

Chapter 2: The Hydrogen Atom

2.1 Central potential and Hamiltonian of the Hydrogen

2.2 The radial wave functions for the Hydrogen Atom

2.3 Energy Eigenvalues for the Hydrogen Atom

2.4 The Transition Spectrum of Hydrogen

2.5 Other Single-Electron Atoms

2.6 Parity, spherical harmonics and atomic orbitals

One of the primary goals in studying quantum mechanics is to understand the physics of atoms. In this chapter, we begin with the hydrogen atom. Building on our knowledge of angular momentum covered in last chapter, we can determine the angular components of the wave function. However, solving for the radial component is necessary to uncover the energy levels. We will classify the resulting wave functions into orbitals, a concept familiar to anyone with a background in chemistry.

2.1 Central potential and Hamiltonian of the Hydrogen

A hydrogen atom consists of a single electron in a bound state around a single proton, held together by the Coulomb force. We will initially assume that the proton is infinitely heavy (relative to the electron) and stationary at the origin. So when we say we are solving the quantum mechanics of the hydrogen atom, it is really the electron in the hydrogen atom that we mean.

To set the scene, and revise the basics of the course, we start from the beginning, with the TDSE of Eq. (3) in Chapter 1:

$$\left(-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x, y, z, t)\right) \Psi(x, y, z, t) = i\hbar \frac{\partial}{\partial t} \Psi(x, y, z, t).$$

For a static, central, potential, we work in spherical polar coordinates, the TISE of Eq. (5) in Chapter 1 now reads:

$$\left(\frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \left[\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2}\right]\right) + V(r)\right) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi).$$

We recognize the factor involving the angular parts is related to the angular momentum operator

$$\hat{L}^2 = -\hbar^2 \left[\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2}\right], \quad (1)$$

such that

$$\left(\frac{-\hbar^2}{2m} \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r}\right] + \frac{\hat{L}^2}{2mr^2} + V(r)\right) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi), \quad (2)$$

is the TISE for the central potential. And we note for later convenience that the factor in square brackets can be written as

$$\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}.$$

The Coulomb potential between the positively charge nucleus (proton) and electron is

$$V(r) = \frac{-e^2}{4\pi\epsilon_0 r}.$$

The fact that this is negative corresponds to this being an attractive force, with energies lower than at infinity, so we expect to find bound states. This expression assumes that the nucleus is infinitely heavy, and point-like, both of which we will come back to later.

We will try separable solutions of the form

$$\psi(r, \theta, \phi) = R(r) Y_{lm}(\theta, \phi). \quad (3)$$

Therefore Eq. (2) becomes

$$\left(\frac{-\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r} \right) R(r) Y_{lm}(\theta, \phi) = E R(r) Y_{lm}(\theta, \phi),$$

and Y_{lm} cancels. Finally, a useful trick, we replace $R(r)$ by

$$R(r) = \frac{U(r)}{r}, \quad (4)$$

we arrive a one-dimensional differential equation for $U(r)$

$$-\frac{\hbar^2}{2m} \frac{d^2 U}{dr^2} + \frac{l(l+1)\hbar^2}{2mr^2} U - \frac{e^2}{4\pi\epsilon_0 r} U = E U. \quad (5)$$

Dimensionless Variables Recall that the Bohr model of the atom had energy levels

$$E_n = \frac{-E_R}{n^2}, \quad \text{with } E_R = \frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2} = 13.6 \text{ eV}, \quad (6)$$

with Rydberg energy unit E_R and radii

$$a_n = a_0 n^2, \quad \text{with } a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = 0.53 \text{ \AA}. \quad (7)$$

Therefore we define dimensionless variables

$$\rho \equiv \frac{r}{a_0}, \quad \tilde{E} \equiv \frac{E}{E_R},$$

which gives

$$-\frac{d^2 U}{d\rho^2} + \frac{l(l+1)}{\rho^2} U - \frac{2}{\rho} U = \tilde{E} U. \quad (8)$$

2.2 The radial wave functions for the Hydrogen Atom

We ended the last section with the radial TISE for hydrogen of Eq. (8),

$$-\frac{d^2U}{d\rho^2} + \frac{l(l+1)}{\rho^2}U - \frac{2}{\rho}U = \tilde{E}U.$$

Before proceeding to solve it, we consider how the solutions might behave for small and large ρ .

Large ρ :

For large ρ , the $1/\rho^2$ and $1/\rho$ terms must both be tiny relative to the constant \tilde{E} on the right-hand side, so

$$-\frac{d^2U}{d\rho^2} \approx \tilde{E}U.$$

Since we are seeking bound states, we must have $\tilde{E} < 0$, so we define

$$\tilde{E} = -b^2,$$

for some real constant b . This has solutions

$$U(\rho) = e^{\pm b\rho}.$$

But the wave function must vanish for large ρ , so it must be that for large ρ ,

$$U(\rho) \rightarrow e^{-b\rho}.$$

Small ρ :

For small ρ , the $l(l+1)/\rho^2$ term must dominate the other two (at least for $l \neq 0$) and we have

$$-\frac{d^2U}{d\rho^2} + \frac{l(l+1)}{\rho^2}U \approx 0.$$

Since $U(0)$ has to be zero, try $U(\rho) \sim \rho^a$ for some constant a .

$$\rightarrow -a(a-1) + l(l+1) = 0 \quad \Rightarrow a = l+1 \text{ or } a = -l.$$

However, $U(0) = 0$ only for $a > 0$, so it must be that for small ρ ,

$$U(\rho) \rightarrow \rho^{l+1}.$$

For $l = 0$, we have to consider the $-2/\rho$ term in the same way, but come to the same conclusion, that $U \sim \rho^1$ in that case.

General solution:

Inspired by those limits, we propose a general solution

$$U(\rho) = \rho^{l+1} e^{-b\rho} f(\rho), \quad \text{with } \tilde{E} = -b^2, \quad (9)$$

where $f(\rho)$ is a smooth function with $f(0) = \text{const.}$ Substituting this in gives us the equation for $f(\rho)$:

$$\rho \frac{d^2 f}{d\rho^2} + 2(l+1-b\rho) \frac{df}{d\rho} + 2(1-b(l+1))f = 0. \quad (10)$$

For those who are frustrated by trial solutions, the mathematical footnote below will help you to solve this equation systematically. The systematic solution shows that $f(\rho)$ must be a polynomial, let us call its degree p .

For $p = 0$, i.e. $f(\rho) = \text{constant}$, we obtain

$$1 - b(l+1) = 0 \quad \Rightarrow \quad b = \frac{1}{l+1} \quad \Rightarrow \quad \tilde{E} = \frac{-1}{(l+1)^2}.$$

For $p = 1$, i.e. $f(\rho) = c_0 + c_1\rho$, we obtain

$$\begin{aligned} 2(l+1-b\rho)c_1 + 2(1-b(l+1))(c_0 + c_1\rho) &= 0 \\ \rightarrow \left[(l+1)c_1 + (1-b(l+1))c_0 \right] - \left[b - (1-b(l+1)) \right] c_1\rho &= 0. \end{aligned}$$

For this to be true for all ρ , the two square brackets must separately be zero:

$$\Rightarrow c_1 = \frac{-c_0}{(l+1)(l+2)} \quad \Rightarrow \quad b = \frac{1}{l+2} \quad \Rightarrow \quad \tilde{E} = \frac{-1}{(l+2)^2}.$$

For $p = 2$, i.e. $f(\rho) = c_0 + c_1\rho + c_2\rho^2$, we obtain three equations and we can solve for three unknowns, with

$$b = \frac{1}{l+3} \quad \Rightarrow \quad \tilde{E} = \frac{-1}{(l+3)^2},$$

and equations for c_1 and c_2 proportional to c_0 .

Mathematical footnote 1

To systematically solve the equation:

1. Represent $f(\rho)$ by its series expansion

$$f(\rho) = \sum_{k=0}^{\infty} c_k \rho^k.$$

Note that for $f(\rho)$ to be well defined for all $\rho \geq 0$, either this series must converge, or it must terminate.

2. Insert $f(\rho)$ into the differential equation, shift the sum over k to a sum over $k - 1$ where necessary, to write the series as

$$\sum_{k=0}^{\infty} [c_{k+1}(\cdots) + c_k(\cdots)] \rho^k = 0.$$

3. Realise that to solve the equation for all ρ , every square bracket term must separately be zero.

$$\Rightarrow c_{k+1} = -\frac{(\cdots)}{(\cdots)} c_k.$$

4. Prove that the series with these coefficients diverges, unless it terminates. i.e. it is not a series but a polynomial. Call its degree p .
5. The requirement that $c_{p+1} = 0$ gives us

$$b = \frac{1}{l + p + 1} \quad \Rightarrow \quad \tilde{E} = \frac{-1}{(l + p + 1)^2}.$$

The other p equations give us the solutions for the coefficients of the polynomial, all proportional to c_0 .

6. Note that the multiplier on the right-hand side of (1) is always negative, so the polynomial has alternating sign. Therefore $f(\rho)$ has p zeroes for $\rho > 0$.

2.3 Energy Eigenvalues for the Hydrogen Atom

To summarise what we have found so far, we have found solutions of Eq. (5) for the radial wave function $U(r)$ with:

- $E = \frac{-E_R}{(l+1)^2}$ described by a $p = 0$ th order polynomial and $l = 0, 1, 2, \dots$
- $E = \frac{-E_R}{(l+2)^2}$ described by a $p = 1$ st order polynomial and $l = 0, 1, 2, \dots$
- $E = \frac{-E_R}{(l+3)^2}$ described by a $p = 2$ nd order polynomial and $l = 0, 1, 2, \dots$ etc.

We define a new quantum number, which will be called the **principal quantum number**, n , such that

$$E_n = \frac{-E_R}{n^2}, \quad n \geq 1. \quad (11)$$

Checking in the list above shows us that a given energy can only be achieved if

$$0 \leq l \leq n - 1 \quad (12)$$

with a $p = (n - 1 - l)$ th order polynomial.

Recall that, for a given l , $L_z = m\hbar$ where

$$-l \leq m \leq l. \quad (13)$$

n and l and m fully parametrize $\psi(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$. They are **good quantum numbers**.

The radial wave functions themselves, $R_{nl}(r)$ are summarized in the following table:

n	$l = 0$	$l = 1$	$l = 2$
1	e^{-r/a_0}		
2	$\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$	$\frac{r}{a_0} e^{-r/2a_0}$	
3	$\left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) e^{-r/3a_0}$	$\frac{r}{a_0} \left(1 - \frac{r}{6a_0}\right) e^{-r/3a_0}$	$\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$

There is a naming convention that comes from spectroscopic physics, which you just have to know, as defined below:

- States with $l = 0$ are called s orbitals, originally for “sharp”
- States with $l = 1$ are called p orbitals, originally for “principal”
- States with $l = 2$ are called d orbitals, originally for “diffuse”.
- States with $l = 3$ are called f orbitals, originally for “fundamental”
- And higher l states just go alphabetically, g , h , ...

So, the $n = 2$, $l = 0$ state, for example, is called $2s$, the $n = 3$, $l = 1$ state is called $3p$, and so on.

You will be expected to recognise wave functions from their algebraic forms. To do this, note:

- The exponential is e^{-r/na_0} : you can just read off n .
- For small r , they are $\left(\frac{r}{a_0}\right)^l$: you can read off l .
- The polynomial in r is degree $n - l - 1$: you can double-check that your values of n and l are consistent.

You rarely need the normalization constants, but if you do, they can be obtained from

$$\int_{r=0}^{\infty} dr \int_{\theta=0}^{\pi} d\theta \int_{\phi=0}^{2\pi} d\phi r^2 \sin \theta |\psi|^2 = 1$$

or

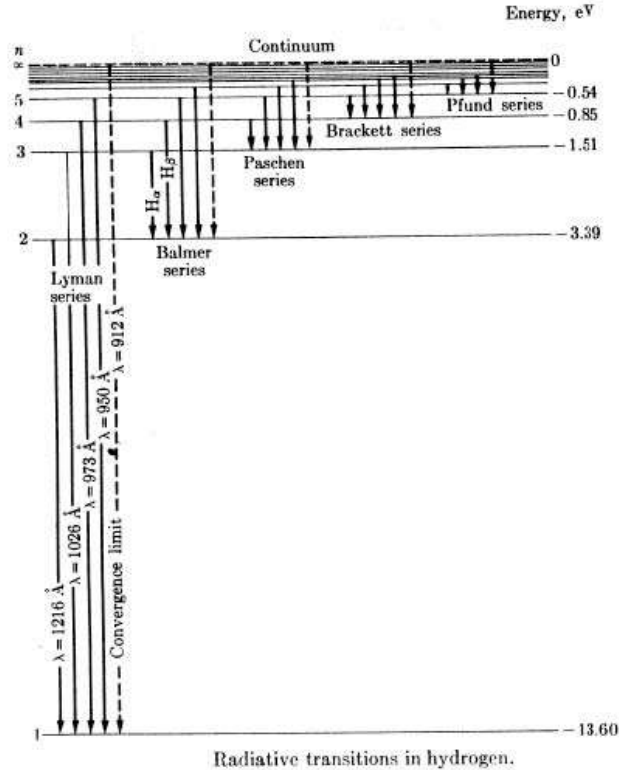
$$\int_{r=0}^{\infty} dr r^2 |R(r)|^2 \times \int_{\theta=0}^{\pi} d\theta \sin \theta \int_{\phi=0}^{2\pi} d\phi |Y_{lm}|^2 = 1. \quad (14)$$

The usual convention is that the $|Y|^2$ integral is normalized to 1 and hence

$$\int_{r=0}^{\infty} dr r^2 |R(r)|^2 = 1. \quad (15)$$

We will further discuss the properties of hydrogen wave functions, particularly the angular parts, $Y_{lm}(\theta, \phi)$, in the last section.

2.4 The Transition Spectrum of Hydrogen



Transitions (shown on the last page) between energy levels involves emission or absorption of a single photon. If a hydrogen atom is in an excited state with principal quantum number n , it can fall down to a lower level $n' < n$ by the emission of a photon with energy

$$h\nu = E_R \left(\frac{1}{n'^2} - \frac{1}{n^2} \right). \quad (16)$$

For a given n' , we get a set of emission frequencies in different frequency ranges, named after their historical discoverers:

- The Lyman series has $n' = 1$ and is in the UV ($\lambda = 91 - 122 \text{ nm}$);
- The Balmer series has $n' = 2$ and is in the UV/visible range ($\lambda = 365 - 656 \text{ nm}$);
- The Paschen series has $n' = 3$ and is in the IR ($\lambda = 820 - 1875 \text{ nm}$).

2.5 Other Single-Electron Atoms

We can also understand the properties of other single-electron atoms from our hydrogen wavefunctions.

The hydrogen atom, the He^+ ion ($Z = 2$) and the Li^{2+} ion ($Z = 3$) all have the same structure, i.e. a single electron orbiting a positively-charged nucleus.

The Coulomb potential is

$$V(r) = \frac{-Z e^2}{4\pi\epsilon_0 r}. \quad (17)$$

We obtain a "Bohr radius" $= a_0/Z$ and energy levels

$$E_n = \frac{-Z^2 E_R}{n^2}. \quad (18)$$

Apart from this factor of Z^2 , these systems have identical energy spectra to hydrogen atoms.

Classically, the electron and the nucleus each orbit their centre of mass, with separation r . This can be taken into account by replacing the electron mass by the reduced mass,

$$\mu = \frac{m_e M_N}{m_e + M_N} = \frac{m_e}{1 + m_e/M_N},$$

so that the energy of the n th level is

$$E_n = \frac{-Z^2 E_R}{n^2} \frac{\mu}{m_e}.$$

This gives a measurable difference between different isotopes of hydrogen, for example:

$$\left(\frac{\Delta E}{E}\right)_{\text{H}} = -0.054\%, \quad \left(\frac{\Delta E}{E}\right)_{\text{D}} = -0.027\%, \quad \left(\frac{\Delta E}{E}\right)_{\text{T}} = -0.018\%.$$

Also, positronium is a bound state (an "atom" of sorts) of an electron and a positron (anti-electron). It also has the same energy spectrum, but with $\mu = m_e/2$.

2.6 Parity, spherical harmonics and atomic orbitals

In this section, we discuss the structural properties of the Hydrogen wave functions (mainly the angular parts), useful in study of the radiations in Chapter 5, and the molecular bonding in Chapter 6.

Under an inversion (parity) transformation $\mathbf{r} \rightarrow -\mathbf{r}$, the Hamiltonian of a Hydrogen atom is invariant, $\hat{H}(-\mathbf{r}) = \hat{H}(\mathbf{r})$. This is easy to see since the Coulomb potential depends on the magnitude r . The eigenfunctions of Hydrogen are then either odd, $\psi(-\mathbf{r}) = -\psi(\mathbf{r})$, or even, $\psi(-\mathbf{r}) = \psi(\mathbf{r})$. So we write

$$\psi(-\mathbf{r}) = \pm\psi(\mathbf{r}). \quad (19)$$

To prove this is so, we can define a parity transformation operator \hat{P} such that

$$\hat{P}\psi(\mathbf{r}) = \psi(-\mathbf{r}).$$

Parity symmetric Hamiltonian means \hat{H} commutes with \hat{P}

$$[\hat{H}, \hat{P}] = 0.$$

So $\psi(\mathbf{r})$ can be eigenfunction of both \hat{H} and \hat{P} . Let λ be the eigenvalue of \hat{P}

$$\hat{P}\psi(\mathbf{r}) = \lambda\psi(\mathbf{r}).$$

But by definition, $\hat{P}\psi(\mathbf{r}) = \psi(-\mathbf{r})$, apply \hat{P} again,

$$\hat{P}^2\psi(\mathbf{r}) = \hat{P}\psi(-\mathbf{r}) = \psi(\mathbf{r}) = \lambda^2\psi(\mathbf{r}),$$

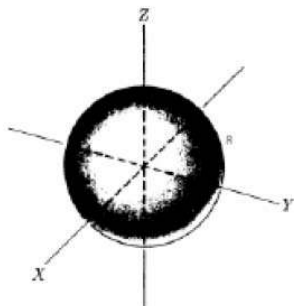
where in the last equation we have used the eigen equation. Therefore $\lambda^2 = 1$ and $\lambda = \pm 1$. The eigenfunction of hydrogen Hamiltonian as given by Eq. (3), a product of the radial and angular parts

$$\psi_{n,l,m}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta, \phi).$$

Parity transformation implies $\theta \rightarrow \pi - \theta$ and $\phi \rightarrow \phi + \pi$. It follows that (see Mathematics footnote 2 at the end)

$$Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}(\theta, \phi). \quad (20)$$

Thus a hydrogen state with angular momentum l has parity $(-1)^l$. The angular parts of the wave functions are described by the spherical harmonics that we determined earlier in Chapter 1.3c.



For $l = 0$ (s states), the wave function is spherically symmetric ($|Y_{0,0}|^2 = \text{constant}$), as we saw in Chapter 1.3c. And it is referred to as s orbital, as shown above.

For $l = 1$, m_l can take 3 values, $0, \pm 1$. The $m_l = 0$ state has a $\cos \theta$ dependence which leads to a dipole-type elongation along the z axis. This is known as a p_z orbital. For $m_l = \pm 1$, the spherical harmonics that we arrived at in Chapter 1.3d do not naturally point along the two Cartesian axes, x and y . This makes it difficult to consider (for example) how the atomic orbitals on one atom may interact with those on another in chemical bonding studied in Chapter 6. However, because the $Y_{1,\pm 1}$ are degenerate eigenstates, it is possible to make 2 symmetrised linear superpositions of $Y_{1,\pm 1}$ which have dipoles lying along the x and y axes. It is in fact these that you may be familiar with from chemistry as p_x and p_y orbitals. Therefore, from the spherical harmonic functions $Y_{1,\pm 1}$ (see the table on Page 20 of Chapter 1)

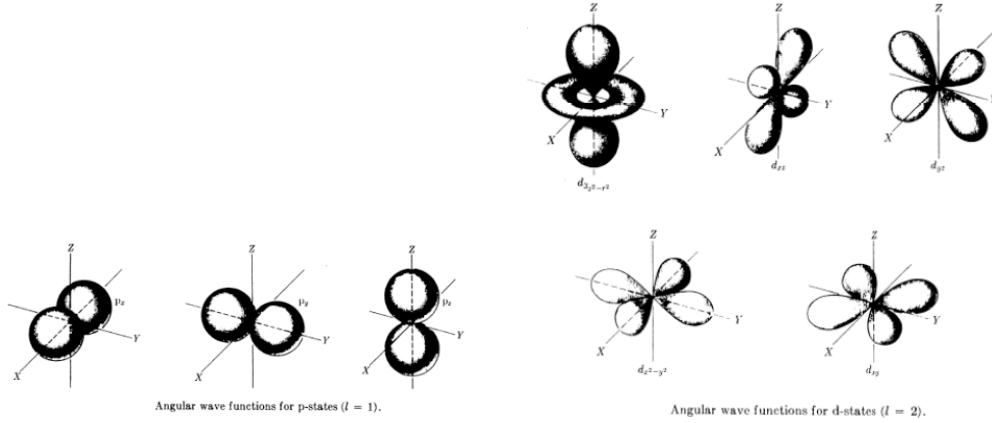
$$Y_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi},$$

the linear combinations:

$$p_x = \frac{1}{\sqrt{2}} (Y_{1,1} - Y_{1,-1}) = -\sqrt{\frac{3}{4\pi}} \sin \theta \cos \phi \quad (21)$$

$$p_y = \frac{i}{\sqrt{2}} (Y_{1,1} + Y_{1,-1}) = -\sqrt{\frac{3}{4\pi}} \sin \theta \sin \phi. \quad (22)$$

The form of these symmetrised functions for $l=1$ and $l=2$ (d orbitals) is shown on the next page.



Any pictorial representation of the *complete orbitals* must recombine the radial **and** angular parts to produce a distribution of the electrons in space. In addition we should note that our schematic representations of the orbitals indicate *probabilities*, rather than certainties of finding electrons. As the orbitals do not have definite radii, we can only define surfaces which represent a 90% (say) probability of finding the electron within it. An example is shown below for a 1s orbital.

Mathematics footnote 2

The parity theorem of Eq. (20) can be proved by examining first the parity of

$$Y_{l,-l}(\theta, \phi) \propto \sin^l \theta \exp(-il\phi).$$

Hence, under a parity transformation,

$$Y_{l,-l}(\pi - \theta, \phi + \pi) = e^{-i\pi l} Y_{l,-l}(\theta, \phi) = (-1)^l Y_{l,-l}(\theta, \phi)$$

as $\sin(\pi - \theta) = \sin \theta$. Using the fact that the raising operator $\hat{L}^+ = \hat{L}_x + i\hat{L}_y$ is invariant under the parity transformation and that $Y_{l,m}$ can be obtained by applying \hat{L}^+ to $Y_{l,-l}$, we conclude that $Y_{l,m}$ has the same parity as $Y_{l,-l}$. Therefore, the parity of $Y_{l,m}$ is given by $(-1)^l$.

Summary of Chapter 2

- As with all central potentials, we could separate the wave function into an angular part, given by the spherical harmonics, and a radial part.
- The total angular momentum L^2 affects the radial wave function, but there is no other coupling between the two parts.

- The energy levels are $E_n = -E_R/n^2$ with $n \geq 1$.
- Each energy level allows L^2 values $l(l+1)\hbar^2$, with $0 \leq l \leq n-1$ (with each therefore allowing L_z values $m\hbar$, with $-l \leq m \leq l$).
- The good quantum numbers are n , l and m .
- States with given n and l values are called orbitals $n'l'$, where ' l ' = s, p, d, f, \dots
- The radial part of the wave function goes like r^l at small r and e^{-r/na_0} at large r , multiplying a polynomial of degree $n-l-1$.
- The emission and absorption spectra can be explained by these energy levels.
- And the results can be applied to any single-electron atom, with appropriate values of Z and μ .
- The parity of the hydrogen wave functions is determined by l : $(-1)^l$.