\mu e^4}{2(\ell+1)^2\hbar^2}$ to be greater than zero, there exists an ℓ_{max} for an eigenvalue $E < 0$ such that $D_{\ell_{max}}^\dagger|E,\ell_{max},m\rangle$ is the zero vector.
As observed above, for the ground state energy, $\ell_{max} = 0$.
We can write $\ell_{max} = n-1$ where $n = 1,2,3,...$ since ℓ_{max} it is a non negative integer. Here $n = 1$ corresponds to the ground state level.
Finally, since $c_{\ell_{max}}^\dagger = c_{n-1}^\dagger$ must vanish, we conclude that

$$E_n = -\frac{\mu e^4}{2\hbar^2 n^2} \tag{2.52}$$

NB This implies that the energy is independent of ℓ.

This is our final answer for the energy eigenvalue of Hydrogen atom using operator methods.
Referring to equations 2.43 and 2.46, the **ground state energy level** we must satisfy

$$D_\ell^\dagger |E, 0, m\rangle = 0 \tag{2.53}$$

Therefore, the ground state energy is

$$\underline{E} = -\frac{\mu e^4}{2\hbar^2} \tag{2.54}$$

which means that the minimum possible value of energy (equation 2.48) is in fact an eigenvalue of the Hamiltonian $\hat{H}$.
Comparing the results with those obtained in Section 2.1 , equation 2.28 , it is clear that they are the same apart from the factor $\frac{1}{4\pi\varepsilon_0}$ which, as mentioned before, is due to use of different units for the potential.

References

[1] Gasiorowicz, Stephen. Quantum Physics. New Jersey: Wiley & Sons, 2003

[2] Manoukian, Edward. B. Quantum Theory: A Wide Spectrum. Dordrecht, The Netherlands: Springer, 2006.

[3] Pendleton, Brian. Mathematics for Physics 4: Fields lecture notes, Edinburgh University

[4] www.wiley.com/college/gasiorowicz

[5] Griffiths, David. j. Introduction to Quantum Mechanics. Upper Saddle River, N.J. : Pearson/Prentice Hall, 2005.