16   The Hydrogen Atom

1. We want to solve the time independent Schrödinger Equation for the hydrogen atom.

2. There are two particles in the system, an electron and a nucleus, and so we can write the Hamiltonian as:
$$H(\vec{r}, \vec{R}) = -\frac{\hbar^2}{2m}\nabla_r^2 - \frac{\hbar^2}{2M}\nabla_R^2 - \frac{Ze^2}{\left|\vec{r} - \vec{R}\right|} \tag{16.1}$$

3. We have already seen earlier that the spherical coordinate system is ideal to solve such problems, on account of the spherical symmetry of atoms.

4. We did go through quite a bit of algebra to write the angular momentum operators in spherical coordinates. Here we will see that the operator ∇^2 there are some rules that we can use to make our life a little simple.

5. But lets see if we can first reduce this problem to a simpler problem.

6. There are two particles, the electron and the nucleus. Lets assume the vector $\vec{R}$ represents the position of the nucleus (mass M) and the let $\vec{r}$ represent the position of the electron (mass m).

7. What is the center of mass of this system? The position of the center of mass is given by the vector:
$$\vec{R}_{CM} \equiv \frac{m\vec{r} + M\vec{R}}{m + M} \tag{16.2}$$

   and lets introduce the vector:
$$\vec{r}_{e-N} \equiv \vec{R} - \vec{r} \tag{16.3}$$

   Or we can write the old coordinates in terms of the new as:
$$\vec{R} = \vec{R}_{CM} + \frac{m}{m + M}\vec{r}_{e-N} \tag{16.4}$$

   and
$$\vec{r} = \vec{R}_{CM} - \frac{M}{m + M}\vec{r}_{e-N} \tag{16.5}$$

   Homework: Show Eqs. (16.4) and (16.5) to be true.

8. So now we have introduced two new coordinates, the center of mass vector, and a vector denoting the position of the electron with respect to the nucleus. (As we will see later this new set of coordinates are more convenient to work with.) Lets see if we can write the kinetic energy of the two particle system in terms of these two new coordinates.

$$T = \frac{p_r^2}{2m} + \frac{p_R^2}{2M}$$

$$
\begin{aligned}
&= \frac{1}{2}M\left|\frac{d\vec{R}}{dt}\right|^2 + \frac{1}{2}m\left|\frac{d\vec{r}}{dt}\right|^2 \\[2mm]
&= \frac{1}{2}M\left|\frac{d\vec{R}_{CM}}{dt} + \frac{m}{m+M}\frac{d\vec{r}_{e-N}}{dt}\right|^2 + \\[2mm]
&\quad \frac{1}{2}m\left|\frac{d\vec{R}_{CM}}{dt} - \frac{M}{m+M}\frac{d\vec{r}_{e-N}}{dt}\right|^2 \\[2mm]
&= \frac{1}{2}(M+m)\left|\frac{d\vec{R}_{CM}}{dt}\right|^2 + \frac{1}{2}\left(\frac{mM}{m+M}\right)\left|\frac{d\vec{r}_{e-N}}{dt}\right|^2
\end{aligned}
\tag{16.6}
$$

9. **Homework: Show Eq. (16.6) to be true. To achieve this realize first that $|\vec{a}|^2 = \vec{a}\cdot\vec{a}$.**

10. Now if we represent the *total mass*, $M_{tot} = (M+m)$ and the *reduced mass*, $\mu = \left(\frac{mM}{m+M}\right)$ then we have

$$
\begin{aligned}
T &= \frac{1}{2}M_{tot}\left|\frac{d\vec{R}_{CM}}{dt}\right|^2 + \frac{1}{2}\mu\left|\frac{d\vec{r}_{e-N}}{dt}\right|^2 \\[2mm]
&= \frac{p_{CM}{}^2}{2M_{tot}} + \frac{p_{e-N}{}^2}{2\mu}
\end{aligned}
\tag{16.7}
$$

11. Now lets see if we can use all this to simplify the hydrogen atom Hamiltonian. Consider the kinetic energy part of the Hamiltonian as seen in Eq. (16.1):

$$
\begin{aligned}
T(\vec{r},\vec{R}) &= -\frac{\hbar^2}{2m}\nabla_r^2 - \frac{\hbar^2}{2M}\nabla_R^2 \\[2mm]
&= \frac{p_r{}^2}{2m} + \frac{p_R{}^2}{2M} \\[2mm]
&= \frac{p_{CM}{}^2}{2M_{tot}} + \frac{p_{e-N}{}^2}{2\mu} \\[2mm]
&= -\frac{\hbar^2}{2M_{tot}}\nabla_{R_{CM}}^2 - \frac{\hbar^2}{2\mu}\nabla_{r_{e-N}}^2
\end{aligned}
\tag{16.8}
$$

and the Hamiltonian for the Hydrogen atom becomes:

$$
H = -\frac{\hbar^2}{2M_{tot}}\nabla_{R_{CM}}^2 - \frac{\hbar^2}{2\mu}\nabla_{r_{e-N}}^2 - \frac{Ze^2}{|r_{e-N}|}
\tag{16.9}
$$

12. Now, the time-independent Schödinger Equation that will be obtained from using this Hamiltonian will be a second order differential equation. Why? Because this Hamiltonian contains second derivative terms.

13. Now note that this Hamiltonian can be written as the sum of two terms one that only depends on R_{CM} and the other that only depends on r_{e-N}. Such Hamiltonians are called separable Hamiltonians and in such cases one can always make the approximation that the solution to the time-independent Schödinger Equation will be of the product form

$$\Psi(R_{CM}, r_{e-N}) = \chi(R_{CM})\psi(r_{e-N}) \tag{16.10}$$

14. Note, we used this separation idea when we reduced the time-dependent Schödinger Equation to the time-independent Schödinger Equation in Section. 8. We also used this exact same idea in solving the angular momentum problem in Eqs. (15.85), (15.85) and (15.86).

15. As must be clear by the repeated use of this idea of separation, "separation of variables" is a powerful approach to solve many kinds of differential equations. We will use it here to solve the Hydrogen atom problem.

16. The time-independent Schödinger Equation for the hydrogen atom is:

$$\left[-\frac{\hbar^2}{2M_{tot}}\nabla^2_{R_{CM}} - \frac{\hbar^2}{2\mu}\nabla^2_{r_{e-N}} - \frac{Ze^2}{|r_{e-N}|}\right]\Psi(R_{CM}, r_{e-N}) = E\Psi(R_{CM}, r_{e-N}) \tag{16.11}$$

$$\left[-\frac{\hbar^2}{2M_{tot}}\nabla^2_{R_{CM}} - \frac{\hbar^2}{2\mu}\nabla^2_{r_{e-N}} - \frac{Ze^2}{|r_{e-N}|}\right]\chi(R_{CM})\psi(r_{e-N})$$
$$= E\chi(R_{CM})\psi(r_{e-N}) \tag{16.12}$$

$$-\frac{\hbar^2}{2M_{tot}}\psi(r_{e-N})\nabla^2_{R_{CM}}\chi(R_{CM}) - \frac{\hbar^2}{2\mu}\chi(R_{CM})\nabla^2_{r_{e-N}}\psi(r_{e-N})$$
$$- \chi(R_{CM})\frac{Ze^2}{|r_{e-N}|}\psi(r_{e-N})$$
$$= E\chi(R_{CM})\psi(r_{e-N}) \tag{16.13}$$

Dividing both sides by $\chi(R_{CM})\psi(r_{e-N})$ we obtain:

$$-\frac{\hbar^2}{2M_{tot}}\frac{1}{\chi(R_{CM})}\nabla^2_{R_{CM}}\chi(R_{CM}) + \frac{1}{\psi(r_{e-N})}\left[-\frac{\hbar^2}{2\mu}\nabla^2_{r_{e-N}}\psi(r_{e-N})\right.$$
$$\left. - \frac{Ze^2}{|r_{e-N}|}\psi(r_{e-N})\right] = E \tag{16.14}$$

And again we will use the same trick that we used in simplifying the time-dependent Schödinger Equation in Section. 8. We note that the first term on the left depends only on R_{CM}. The second term on the left depends only on r_{e-N}. But they add up to a constant E. The only way that can hold true is if both of these two terms are independently equal to a constant. (*Sound familiar?*)

17. Now if we were to say that $E = E_\mu + E_{R_{CM}}$ such that:

$$-\frac{\hbar^2}{2M_{tot}} \frac{1}{\chi(R_{CM})} \nabla^2_{R_{CM}} \chi(R_{CM}) = E_{R_{CM}} \tag{16.15}$$

and

$$\frac{1}{\psi(r_{e-N})} \left[-\frac{\hbar^2}{2\mu} \nabla^2_{r_{e-N}} \psi(r_{e-N}) - \frac{Ze^2}{|r_{e-N}|} \psi(r_{e-N}) \right] = E_\mu \tag{16.16}$$

then Eq. (16.15) above is simply:

$$-\frac{\hbar^2}{2M_{tot}} \nabla^2_{R_{CM}} \chi(R_{CM}) = E_{R_{CM}} \chi(R_{CM}) \tag{16.17}$$

which has a form identical to the particle in a box time-independent Schrödinger Equation, but notice that we will have no boundary conditions for this particular case of R_{CM}. (That is the center of mass of the hydrogen atom is not confined to remain inside in any space as the particle-in-a-box was, that is the hydrogen atom as unconfined translational motion.) And recall that it was the boundary conditions of confinement that enforced discrete states (or quantization of energy levels) for the particle-in-a-box case. And since there is no confinement of center-of-mass here we may expect the eigenstates in Eq. (16.17) to be continuous, that is defined for all energies. The general solution to Eq. (16.17) is:

$$\chi(R_{CM}) = A \exp\left[\imath k R_{CM} \right] + B \exp\left[-\imath k R_{CM} \right] \tag{16.18}$$

here $k = \frac{\sqrt{2M_{tot}E_{R_{CM}}}}{\hbar}$ as in the particle in a box case. Another important condition that arises from here is that

$$E_{R_{CM}} = \frac{\hbar^2 k^2}{2M_{tot}} > 0 \tag{16.19}$$

18. Now lets consider Eq. (16.16) which represents the "internal structure" of the hydrogen atom.

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2_{r_{e-N}} \psi(r_{e-N}) - \frac{Ze^2}{|r_{e-N}|} \psi(r_{e-N}) \right] = E_\mu \psi(r_{e-N}) \tag{16.20}$$

Notice that this equation depends on the relative displacement of the electron with respect to the hydrogen nucleus. Hence we have achieved a separation of variables as stated earlier. Thus the total energy of hydrogen atom is $E = E_\mu + E_{R_{CM}}$, where $E_{R_{CM}}$ is non-negative as shown earlier and corresponds to the translational motion of the center-of-mass, and E_μ is the internal energy due to the relative motion of the electrons and nucleus which is what we are about to discuss now.

19. As noted in the angular momentum case it is always convenient to choose a coordinate system that represents the symmetry of the problem. In this case, again, there is an inherent spherical symmetry that is enforced by the potential. What is meant by this statement is that as the electron moves on the surface of a sphere of any radius, with the nucleus at the center of

the sphere, it feels the same potential all through since the potential energy is only a function of $|r_{e-N}|$. This is called spherical symmetry!! In general, we should note that the symmetry of the problem is that enforced by the potential energy function and the subject of group theory is based on exploiting such symmetries to simplify problems of quantum mechanics and in many cases obtain accurate qualitative results without doing much of algebra! [2]

20. Back to Eq. (16.20) we need to write $\nabla^2_{r_{e-N}}$ in spherical coordinates.

21. We could go through the same algebra that we did earlier (during the angular momentum study) and we would get the correct form of the Laplacian $\nabla^2_{r_{e-N}}$. Alternately, we could introduce a more general approach here that will tell us how to derive the Laplacian in any arbitrary coordinate system which could be useful for us to avoid tedious algebra in the future. We will choose the second approach.

22. We will first introduce a concept called the metric tensor. These two words essentially mean "length element". And the length element has to be different in different coordinate systems. While in the Cartesian coordinate system the length elements would be along the x, y and z directions, in a spherical coordinate system the length elements would be along the r, θ and ϕ directions, which are obviously different. The metric tensor is a matrix that basically tells us how these length elements relate to each other when we go from one coordinate system to another. (In the present case we want to go from the Cartesian to the spherical coordinate system.)

23. The metric tensor is defined in the following fashion for a transformation from $\{x, y, z\} \to \{u_1, u_2, u_3\}$. (Note that for a spherical coordinate system $\{u_1, u_2, u_3\} \equiv \{r, \theta, \phi\}$.)

$$g_{i,j} = \frac{\partial x}{\partial u_i}\frac{\partial x}{\partial u_j} + \frac{\partial y}{\partial u_i}\frac{\partial y}{\partial u_j} + \frac{\partial z}{\partial u_i}\frac{\partial z}{\partial u_j} \tag{16.21}$$

where i, j can be 1, 2, 3, for the coordinate system transformation that we are interested in.

24. For illustration we can write down the metric tensor for the $\{x, y, z\} \to \{r, \theta, \phi\}$ transformation as (using Eqs. (15.73))

$$\begin{aligned}
g_{1,1} &= \frac{\partial x}{\partial r}\frac{\partial x}{\partial r} + \frac{\partial y}{\partial r}\frac{\partial y}{\partial r} + \frac{\partial z}{\partial r}\frac{\partial z}{\partial r} = 1 \\
g_{2,2} &= \frac{\partial x}{\partial \theta}\frac{\partial x}{\partial \theta} + \frac{\partial y}{\partial \theta}\frac{\partial y}{\partial \theta} + \frac{\partial z}{\partial \theta}\frac{\partial z}{\partial \theta} = r^2 \\
g_{3,3} &= \frac{\partial x}{\partial \phi}\frac{\partial x}{\partial \phi} + \frac{\partial y}{\partial \phi}\frac{\partial y}{\partial \phi} + \frac{\partial z}{\partial \phi}\frac{\partial z}{\partial \phi} = r^2 \sin^2 \theta
\end{aligned}$$

$$\tag{16.22}$$

And we also find that $g_{1,2} = g_{2,1} = g_{1,3} = g_{3,1} = g_{2,3} = g_{3,2} = 0$.

---

[2]In fact group theory is useful to simplify the solution of any partial differential equation, and the Schrödinger Equation is one such equation. But we will not concern ourselves with these more general arguments during the current course.

25. So how does the metric tensor help us? It turns out that the Laplacian for such *orthogonal* coordinate systems (where $g_{i,j} = 0$ for $i \neq j$) can be written as:

$$\nabla^2 = \sum_i \frac{1}{g^{1/2}} \frac{\partial}{\partial u_i} \left[\frac{g^{1/2}}{g_{i,i}} \right] \frac{\partial}{\partial u_i} \tag{16.23}$$

where g is the determinant of the metric tensor. Hence in our case $g = g_{1,1} \times g_{2,2} \times g_{3,3}$ since the off-diagonal elements are zero. The gradient operator is given by:

$$\nabla = \sum_i \frac{\vec{u_i}}{\sqrt{g_{i,i}}} \frac{\partial}{\partial u_i} \tag{16.24}$$

Hence the Laplacian for $\{x, y, z\} \rightarrow \{r, \theta, \phi\}$ is:

$$\nabla^2 = \frac{1}{r^2 \sin \theta} \left\{ \frac{\partial}{\partial r} \left[r^2 \sin \theta \frac{\partial}{\partial r} \right] + \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial}{\partial \theta} \right] + \frac{\partial}{\partial \phi} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right] \right\} \tag{16.25}$$

Homework: Go ahead and show that Eq. (16.26) is correct by working out the algebra.

26. Recognize that the θ and ϕ dependent operators lead to a term that is identical to the $\mathbf{L}^2$ operator derived in the spherical harmonics section, that is in Eq. (15.83).

27. Hence the solutions to the spherical harmonics problem are the same as those for a **rigid rotor** that is used in rotational spectroscopy!! If you were to only consider the θ and ϕ components of the operator above, (that is kinetic energy on the surface of sphere):

$$\nabla^2_{\theta,\phi} = \frac{1}{r^2 \sin \theta} \left\{ \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial}{\partial \theta} \right] + \frac{\partial}{\partial \phi} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right] \right\} \tag{16.26}$$

and plugging this into an SE leads to the eigenvalues:

$$E_{rot,J} = \frac{\hbar^2}{2I} J(J+1) \tag{16.27}$$

where I is the moment of inertia. **Homework: Prove the equation above. It suffices to show how the SE relates to a previous problem, whose eigenvalues and eigenvectors are we have already stated. What are the eigenvectors of the rigid rotor?**

28. So now lets go ahead and simplify Eq. (16.26).

$$\begin{aligned}
\nabla^2 &= \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial}{\partial r} \right] + \frac{1}{r^2} \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \\
\nabla^2 &= \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial}{\partial r} \right] + \frac{1}{r^2} \left[\cot \theta \frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \theta^2} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]
\end{aligned} \tag{16.28}$$

Notice the similarity between the square bracketed term and the angular momentum operator in Eq. (15.83). Thus we can rewrite Eq. (16.20) as

$$
-\frac{\hbar^2}{2\mu}\left\{\frac{1}{(r_{e-N})^2}\frac{\partial}{\partial r_{e-N}}\left[(r_{e-N})^2\frac{\partial}{\partial r_{e-N}}\right]\right\}
$$

$$
-\frac{\hbar^2}{2\mu(r_{e-N})^2}\left[\cot\theta\frac{\partial}{\partial\theta}+\frac{\partial^2}{\partial\theta^2}\quad+\quad\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(r_{e-N},\theta,\phi)
$$

$$
-\frac{Ze^2}{r_{e-N}}\psi(r_{e-N},\theta,\phi)\quad=\quad E_\mu\psi(r_{e-N},\theta,\phi)\tag{16.29}
$$

Here we have gone back to using r_{e-N} for the radial coordinate which explains why the equation has become so long. Now using the definition of the $\mathbf{L}^2$ operator in Eq. (15.83),

$$
\left[-\frac{\hbar^2}{2\mu}\left\{\frac{1}{r_{e-N}^2}\frac{\partial}{\partial r_{e-N}}\left[r_{e-N}^2\frac{\partial}{\partial r_{e-N}}\right]\right\}\quad+\quad\frac{1}{2\mu r_{e-N}^2}\mathbf{L}^2\right]\psi(r_{e-N},\theta,\phi)
$$

$$
-\frac{Ze^2}{r_{e-N}}\psi(r_{e-N},\theta,\phi)\quad=\quad E_\mu\psi(r_{e-N},\theta,\phi)\tag{16.30}
$$

or

$$
\left\{-\frac{\hbar^2}{2\mu r_{e-N}^2}\frac{\partial}{\partial r_{e-N}}\left[r_{e-N}^2\frac{\partial}{\partial r_{e-N}}\right]\quad-\quad\frac{Ze^2}{r_{e-N}}\right\}\psi(r_{e-N},\theta,\phi)
$$

$$
+\frac{1}{2\mu(r_{e-N})^2}\mathbf{L}^2\psi(r_{e-N},\theta,\phi)\quad=\quad E_\mu\psi(r_{e-N},\theta,\phi)\tag{16.31}
$$

29. From the last couple of equations we notice that $\mathbf{L}^2$ is the only part of the Hamiltonian operator that depends on θ and ϕ. Hence we can see why $[H,\mathbf{L}^2]=0$, and similarly the commutator of the Hamiltonian with $\mathbf{L}_z$ is also zero.

30. We also notice from Eq. (16.31) that the Hamiltonian has a separable form that we discussed earlier. On account of this, we propose the solution to this differential equation to be:

$$
\psi(r_{e-N},\theta,\phi)=\mathcal{R}(r_{e-N})\mathcal{Y}_{l,m_l}(\theta,\phi)\tag{16.32}
$$

where $\mathcal{Y}_{l,m_l}(\theta,\phi)$ are the spherical harmonics, the solution to the angular momentum part as discussed earlier. **Homework: Note that we have also studied other ways of obtaining the eigenstates for the particle on the surface of a sphere and we have been able to physically rationalize the nature of these functions. Here, please provide a one or two simple reasons as to why** $-l\leq m_l\leq+l$**.**

31. Now using Eq. (16.32) in Eq. (16.31) and noting that $\mathcal{Y}_{l,m_l}(\theta,\phi)$ eigenstates of $\mathbf{L}^2$ with eigenvalues $\hbar^2 l(l+1)$

$$
\mathcal{Y}_{l,m_l}(\theta,\phi)\left\{-\frac{\hbar^2}{2\mu r_{e-N}^2}\frac{\partial}{\partial r_{e-N}}\left[r_{e-N}^2\frac{\partial}{\partial r_{e-N}}\right]\quad-\quad\frac{Ze^2}{r_{e-N}}\right\}\mathcal{R}(r_{e-N})
$$

$$+\frac{\hbar^2 l(l+1)}{2\mu(r_{e-N})^2}\mathcal{R}(r_{e-N})\mathcal{Y}_{l,m_l}(\theta,\phi) = E_\mu \mathcal{R}(r_{e-N})\mathcal{Y}_{l,m_l}(\theta,\phi)$$

(16.33)

Dividing by $\mathcal{Y}_{l,m_l}(\theta,\phi)$ (we have been doing this dividing stuff for quite sometime now, right?)

$$\left\{-\frac{\hbar^2}{2\mu r_{e-N}^2}\frac{\partial}{\partial r_{e-N}}\left[r_{e-N}^2\frac{\partial}{\partial r_{e-N}}\right] - \frac{Ze^2}{r_{e-N}}\right\}\mathcal{R}(r_{e-N})$$

$$+\frac{\hbar^2 l(l+1)}{2\mu(r_{e-N})^2}\mathcal{R}(r_{e-N}) = E_\mu \mathcal{R}(r_{e-N}) \qquad (16.34)$$

which is a second order differential equation for $\mathcal{R}(r_{e-N})$ The solutions to this equation are related to what are known as the Laguerre polynomials.

32. How do we solve Eq. (16.34).

33. Lets first analyze the equation. The term involving the derivatives can be interpreted as a second derivative operator and hence a radial kinetic energy (notice the angular kinetic energy was discussed above) of r_{e-N}. The two other terms are like an effective potential: $\frac{\hbar^2 l(l+1)}{2\mu(r_{e-N})^2} - \frac{Ze^2}{r_{e-N}}$. This is an effective potential since it involves the true potential: $\left[-\frac{Ze^2}{r_{e-N}}\right]$, plus an additional potential that includes the influence of the angular dependence. Hence this is a "spherically averaged" potential. Hence the net effective potential has the following functional form:

34. We would now like to go to reduced units, to make our differential equation simpler looking. We may first rewrite Eq. (16.34) by multiplying throughout by $-\frac{2\mu}{\hbar^2}$ and collecting terms on one side to obtain

$$\left\{\frac{1}{r_{e-N}^2}\frac{\partial}{\partial r_{e-N}}\left[r_{e-N}^2\frac{\partial}{\partial r_{e-N}}\right] - \frac{l(l+1)}{(r_{e-N})^2} + \frac{2\mu}{\hbar^2}\left(E_\mu + \frac{Ze^2}{r_{e-N}}\right)\right\}$$

$$\mathcal{R}(r_{e-N}) = 0$$

(16.35)

35. Then to make the equation look simpler we make the following substitutions:

$$\alpha^2 = -\frac{2\mu E_\mu}{\hbar^2}$$
$$\lambda = \frac{\mu Z e^2}{\hbar^2 \alpha}$$
$$\rho = 2\alpha r_{e-N} \tag{16.36}$$

to obtain

$$\left\{\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left[\rho^2\frac{\partial}{\partial\rho}\right] - \frac{l(l+1)}{(\rho)^2} - \frac{1}{4} + \frac{\lambda}{\rho}\right\}\mathcal{R}(\rho) = 0 \tag{16.37}$$

36. **Homework: Obtain Eq. (16.37) from Eq. (16.35) using the definitions above.**

37. To solve Eq. (16.42) we will use a power series approach. But before we do this, we analytically solve Eq. (16.37) in some limiting values of ρ (for example we will first solve this equation for the case of large and small ρ). This is done to simplify our problem. Then we take these solutions for the limiting cases and multiply it with a power series with unknown coefficients. You will see what I mean in a little while.

38. First lets see if we can solve Eq. (16.37) **for the case of large** ρ. But before we proceed, realize that:

$$\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left[\rho^2\frac{\partial}{\partial\rho}\right] \equiv \frac{\partial^2}{\partial\rho^2} + \frac{2}{\rho}\frac{\partial}{\partial\rho}. \tag{16.38}$$

Using this in Eq. (16.37), for $\rho \to \infty$ we obtain:

$$\frac{\partial^2}{\partial\rho^2}\mathcal{R}(\rho) - \frac{1}{4}\mathcal{R}(\rho) = 0 \tag{16.39}$$

This equation looks familiar!! (similar to PIB, do you see?). The solution is:

$$\mathcal{R}(\rho) = A\exp\left[-\rho/2\right] + B\exp\left[\rho/2\right] \tag{16.40}$$

If α were imaginary, the states are unbound!! $\mathcal{R}(\rho)$ is totally delocalized and there is always a probability of finding the electron infinitely far from the nucleus. This corresponds to an ionized state of the hydrogen atom (free electron) !! The energy is positive. *But if α is real, E_μ is negative and the wavefunction must be finite for all ρ* (which is proportional to r_{e-N}). Hence $B = 0$ in this case. (Because $\exp\left[\rho/2\right]$ would blow up for large ρ.)

39. **For the case of small** ρ: Before we proceed further we simplify Eq. (16.37). Why? We need a simpler equation to solve under the condition of small ρ. After-all, we are obtaining these solutions to large and small ρ to help us in solving Eq. (16.37) completely. Hold-on, and you will see what I mean.

Now note that

$$\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left[\rho^2\frac{\partial}{\partial\rho}\right] \equiv \frac{1}{\rho}\frac{\partial^2}{\partial\rho^2}\rho \tag{16.41}$$

and since there is a $1/\rho$ dependence in all terms of Eq. (16.37) (except the 1/4 term), lets substitute $\mathcal{R} = \mathcal{U}/\rho$ and use Eq. (16.41) to further simplify Eq. (16.37):

$$\left\{\frac{\partial^2}{\partial\rho^2} - \frac{l(l+1)}{(\rho)^2} - \frac{1}{4} + \frac{\lambda}{\rho}\right\}\mathcal{U}(\rho) = 0 \tag{16.42}$$

Now as $\rho \to 0$ the second term dominates and is much larger than the third and fourth terms, and the equation becomes:

$$\frac{\partial^2}{\partial\rho^2}\mathcal{U}(\rho) - \frac{l(l+1)}{(\rho)^2}\mathcal{U}(\rho) = 0 \tag{16.43}$$

which has the solution

$$\mathcal{U}(\rho) = A'\frac{1}{\rho^l} + B'\rho^{l+1} \tag{16.44}$$

And again the requirement of finiteness of $\mathcal{R}$ (note: $\mathcal{R} = \mathcal{U}/\rho$) sends A' to zero. (Note: $\mathcal{R} \equiv \mathcal{U}/\rho$ has to finite as $\rho \to 0$ sends A' to zero.)

40. So we have two asymptotic solutions that we can use. We want the wavefunction to approach these asymptotic values, but for intermediate values of ρ what is the value of $\mathcal{R}(\rho)$? To obtain this we make the substitution:

$$\mathcal{R}(\rho) = \exp\left[-\rho/2\right]\rho^l F(\rho) \tag{16.45}$$

and let

$$F(\rho) = \sum_{i=0}^{\infty} c_i\rho^i \tag{16.46}$$

Substitute this in Eq. (16.42) and we need to solve for the coefficients c_i. Multiply both sides by $\exp\left[-\rho/2\right]$ and then one equate equal powers of ρ to obtain

$$c_{i+1} = \frac{(i+l+1) - \lambda}{(i+1)(i+2l+2)}c_i = c_i\Gamma_{i,l} \tag{16.47}$$

This is called a recursion relation. The polynomial $F(\rho)$ are called the Laguerre polynomials.

Now, as $i \to \infty$, $C_{i+1} \approx c_i/i$. For large i, $F(\rho)$ diverges. (Note: for large ρ $C_{i+1} \approx c_i/i$ which yields $F(\rho) \propto \sum_i(1/i!)\rho^i \approx \exp\rho$ which diverges for large values of ρ. **This is clearly non-physical since the wavefunction should be finite.** Hence, we need to somehow truncate the series for some finite i_{max} so as to control $F(\rho)$ from blowing up. How do we do that? We could do that by requiring that the numerator of Eq. (16.47) go to zero for $i = i_{max}$. Then

$$i_{max} + l + 1 = \lambda \equiv n \tag{16.48}$$

and then $c_i = 0$ for all $i \geq i_{max}$. Hence the series truncates and the wavefunction remains finite.

41. In addition, i_{max} is non-negative, since it is the maximum value that i can have, hence $n \geq (l+1)$. This is obviously an important result that we have all seen before. (For $n = 3$ (where n is the principal quantum number), l (the azimuthal quantum number can only have values $l = 0, 1, 2$, that 3s, 3p and 3d orbitals. This result directly appears from the above series truncation, which in turn is a result of the boundary conditions.

42. But now λ depends upon E the energy as given in the first two of Eq. (16.36). Using Eqs. (16.36)

$$n^2 = \lambda^2 = \frac{\mu^2 Z^2 e^4}{\hbar^4 \alpha^2} = -\frac{\mu Z^2 e^4}{2\hbar^2 E_\mu} \qquad (16.49)$$

and hence

$$E_\mu = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2} \qquad (16.50)$$

And now this energy is negative!! (Recall the earlier center of mass energy levels were all greater than zero and formed a continuous spectrum.) Furthermore, n is an integer and hence the energy in Eq. (16.50) is quantized. *Again we got quantization by enforcing the boundary conditions. Here we used the fact that the wavefunction has to be finite and that gave us a maximum i_{max} which lead to a discrete set of states.*

43. We will go ahead and note here that what we have derived is true for a one-electron one nucleus system. Hence not only is the energy in Eq. (16.50) a valid expression for the hydrogen atom, but it is also from for He^+, Li^{2+} and so on.

44. Hence the energy levels look as follows:

45. From Eq. (16.48) we also see that the minimum value of n is 1. (That is n cannot be zero.) Hence the minimum energy for the hydrogen atom is $E_\mu^{n=1} = -\frac{\mu Z^2 e^4}{2\hbar^2}$. (Note that the lowest value of the potential is $r_{e-N} \to 0$ when the potential energy tends to $-\infty$. Hence like in the particle in a box case, the lowest energy state does not correspond to the lowest potential energy value. Zero point energy is how we referred to this phenomenon in the particle-in-a-box case. But now we see the same thing happens in hydrogen atom as well.)

46. **Quantum number of the hydrogen atom:** We see that there are three quantum numbers now, l, m and n. From Eq. (16.48) $n > l$. Since they are both integers $0 < l < (n-1)$. We have already seen the range of values that m can have. But the energy only depends on n.

47. **Eigenstates of the hydrogen atom:** We have seen that the wavefunction for the hydrogen atom has the form:

$$\{A \exp[\imath k R_{CM}] + B \exp[-\imath k R_{CM}]\} \exp[-\rho/2] \rho^l F(\rho) \mathcal{Y}_{l,m_l}(\theta, \phi) \qquad (16.51)$$

Some solutions are illustrated on the next page. We note that in this expression we have associated Legendre polynomials as well as associated Laguerre polynomials. These are two special functions that we have seen so far. There are a great number of special functions and we will also encounter the Hermite polynomials when we study the Harmonic oscillator.

48. **Homework: The electron mass is often used in many books instead of the reduced mass μ. Show that using the mass of an electron instead of μ is a good approximation. (Use the definition of μ.) What does this physically mean regarding the mass of the nucleus?**

49. Using the mass of the electron instead of the reduced mass, one defines the Bohr radius as:

$$a_0 = \frac{\hbar^2}{me^2} = 0.52918 \text{Å} \tag{16.52}$$

where we have used m to represent the mass of the electron as done earlier. This is the radius of the circle inside which the electron moved in the old Bohr theory!! (Below we will present some expressions for the lower energy wavefunctions for the hydrogen atom and then we will be in a position to interpret what fraction of the electron density really stays inside a_0 for the ground state of hydrogen.) The energy expression then becomes:

$$E_\mu = -\frac{Z^2 e^2}{2a_0 n^2} \tag{16.53}$$

but only if we assume that the electron mass can replace the reduced mass!! You guys will have the opportunity to work out when this is the case (homework above).

50. In the old Bohr model, the energy is actually given by Eq. (16.53). Hence Bohr had it right for the hydrogen atom. But that approach failed for larger systems and was replaced by quantum mechanics.

51. **Nodes:** The radial part of the solution (the part that depends on ρ) can be zero at finite values of ρ. These are points in space where the electron density is zero. (Remember from the particle in a box that such points could exist inside the box.) These special points are called "nodes" of the wavefunction. From the form of the solution can we find out the nodes of the wavefunction. Or at least can we find out how many nodes each wavefunction might have? Turns out we can. Note that the wavefunction is a polynomial in ρ. See Eqs. (16.45), (16.46), (16.47) and (16.48). From these equations we know that $\mathcal{R}(\rho)$ is a finite polynomial in ρ. We also know the order of this polynomial by looking at these equations. It is: $n-l-1$. Any polynomial of order N, has N roots. What does this mean? It means that if you set a function that is a polynomial of order N equal to zero, then we can get N solutions. For example a quadratic equation has 2 solutions, a cubic equation has 3 solutions, a quartic equation has 4 and so on. So an N-th order polynomial equation should have N solutions. So the number of nodes in the hydrogen atom solution should be $n - l - 1$.

52. **Probability current for the hydrogen atom**

$$\mathcal{J} = \frac{\hbar}{\mu} \mathcal{I} \left[\psi^*(x,t) \nabla \psi(x,t) \right] \tag{16.54}$$

For ∇ in spherical coordinates we can use Eq. (16.24) and definitions in that same page to obtain:

$$\nabla = \vec{r_{e-N}} \frac{\partial}{\partial r_{e-N}} + \vec{\theta} \frac{\partial}{\partial \theta} + \frac{\vec{\phi}}{r_{e-N} \sin \theta} \frac{\partial}{\partial \phi} \tag{16.55}$$

Now its only the ϕ dependent part in Eq. (16.71) that has an imaginary term in it:

$$
\begin{aligned}
\psi_{n,l,m}(\rho, \theta, \phi; t) \quad &\propto \quad \exp\left[-\rho/2\right] \rho^l F(\rho) \mathcal{P}_{l,m}(\cos\theta) \exp\left\{\imath m\phi\right\} \\
&\exp\left[-\imath E_{\mu,n} t/\hbar\right]
\end{aligned}
\tag{16.56}
$$

This leads to

$$
\mathcal{J} = \vec{\phi}\frac{m\hbar}{\mu r_{e-N} \sin\theta} \left|\psi_{n,l,m}\right|^2
\tag{16.57}
$$

proportional to the m quantum number. The fact that it is directed along $\vec{\phi}$ implies it is a *rotating wave*!!

Now interestingly, the magnetic moment inside a small volume element is defined as:

$$
d\vec{M} = \frac{1}{2}\vec{r} \times e\mathcal{J}dV
\tag{16.58}
$$

So, now you know where an orbital magnetic moment comes from, it comes from the flux. *Seems like Faraday's' law applies here too!!*

Using Eq. (16.58) and the definition of flux the orbital magnetic moment is:

$$
M = -\frac{e}{2\mu} \left\langle \psi \left| \mathbf{L} \right| \psi \right\rangle
\tag{16.59}
$$

and the orbital magnetic moment operator is:

$$
\mathbf{M} = -\frac{e}{2\mu}\mathbf{L} = \frac{g_e\beta}{\hbar}\mathbf{L}
\tag{16.60}
$$

where $\beta = \frac{e\hbar}{2\mu}$ is called the *Bohr magneton*, a unit of the magnetic moment. The orbital g-factor $g_e = 1$ for the hydrogen. This also means:

$$
\mathbf{M_z} = -\frac{e}{2\mu}\mathbf{L_z} = \frac{g_e\beta}{\hbar}\mathbf{L_z}
\tag{16.61}
$$

Does this remind you of Eq. (2.2), very early!!

These can get you NMR chemical shifts in a complicated system!! Leads into Zeeman effect next.

53. **Splitting the m quantum numbers: Zeeman effect**: We noticed that the 2p orbital is triply degenerate, each degenerate state characterized by m values in the range +1 to -1 (since for p orbital, $l = 1$). The 3d orbital has a degeneracy of 5, each degenerate state characterized by m values in the range +2 to -2 (since for the d orbital $l = 2$). We notice further from the solution to the hydrogen seen previously that two wave functions with magnetic quantum numbers +m and -m only differ due to $\exp\left[\imath m\phi\right]$ factor. Notice from Eqs. (15.87) and (15.86) (from the Spherical harmonics handout) that $\mathcal{P}_{l,m}$ only depends on $|m|$ which is the same for $\pm m$. It is only the $\exp\left[\imath m\phi\right]$ factor in Eq. (16.72) that makes these functions

different. Furthermore, the energy for the $\pm m$ levels are the same as the energy in Eq. (16.50) does not depend on m (which is why all the 2p orbitals for example have the same energy).

Is there a way we can split this degeneracy? We recall from the Stern-Gerlach experiment that the z-component of the spin angular momentum interacts with an external magnetic field to give rise to a force on the silver atoms. Why does this happen? The angular momentum of a charged particle creates an internal magnetic field which interacts with the external magnetic field. But is spin angular momentum the only kind of angular momentum in a molecular system? No we know at least one more and that is the orbital angular momentum. Hence the orbital angular momentum can also interact with an external magnetic field like the spin angular momentum does.

Using Eqs. (2.1) and (2.2) and realizing that force is the Negative of the derivative of the potential energy with respect to distance, We see that

$$E_B = CBS_z \qquad (16.62)$$

A similar energy exists due to the orbital angular momentum and in that case the Constant is just the definition of the Bohr-magneton:

$$E_B = \frac{\beta_e}{\hbar}BL_z \qquad (16.63)$$

where β_e is the Bohr magneton of an electron and $\beta_e = \frac{e\hbar}{2m_e}$.

And so now we are in a position to write the new Hamiltonian of the Hydrogen Atom in the presence of the magnetic field as

$$H_B = H + \frac{\beta_e}{\hbar}BL_z \qquad (16.64)$$

where H is the Hydrogen atom Hamiltonian of Eq. (16.1). Since L_z commutes with H, the eigenstates of the Hamiltonian in Eq. (16.64) will be the same as the Hydrogen atom eigenstates. But now the eigenvalues get an additional m dependent term due the $\frac{\beta_e}{\hbar}BL_z$ factor since

$$H_B\Psi = \left[H + \frac{\beta_e}{\hbar}BL_z\right]\Psi = [E_{R_{CM}} + E_\mu + \beta_e Bm]\Psi \qquad (16.65)$$

where $E_{R_{CM}}$ and E_μ are given by Eqs. (16.19) and (16.49), Ψ is the full hydrogen atom wavefunction discussed earlier.

So the m quantum number states can be split in this fashion. This effect is called the Zeeman effect.

54. Using the final expressions for the internal part of the wavefunction of the hydrogen atom (that is we are not including the center of mass portion here) the lower energy states of the

hydrogen atom have the following functional forms:

$$\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\exp\left[-r/a_0\right] \tag{16.66}$$

$$\psi_{2s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{3/2}\left(2-\frac{Zr}{2a_0}\right)\exp\left[-Zr/(2a_0)\right] \tag{16.67}$$

$$\psi_{2p_{m=-1}} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{5/2}r\exp\left[-Zr/(2a_0)\right]\sin\theta\exp\left(-\imath\phi\right) \tag{16.68}$$

$$\psi_{2p_{m=0}} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{5/2}r\exp\left[-Zr/(2a_0)\right]\cos\theta \tag{16.69}$$

$$\psi_{2p_{m=1}} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{5/2}r\exp\left[-Zr/(2a_0)\right]\sin\theta\exp\left(\imath\phi\right) \tag{16.70}$$

The p-orbitals all have the same energy since the energy of the Hydrogen atom does not depend on the l quantum number. Hence $\psi_{2p_{m=-1}}$, $\psi_{2p_{m=0}}$ and $\psi_{2p_{m=1}}$ are degenerate states. It is $\psi_{2p_{m=0}}$ that is called the ψ_{2p_z} state. The ψ_{2p_x} and ψ_{2p_y} states are actually linear combinations of $\psi_{2p_{m=-1}}$ and $\psi_{2p_{m=1}}$. And since these are degenerate states ψ_{2p_x} and ψ_{2p_y} are eigen-kets that have the same energy as $\psi_{2p_{m=-1}}$ and $\psi_{2p_{m=1}}$. *But notice that ψ_{2p_x} and ψ_{2p_y} are not eigenstates of* $\mathbf{L_z}$ *anymore.*

55. **Generating functions**: We went through some detail here but did not quite derive everything. Now, if we want to write down the solution to the hydrogen atom for any given state (for example 5p$_{+1}$), how do we do that? Is there a way to directly write down the solution without bothering to do the derivation as we now have a general idea as to how things are derived? Turns out yes. And here we introduce what are known as generating functions for the various polynomials that form the solutions to the hydrogen atom. As the name suggests generating functions are simple functions that may be used to *generate* these solutions.

56. As noted earlier, the solution to the hydrogen atom for the internal degrees of freedom is given by
$$\exp\left[-\rho/2\right]\rho^l F(\rho)\mathcal{Y}_{l,m_l}(\theta,\phi) \tag{16.71}$$

where $F(\rho)$ are proportional to the Laguerre polynomials and

$$\mathcal{Y}_{l,m_l}(\theta,\phi) \propto \mathcal{P}_{l,m}(\cos\theta)\exp\left\{\imath m\phi\right\} \tag{16.72}$$

where $\mathcal{P}_{l,m}(\cos\theta)$ are the associated Legendre polynomials. Hence if we know how to write down the Legendre polynomials and the Laguerre polynomials for arbitrary n, l, m, we can write down the solution of the hydrogen atom for any orbital!! So how do we do this?

(a) Turns out the following mathematical relations hold and these help us to write down the solutions for any general orbital that we need.

$$\mathcal{P}_{l,m}(z) = \frac{1}{2^l l!} \sqrt{\frac{(2l+1)}{2} \frac{(l-|m|)!}{(l+|m|)!}}$$

$$\left(1-z^2\right)^{(|m|/2)} \frac{d^{(l+|m|)}\left(z^2-1\right)^l}{dz^{(l+|m|)}} \tag{16.73}$$

$$\mathcal{L}_{n,l}(\rho) = \frac{d^{2l+1}}{d\rho^{2l+1}}\left[\exp\left(\rho\right)\frac{d^{n+l}\left(\rho^{n+l}\exp\left(-\rho\right)\right)}{d\rho^{n+l}}\right] \tag{16.74}$$

and $F(\rho) = \mathcal{L}_{n,l}(\rho)/\rho$.

(b) **Volume Element:** We discussed earlier how we can transform a general Laplacian in Cartesian coordinates to any other coordinate system (for example the spherical coordinate system). In addition to the Laplacian there turns out another quantity that one needs when transforming coordinate systems. This is known as the volume element. Remember that when you perform a one-dimensional integration what you do is multiply the integrand with a quantity, dx. This quantity is dx is a one-dimensional "measure" or *length element* along the x direction. Similarly when you perform the three-dimensional integration what we do is multiply by a three-dimensional *volume element*, $dxdydz$. But this is the volume element in Cartesian coordinates. What does one do if we needed this is spherical coordinates? We need to transform the volume element to the new coordinate system. Using the definitions for the spherical coordinates in Eq. (15.73) it turns out that the volume element in spherical coordinates is given as:

$$r^2 dr \sin\theta d\theta d\phi \tag{16.75}$$

But is there a way we could do this in a general fashion using the definition of the metric tensor we introduced earlier? Turns out yes and the general expression is:

$$dv = \sqrt{g} du_1 du_2 du_3 \tag{16.76}$$

where g is the determinant of the metric tensor as seen earlier. We recall from Eqs. (16.22) that $\sqrt{g} = r^2 \sin\theta$, which proves Eq. (16.75).

(c) As a special case of the volume element in Eq. (16.75) we write what is a spherical shell element. This volume element does not depend on θ and ϕ can be used when the integrand does not have angular dependence. This is for example the case if one were to find the expectation value of position with respect to the 1s orbital:

$$\langle\psi_{1s}|r|\psi_{1s}\rangle = \int r^2 dr \sin\theta d\theta d\phi \left[\frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 \exp\left[-2r/a_0\right]r\right]$$

$$= \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 \left[\int_0^\infty r^3 \exp\left[-2r/a_0\right]dr\right]\left[\int_0^\pi sin\theta d\theta\right]\left[\int_0^{2\pi} d\phi\right]$$

$$= \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 \left[\int_0^\infty r^3 \exp\left[-2r/a_0\right]dr\right] 4\pi \tag{16.77}$$

This is how you integrate to obtain an expectation value. In general, of course, The integrand may depend on θ and ϕ. But if not the problem can be Simplified as shown above.

(d) **Homework:** Calculate the expectation value of position for the ground electronic state (1s). Compare this expectation value to the Bohr radius. What is the probability of finding the electron inside a sphere $r < a_0$?

(e) **Homework:** Derive relations for $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p \rangle$ and $\langle p^2 \rangle$ for the $2p_{+1}$ orbital of the hydrogen atom and use this to obtain the uncertainty product.

(f) **Homework:** Using the energy expression, calculate the ground state energy of the hydrogen atom.