

LECTURE 4

Content

In this lecture we will discuss a simple model of the hydrogen atom - the **Bohr model**. We shall see how applying quantisation rules leads to a discrete electronic energy spectrum for the hydrogen atom, and find an equation for the wavelength of light absorbed or emitted in an electronic transition. We shall compare the predictions of this simple model with the experimental values. Lastly we shall state the Correspondence Principle, and see how it applies to the energy spectrum of hydrogen.

Outcomes

At the end of this lecture you will:

- be able to describe the Bohr model of the atoms
- apply this description to hydrogen-like atoms to calculate the energy spectra
- be able to apply quantisation rules
- know the significance of the principal quantum number
- be able to use the Rydberg formula to calculate transition energies
- know the Correspondence Principle

2 ONE-ELECTRON ATOMS

The simplest atom - hydrogen - is a good place to start when trying to devise a model for atomic structure. The model can also be fairly simply applied to other atoms that are 'hydrogen-like', such as He^+ .

2.1 THE BOHR ATOM

The Rutherford nuclear picture of the atom could not explain why electrons circling the positively charged nucleus (and hence being accelerated) did not radiate continuously and lose their energy.

For the hydrogen atom this problem was partly solved by Niels Bohr's 'quantum-classical hybrid' model for a one-electron atom.

This model is still very useful nowadays in order to yield estimates for energies, frequencies, size of an excited atom etc - in fact you may have used it in the diffraction grating spectrometer experiment in Lab 2 - but **BEWARE**, it has its limitations.

2.2 DERIVATION OF THE BOHR ATOM

Bohr's postulates (1913):

1. The electron moves in certain allowed circular classical orbits about the nucleus without radiating
2. Emission or absorption of radiation by an atom is associated with a transition between these states.

The allowed orbits, called *stationary states*, are those for which the angular momentum:

$$L = n\hbar , \quad (1)$$

with $\hbar = h/2\pi$ and $n=1,2,3,\dots$

i.e. L is an integral multiple of \hbar

In these orbits, the Coulomb force between nucleus and electron is balanced by the centripetal force.

Assuming the nucleus is infinitely heavy, i.e. it remains stationary while the electron performs a circular orbit, and that the radius of the orbit is r :

$$\underbrace{\frac{Ze^2}{4\pi\epsilon_0 r^2}}_{\text{Coulomb}} = \underbrace{\frac{m_e v^2}{r}}_{\text{Centripetal}} . \quad (2)$$

From the quantization of L , $L = n\hbar$ (which occurs because the circumference of the orbit must be an integral number of de Broglie wavelengths):

$$v = \frac{n\hbar}{m_e r}. \quad (3)$$

So, substituting for v in Eq.(2)

$$\frac{Ze^2}{4\pi\epsilon_0 r} = m_e \left[\frac{n\hbar}{m_e r} \right]^2. \quad (4)$$

we can now work out the allowed radius, for each quantized state n , for the circular orbits:

$$r_n = \frac{4\pi\epsilon_0 \hbar^2 n^2}{Ze^2 m_e}. \quad (5)$$

For $n = 1$, $r_{n=1} = \frac{4\pi\epsilon_0 \hbar^2}{Ze^2 m_e}$.

For $Z = 1$ (hydrogen) this is called the **Bohr radius**, a_0 .

Note that the quantisation of L has lead to the quantisation of r , i.e. only certain radii of the orbits are allowed, and the $r_n \propto n^2$.

We can eliminate r in the equation for the velocity:

$$v_n = \frac{Ze^2}{4\pi\epsilon_0 n\hbar}. \quad (6)$$

Unsurprisingly the velocity is quantised, and $v_n \propto n^{-1}$.

Knowing v we can work out the total kinetic energy, T , for each quantum state, since $T = \frac{1}{2}m_e v^2$.

Knowing r we can work out the potential energy, V , since $V = -\frac{Ze^2}{4\pi\epsilon_0 r}$ (i.e. the Coulomb potential we used earlier):

$$T = \frac{1}{2}m_e \left[\frac{Ze^2}{4\pi\epsilon_0 n\hbar} \right]^2, \quad (7)$$

and

$$V = -m_e \left[\frac{Ze^2}{4\pi\epsilon_0 n\hbar} \right]^2 \quad (8)$$

So the **total energy** (kinetic + potential) is:

$$E = T + V \quad (9)$$

Hence:

$$E_n = -\frac{1}{2} \left[\frac{Ze^2}{4\pi\epsilon_0 n\hbar} \right]^2. \quad (10)$$

Re-arranging,

$$E_n = -\frac{m_e}{2\hbar^2} \left[\frac{Ze^2}{4\pi\epsilon_0} \right]^2 \frac{1}{n^2} \quad (11)$$

for $n = 1, 2, 3, \dots$.

Voilà! The energy is quantised, and $E_n \propto n^{-2}$ (Note that the energy is negative, since we have a bound state). This is an *extremely* important result.

The amount of energy the electron may have is not continuous - it is quantised, i.e. the electron may only occupy particular **states**, labelled by the integer n , known as the **principal quantum number**.

2.3 TRANSITIONS

2.3.1 The theory

So the electron in its orbit around the nucleus may only occupy certain states with discrete energies. It may make transitions between these states by exchanging energy. Here we'll consider radiative transition which involve the exchange of a photon.

If the electron jumps from an initial state i with principal quantum number n_i to a final state f with n_f , we have, for the difference in energy:

$$|E_{n_i} - E_{n_f}| = \left| \frac{m_e}{2\hbar^2} \left[\frac{Ze^2}{4\pi\epsilon_0} \right]^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \right| \quad (12)$$

The difference in energy is accounted for by a photon with frequency

$$h\nu_{if} = |E_{n_i} - E_{n_f}| \quad (13)$$

If $n_i < n_f$, a photon will be absorbed and the process is called excitation. If, on the other hand $n_i > n_f$ a photon will be emitted and the process is de - excitation.

The wavelength of the photon will be:

$$\frac{1}{\lambda_{ij}} = \frac{\nu_{if}}{c} = \left| \underbrace{\frac{m_e}{4\pi\hbar^3 c} \left[\frac{Ze^2}{4\pi\epsilon_0} \right]^2}_{\text{constants}} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \right| \quad (14)$$

2.3.2 The observations

In 1885 **Balmer**¹ discovered a set of lines in the spectrum of hydrogen, that is a set of discrete emitted wavelengths that were well fitted by the formula:

$$\lambda_p = 3646 \frac{p^2}{p^2 - 4} \quad (15)$$

for $p = 3, 4, 5, \dots$, and λ_p measured in angstroms ($1 = 1\text{\AA} \times 10^{-10}\text{m}$).

Rydberg² and later **Ritz**³ found that by calculating $1/\lambda$ for each line then the sums of $1/\lambda$ for pairs of lines are equal to $1/\lambda$ for a different lines in the series. This is known as the Rydberg-Ritz combination principle.

This knowledge was combined into the empirical equation for the wavelengths in the hydrogen spectrum:

$$\frac{1}{\lambda_{if}} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (16)$$

where $R=109677.58 \text{ cm}^{-1}$ is the **Rydberg constant**. This is the same form as we have just derived from the Bohr model. So far, so good.

¹*Ann. Phys.* **25**, 80 (1885)

²*Report of Intl. Phys. Cong. at Paris*, ii, 200 (1900)

³*Phys. Z.* **9** 521 (1908), *Astrophys. J.* **28** 237 (1908)

2.3.3 Compare theory to experiment

The Bohr model predicts that the collection of constants in the above equation:

$$R_{\infty} = \frac{m_e}{4\pi\hbar^3 c} \left[\frac{e^2}{4\pi\epsilon_0} \right]^2 = 109737 \text{cm}^{-1} \quad (17)$$

with $Z = 1$ for hydrogen. (the symbol ∞ makes reference to the fact that we are assuming the mass of the nucleus to be infinite). The discrepancy is $\Delta R/R \simeq 5 \times 10^{-4}$.

2.4 LYMAN, BALMER AND PASCHEN SPECTRAL SERIES

- Lyman series $n = 2, 3, 4, 5\dots \rightarrow 1$ (u.v.) [observed 1906]
- Balmer series $n = 3, 4, 5\dots \rightarrow 2$ (optical) [1895]
- Paschen series $n = 4, 5\dots \rightarrow 3$ (Infra Red) [1908]

The limit of the Lyman series is 912 \AA (in u.v.) corresponding to the ionisation energy of hydrogen $R_\infty = 109737 \text{ cm}^{-1}$.

The next series are Brackett [1922] (transitions to $n = 4$) and Pfund [1925] (to $n = 5$), followed by Humphreys ($n = 6$) and Hansen-Strong ($n=7$) but the lines of the series tend to overlap.

Lines within a series are designated as follows:

$\Delta n = n_i - n_f $	label
1	α
2	β
3	γ
4	δ

Problem: Calculate the first ionisation energy of hydrogen in electron volts.

Solution: This is the transition from $n = 1 \rightarrow n = \infty$,
so:

$$E = \frac{hc}{\lambda_{1\infty}} = hcR_{\infty} \left[\frac{1}{1} - \frac{1}{\infty} \right] \quad (18)$$

giving $E = 2.2 \times 10^{-18} \text{J} \equiv 13.6 \text{eV}$.

Remember this!

2.5 THE CORRESPONDENCE PRINCIPLE

Bohr also formulated the Correspondence Principle, which gives a (partial) rule of thumb for the transition from microscopic, quantal behaviour to macroscopic, classical behaviour.

In the limit of large quantum numbers $n \rightarrow \infty$,
QM results should tend to the classical results.

E.g.: $E_n \propto -1/n^2$ as $n \rightarrow \infty$ $E_n \rightarrow$ smooth function.
That is, discreteness of quantum states \rightarrow continuum.

LECTURE 4 SUMMARY

- The Bohr model is a simple model of hydrogen and hydrogen-like atoms.
- It assumes circular electron motion around a stationary nucleus
- Nevertheless, it produces surprisingly good agreement with experimental data
- Electrons are only allowed to occupy certain discrete states
- In hydrogen, the energies of these states scale as $E \propto n^{-2}$
- Transitions between these states involve the exchange of a photon, the energy of which is found from the Rydberg formula
- The Correspondence Principle: in the limit of large quantum numbers $n \rightarrow \infty$, QM results should tend to the classical results

Before next time: calculate the Bohr radius, a_0 , from the equation given in this lecture.

LECTURE 5

Content

In this lecture we will analyse and criticise the Bohr model more closely - discussing the approximations made in the model, and highlighting its failings. We will introduce the convenient atomic units and spectroscopic units and review the quantum treatment of orbital angular momentum.

Outcomes

After this lecture you will

- know the definition of, and be able to use, the reduced mass of a system
- be able to criticise the simple Bohr model of the atom
- know and be able to use atomic and spectroscopic units
- recall the quantum treatment of angular momentum

2.6 EFFECTS OF FINITE NUCLEAR MASS

In the Bohr model we considered the mass of the nucleus to be infinite. While this is a reasonable approximation, as it is indeed very much heavier than the electron, corrections due to the finite mass are important—isotopes (i.e. the same element but a different nuclear mass) behave differently:

- The spectral line frequencies differ for deuterium (D) and hydrogen (H).
- The reaction $\text{H} + \text{D}^+ \rightarrow \text{D} + \text{H}^+$ is exothermic ($T \sim 40 \text{ K}$) since the binding energy for deuterium is larger, i.e., $E_{n=1}^{\text{D}} < E_{n=1}^{\text{H}}$.

So we must consider the **reduced mass**, μ , in the Bohr atom.

Definition: the reduced mass, μ , is the effective mass of a system once the Centre of Mass motion is separated off.

The ratio of the masses is $M_p/m_e = 1836$ and the separation is:

$$\underline{r} = \underline{r}_e - \underline{R}_p \tag{19}$$

The relative velocity is thus $d\underline{r}/dt = \underline{v}$

The *centre of mass* remains at rest. It is at the origin, so taking moments,

$$M_p \underline{R}_p + m_e \underline{r}_e = 0 , \quad (20)$$

so from Eq. (19):

$$\underline{R}_p = -\frac{m_e}{m_e + M_p} \underline{r} \quad (21)$$

and

$$\underline{r}_e = \frac{M_p}{m_e + M_p} \underline{r} \quad (22)$$

Then, for the angular momentum, L :

$$L = M_p \omega R_p^2 + m_e \omega r_e^2 \quad (23)$$

$$= M_p \frac{m_e}{(m_e + M_p)} v r + m_e \frac{M_p}{(m_e + M_p)} v r \quad (24)$$

$$= \mu v r . \quad (25)$$

where we have substituted for $(R_p)^2$ and $(r_e)^2$, and set $r\omega = v$, and introduced the **reduced mass**, $\mu = \frac{m_e M_p}{(m_e + M_p)}$.

Similarly, for the total kinetic energy:

$$\dot{\underline{R}}_p = -\frac{m_e}{m_e + M_p} \underline{v} ; \quad (26)$$

and

$$\dot{\underline{r}}_e = \frac{M_p}{m_e + M_p} \underline{v} . \quad (27)$$

i.e. we take the first derivative of the position vector to get the velocity vector.

So:

$$T = \frac{1}{2}M_p\dot{R}_p^2 + \frac{1}{2}m_e\dot{r}_e^2 \quad (28)$$

$$= \frac{1}{2}M_p\frac{m_e^2}{(m_e + M_p)^2}v^2 + \frac{1}{2}m_e\frac{M_p^2}{(m_e + M_p)^2}v^2 \quad (29)$$

$$= \frac{1}{2}\frac{m_eM_p}{(m_e + M_p)}v^2 \quad (30)$$

$$= \frac{1}{2}\mu v^2 . \quad (31)$$

Hence, in the Bohr atom expressions we replace m_e by $\mu = \frac{m_eM_p}{(m_e+M_p)}$.

In general we can approximate $\mu \sim m_e$ (but the difference accounts for the difference between R and R_∞). Otherwise we use,

$$E_n \propto -\frac{\mu Z^2}{n^2} \quad (32)$$

and

$$r_n \propto \frac{n^2}{Z\mu} . \quad (33)$$

Example If a hydrogenic atom was made up of a proton and an anti-proton would it be larger or smaller than a conventional atom?

The reduced mass is $\mu = M_p/2$ so, the Bohr radius for this ‘protonium’ atom, r' is:

$$r'_{n=1} = \frac{2}{1836} r_{n=1}. \quad (34)$$

So this atom would be a lot smaller.

2.7 ASSESSMENT OF THE BOHR MODEL

- Predictions for energy levels of H and other one-electron (hydrogenic) atoms are good, however
- It could not explain quantitatively transitions between states.
- It could not be extended to other atoms, even helium, but it does work well for hydrogenic atoms, with only one electron such as He^+ or Li^{2+} (i.e., lithium with two electrons removed).
- Need for quantum mechanics developed by Schrödinger, Heisenberg et al.

2.8 ATOMIC UNITS AND WAVENUMBERS

2.8.1 ATOMIC UNITS

When working with atoms it is convenient to use a new set of units.

We define:

- unit of mass = m_e
- unit of charge = e
- unit of length=Bohr radius = a_0

So $\hbar = 4\pi\epsilon_0 = a_0 = e = m_e = 1$.

Problem What is the radius of the n th eigenstate of the Bohr atom in atomic units?

Solution

$$r_n = \frac{4\pi\epsilon_0\hbar^2 n^2}{Ze^2 m_e} = \frac{n^2}{Z} . \quad (35)$$

Of course for $Z = 1$ (hydrogen) and $n = 1$ (ground state) we have $r_1 = a_0 = 1$, the **Bohr radius**.

In *SI* units the Bohr radius is $a_0 = 0.529 \times 10^{-10} \text{m}$ (as I hope you calculated after the last lecture...)

The **energy** of the n th eigenstate:

$$E_n = -\frac{m_e}{2\hbar^2} \left[\frac{Ze^2}{4\pi\epsilon_0} \frac{1}{n^2} \right] = -\frac{Z^2}{2n^2}. \quad (36)$$

So the ground state energy (or ionisation energy) of hydrogen, assuming infinite mass is:

$$E_{n=1} = -1/2 \text{ a.u.} \equiv -13.605 \text{ eV} \equiv -2.18 \times 10^{-18} \text{ J}$$

The atomic unit of energy is often called the **Hartree**:

$$1 \text{ Hartree} = 27.21 \text{ eV}$$

The speed of the electron in the ground (lowest) state of hydrogen is (from previous lecture):

$$v = \frac{e^2}{4\pi\epsilon_0\hbar} = 1 \text{ a.u.} = \alpha c$$

where $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \simeq \frac{1}{137}$ is the fine structure constant.

It is easiest to introduce a constant which determines the units: $R_\infty = |E_{n=1}|$, the **Rydberg constant**. The ∞ subscript indicates that it is the ground state energy of hydrogen assuming infinite mass. Then

$$E_n = -R_\infty \frac{Z^2}{n^2} \quad \left(\text{strictly, } E_n = -R_\infty \frac{\mu}{m_e} \frac{Z^2}{n^2} \right). \quad (37)$$

The ionisation energy of hydrogen is $|E_{n=1}|$ since it is the energy which must be supplied to the atom to *remove* the electron. Another energy unit can be defined: *Rydberg* = $\frac{1}{2}$ *Hartree*

That probably looks over-complicated, and you're probably thinking "What's the point?" It's all about convenience really, and ease of comparison. There's no point in using metres and seconds when the phenomena we're trying to describe occur on much smaller (or, indeed, much larger) timescales. Atomic units makes comparison with a 'standard' that much easier.

2.8.2 SPECTROSCOPIC UNITS: WAVENUMBERS

Wavenumbers or cm^{-1} are the units favoured by spectroscopists. They are quite odd since they have dimension $[\text{Length}]^{-1}$. One advantage is that if the energies of quantum states are given in this unit one can rapidly infer the wavelength of radiation emitted in transitions between two states.

Consider the energy difference between two states of a hydrogen-like atom (in the infinite mass approximation):

$$E_n - E_m = Z^2 R_\infty \left[\frac{1}{m^2} - \frac{1}{n^2} \right]. \quad (38)$$

This energy difference may appear as radiation of wavelength λ where

$$\frac{hc}{\lambda} = Z^2 R_\infty \left[\frac{1}{m^2} - \frac{1}{n^2} \right]. \quad (39)$$

So we write:

$$\lambda^{-1} = Z^2 \tilde{R}_\infty \left[\frac{1}{m^2} - \frac{1}{n^2} \right]. \quad (40)$$

Now \tilde{R}_∞ defines the unit of the **wavenumber**. (Note: **Beware!** we usually drop the tilde. This could lead to confusion, so check the *dimensions* and the *units* on each side of the equation.)

For the expression $E_n = R_\infty Z^2/n^2$ we can use:

- $R_\infty = 109737 \text{ cm}^{-1}$
- $R_\infty = \frac{1}{2} \text{ a.u.}$
- $R_\infty = 13.605 \text{ eV}$

Remember: These are just different ways of expressing the same quantity, which is the amount of energy needed to remove an electron from the ground state of hydrogen to infinity.

Problem: Excited He^+ ions in a sample are observed to emit radiation at 30.38 nm and 25.63 nm.

What transitions does this radiation correspond to and what other spectral line might one expect ?

Use $R_\infty = 109737 \text{ cm}^{-1}$.

Solution: For the Rydberg formula we have:

$$\lambda^{-1} = Z^2 R_\infty \left[\frac{1}{m^2} - \frac{1}{n^2} \right] \quad (41)$$

Transition 1 has $\lambda_1 = 30.38\text{nm} = 30.38 \times 10^{-7}\text{cm}$. So:

$$\left[\frac{1}{m_1^2} - \frac{1}{n_1^2} \right] = \frac{1}{\lambda_1 Z^2 R_\infty} = \frac{3}{4} \quad (42)$$

The transition is therefore from $n = 2$ to $m = 1$.

Transition 2 has $\lambda_2 = 25.63\text{nm} = 25.63 \times 10^{-7}\text{cm}$. So:

$$\left[\frac{1}{m_2^2} - \frac{1}{n_2^2} \right] = \frac{1}{\lambda_2 Z^2 R_\infty} = \frac{8}{9} \quad (43)$$

The transition is therefore from $n = 3$ to $m = 1$.

We may expect a transition from $n = 3$ to $m = 2$, which would have wavelength λ_3 :

$$\lambda_3^{-1} = \lambda_2^{-1} - \lambda_1^{-1}, \quad (44)$$

by the Rydberg-Ritz Combination Principle. This gives $\lambda_3 = 163.92\text{nm}$.

2.9 REVIEW OF QUANTUM ANGULAR MOMENTUM AND SPHERICAL HARMONICS

Classically, orbital angular momentum, \underline{L} , is given by

$$\underline{L} = \underline{r} \times \underline{p} \quad (45)$$

so that the components are:

$$\begin{aligned} L_x &= yp_z - zp_y \\ L_y &= zp_x - xp_z \\ L_z &= xp_y - zyp_x. \end{aligned}$$

Quantum mechanically we use the *momentum operator* $\hat{p} = -i\hbar\nabla$ and *position operator* \hat{r} which give the *angular momentum operator* $\hat{\underline{L}}$ whose components and length are given by

$$\begin{aligned} \hat{L}_x &= -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\ \hat{L}_y &= -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\ \hat{L}_z &= -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \\ \hat{\underline{L}}^2 &= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \end{aligned} \quad (46)$$

and the **commutation relations** are $[\hat{L}_i, \hat{L}_j] = i\hbar\hat{L}_k$, i, j, k stand for x, y and z

Task for next lecture: verify this commutation relation for $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$

As a consequence the components of $\hat{\underline{L}}$ **cannot be assigned definite values simultaneously** (unless $\hat{\underline{L}} = 0$).

However, $[\hat{\underline{L}}^2, \hat{L}_j] = 0$, i.e. $[\hat{\underline{L}}^2, \hat{L}_z] = 0$

so that we can have **simultaneous eigenfunctions of $\hat{\underline{L}}^2$ and one component of $\hat{\underline{L}}$** (note in general we choose \hat{L}_z).

To understand this, picture $\hat{\underline{L}}$ precessing about the z -axis (we can always rotate the reference frame for this to be the case, see diagram).

The precessional motion preserves $\hat{\underline{L}}^2$ and \hat{L}_z . But the average value of \hat{L}_x and \hat{L}_y are zero.

It is easier to use **spherical polar coordinates**, (r, θ, ϕ) .

$$\begin{aligned} x &= r \sin \theta \cos \phi & 0 \leq r \leq \infty \\ y &= r \sin \theta \sin \phi & 0 \leq \theta \leq \pi \\ z &= r \cos \theta & 0 \leq \phi \leq 2\pi \end{aligned}$$

which gives

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi} \quad (47)$$

$$\hat{\underline{L}}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad (48)$$

The simultaneous eigenfunctions of \hat{L}^2 and \hat{L}_z are called **spherical harmonics**, denoted $Y_{lm}(\theta, \phi)$, and the eigenvalue equations are

$$\hat{L}^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi) \quad (49)$$

$$\hat{L}_z Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi) \quad (50)$$

where $l = 0, 1, 2, \dots$ are the **orbital angular momentum quantum numbers**,

and $m(= m_l) = 0, \pm 1, \pm 2, \pm 3, \dots, \pm l$ are the **orbital angular momentum magnetic quantum numbers** and there are $2l + 1$ values.

Note that l is related to the magnitude of \hat{L} , and m is related to the magnitude of \hat{L}_z by eqs 49 and 50 .

So we find that angular momentum is quantized but not in the same way as in the Bohr picture where we had $L = n\hbar^2$

The spherical harmonics are separable in functions of θ and ϕ :

$$Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta)\Phi_m(\phi) \quad (51)$$

where $\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}$ and $\Theta_{lm}(\theta) \propto P_l^m(\cos\theta)$, the Associated Legendre Polynomial.

$$Y_{lm}(\theta, \phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi} \left[\frac{(2l+1)(l-|m|)!}{2(l+|m|)!} \right]^{1/2} P_l^{|m|}(\cos\theta) \quad (52)$$

The parity of $Y_{lm}(\theta, \phi)$

The parity operator, \hat{P} , corresponds to an inversion of a vector \underline{r} through the origin and is defined by the relation

$$\hat{P}f(\underline{r}) = f(-\underline{r}) \quad (53)$$

If $\hat{P}f(\underline{r}) = f(+\underline{r})$, i.e. $f(-\underline{r}) = f(+\underline{r})$, then the function is said to be **EVEN**.

If $\hat{P}f(\underline{r}) = -f(\underline{r})$, i.e. $f(-\underline{r}) = -f(\underline{r})$, then the function is said to be **ODD**.

Now $\underline{r} \rightarrow -\underline{r}$ gives

$\theta \rightarrow \pi - \theta$ Note: we take θ as shortest angle between $-\underline{r}$ and positive z -axis as $0 \leq \theta \leq \pi$.

$\phi \rightarrow \pi + \phi$. Note $0 \leq \phi \leq 2\pi$

As the parity of P_l^m is given by $(-1)^{l-m}$ and that of $e^{im\phi}$ by $(-1)^m$, we have

$$\begin{aligned} \hat{P}Y_{lm}(\theta, \phi) &= Y_{lm}(\pi - \theta, \pi + \phi) \\ &= (-1)^l Y_{lm}(\theta, \phi) \end{aligned} \quad (54)$$

so the **parity** of $Y_{lm}(\theta, \phi)$ is $(-1)^l$ and

$Y_{lm}(\theta, \phi)$ is EVEN if l is even and ODD if l is odd.

Plot of spherical harmonic probability amplitude

LECTURE 5 SUMMARY

- finite nuclear mass effects are important
- the reduced mass is the effective mass of a system once the centre of mass motion is separated off
- Bohr model of the atom is OK... but not good enough
- atomic units, $\hbar = 4\pi\epsilon_0 = a_0 = e = m_e = 1$, and spectroscopic units (wavenumbers) are useful
- a quantum description of angular momentum is needed
- the operators \hat{L}^2 and \hat{L}_z have simultaneous eigenfunctions, which are the **spherical harmonics**

LECTURE 6

Content

In this lecture we will recap the form of the solution to the radial part of the Schrödinger equation for a hydrogen atom, and compare the solutions to the simple Bohr model. We will look at the degeneracy of the energy levels. Spectroscopic notation will be introduced. The spin part of the wavefunction will be introduced and the unavoidable conclusion that antiparticles are necessary to justify this will be discussed.

Outcomes

At the end of this lecture you will:

- recall the radial solutions to the Schrödinger equation for a hydrogen atom
- know that these represent a probability density
- be able to contrast these solutions with the simple Bohr model
- know spectroscopic notation
- know that the total wavefunction requires a spin component, and that this predicts the existence of antiparticles

2.10 REVIEW OF QUANTUM TREATMENT OF ONE ELECTRON ATOMS

Time-independent Schrödinger eq. for one electron-atoms (in a. u.)

$$\hat{H}\Psi_{nlm}(\underline{r}) = \left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} \right] \Psi_{nlm}(\underline{r}) = E_n \Psi_{nlm}(\underline{r}) \quad (55)$$

where $\Psi_{nlm}(\underline{r}) = R_{nl}(r)Y_{lm}(\theta, \phi)$ can be written as a product of the **radial** and **angular** eigenfunctions of \hat{H} . We solved the angular part last time, so now we will look at the radial part.

Radial Wavefunction (A recap without proofs)

$$R_{nl}(\rho) = N_{nl}e^{-\rho/2}\rho^l L_{nl}(\rho) \quad (56)$$

where we have used **scaled variables**:

$$\rho = \frac{2Z}{n}r \quad (57)$$

$N_{nl} = \left\{ \left(\frac{2Z}{na_0} \right)^2 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right\}^{1/2}$ is a constant for given n, l and Z .

and $L_{nl}(\rho)$ are the **Associated Laguerre Polynomials**

$$L_{nl}(\rho) = \sum_{k=0}^{n_r} (-1)^{k+1} \frac{[(n+l)!]^3}{(n_r - k)!(2l+1+k)! k!} \rho^k \quad (58)$$

with $n_r = n - l - 1$.

Look at the behaviour for large ρ where the exponential term, $e^{-\rho/2}$, dominates So:

- as $r \rightarrow \infty$ we have $R_{nl} \rightarrow 0$ ($\rho \propto r$), as expected since the e^- is bound to the atom.
- The larger Z the faster the exponential decay ($\rho \propto Z$), the e^- is closer to the nucleus.
- The larger n , the slower the decay ($\rho \propto n^{-1}$). Excited states are more extended.

For normalized wavefunction we require:

$$\begin{aligned} \int |\Psi_{nlm}|^2 d\tau &= \int_0^\infty |R_{nl}(r)|^2 r^2 dr && (59) \\ &\times \int_0^\pi |Y_{lm}(\theta, \phi)|^2 \sin\theta d\theta d\phi \\ &= 1 \end{aligned}$$

Notes:

- $r^2 R_{nl}^2$ gives the **probability density** of finding the e^- at a distance r from the nucleus. So to ‘visualize’ the radial function we can look at the integrand of the radial integral as shown in figures for the hydrogen atom.
- Number of peaks in $r^2 R_{nl}^2$ is equal to $n-l$ (From Laguerre Polynomial).
- For a given n the probability of finding the e^- near the nucleus decreases as l increases, because the centrifugal barrier pushes the e^- out. So the low- l orbitals are called penetrating.

Contrast with the Bohr model: we no longer have a uniquely defined radius for the electronic orbit, we have a probability of finding the electron at a distance, r , from the nucleus.

We can define a *mean* radius, but note that in general this is **not** the same as the *most probable* radius.

The radial probability distribution has $n-l$ maxima: for the $(n, l) = (1, 0)$ orbital this means there is one maximum.

Problem:

For the the $(n, l) = (1, 0)$ orbital of hydrogen, wavefunction

$$\psi_{10} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} \exp(-r/a_0) \quad (60)$$

find the most probable radius

Solution

The *probability density* is (the factor of 4π arising from the (θ, ϕ) integration):

$$P_{10}(r) = 4\pi r^2 |R_{10}|^2 = r^2 \underbrace{\frac{4\pi}{\pi} \left(\frac{1}{a_0} \right)^3}_{\text{constant, } \alpha} \exp(-2r/a_0) \quad (61)$$

This is maximum where $\frac{dP_{10}(r)}{dr} = 0$, so:

$$\frac{dP_{10}(r)}{dr} = 2r\alpha \exp(-2r/a_0) + r^2\alpha \frac{-2}{a_0} \exp(-2r/a_0) = 0 \quad (62)$$

so

$$r \left(1 - \frac{r}{a_0} \right) = 0 \quad (63)$$

This has solutions where $r = 0$ (trivial), or $r = a_0$, i.e. the most probable radius is the *Bohr radius*!

To calculate the *average* radius is tedious, as we have to evaluate:

$$\langle r \rangle = \int_0^\infty r P(r) dr = \int_0^\infty 4r^3 \left(\frac{Z}{a_0} \right)^3 \exp(-2Zr/a_0) dr \quad (64)$$

which involves integration by parts **three** times.

Instead I will state a result, that:

$$\langle r \rangle = \frac{a_0}{2Z} [3n^2 - l(l+1)] \quad (65)$$

so we can immediately calculate $\langle r \rangle = 3a_0/2$.

The reason this is larger than the most likely radius is the long tail in the radial probability density.

The first few radial eigenfunctions for a hydrogen-like atom are:

$$\begin{aligned} R_{10}(r) &= 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \\ R_{20}(r) &= 2 \left(\frac{Z}{2a_0} \right)^{3/2} \left(1 - \frac{Zr}{2a_0} \right) e^{-Zr/2a_0} \\ R_{21}(r) &= \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \\ R_{30}(r) &= 2 \left(\frac{Z}{3a_0} \right)^{3/2} \left(1 - \frac{2Zr}{3a_0} + \frac{2(Zr)^2}{27a_0^2} \right) e^{-Zr/3a_0} \\ R_{31}(r) &= \frac{4\sqrt{2}}{3} \left(\frac{Z}{3a_0} \right)^{3/2} \frac{Zr}{a_0} \left(1 - \frac{Zr}{6a_0} \right) e^{-Zr/3a_0} \\ R_{32}(r) &= \frac{2\sqrt{2}}{27\sqrt{5}} \left(\frac{Z}{3a_0} \right)^{3/2} \left(\frac{Zr}{a_0} \right)^2 e^{-Zr/3a_0} \end{aligned}$$

Radial part of the wavefunction for hydrogen

The energy eigenvalues obtained by solving the Schrödinger equation are

$$E_n = -\frac{1}{2n^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right) \frac{\mu}{\hbar^2} \quad (66)$$

Compare this with the expression we obtained using the Bohr model in Lecture 4.

Note: E_n **only** depends on n , but for each value of n we have n values of l ($= 0, 1, 2, \dots, n-1$) and for each each value of l we have $(2l + 1)$ values of m ($0, \pm 1, \pm 2, \pm 3, \dots, \pm l$).

Hence the **total** number of states with the same E_n , i.e. total degeneracy with respect to l and m is

$$\sum_{l=0}^{n-1} (2l + 1) = n^2 \quad (67)$$

Task for next lecture: verify that this is true

The degeneracy with respect to m is a feature of a central potential, $V = V(r)$.

The degeneracy with respect to l is characteristic of the $\frac{1}{r}$ potential (*cf* planetary orbits), and is removed if the dependence on r is modified. This was formerly known as an “accidental” degeneracy, as there was no “obvious” reason for it. Of course that rather depends on what you mean by “obvious” ...

Advance warning: The lifting of this degeneracy when the potential is modified by a small perturbation will become very important in later lectures, so *make sure you're familiar with it now*.

Spectroscopic notation.

Each level is labelled by principal and angular momentum quantum numbers, nl , where l is represented by a letter:

$$l = \begin{array}{cccccc} 0 & 1 & 2 & 3 & 4 & \dots \\ s & p & d & f & g & \end{array}$$

s stands for ‘sharp’, p for ‘principal’, d for ‘diffuse’ and f for ‘fundamental’ or sometimes ‘fine’ (the reasons for these names are historical, and while interesting they are not terribly important for this course).

So the ground state (g.s.) of H is labelled 1s — that is, $n = 1$ and $s \Rightarrow l = 0$ — the first excited states 2s and 2p — that is $n = 2$ and $l = 0$ or 1, and so on. Note again how l takes values from $0 \rightarrow n - 1$.

Transitions between states with any Δn are allowed but as we will see there is a restriction on l and m ; $\Delta l = \pm 1$ and $\Delta m = 0, \pm 1$ (this is called the **electric-dipole selection rule**).

We may also label the n quantum numbers by

$$n = \begin{array}{cccccc} 1 & 2 & 3 & 4 & \dots \\ K & L & M & N & \end{array}$$

This is especially used in notation for X-ray spectra, which we will return to later in the course, so **learn it now!**

2.11 ELECTRON SPIN (AND ANTIPARTICLES)

As experimental techniques improved, many transitions were found to exhibit what became known as *fine structure* e.g., the $2p \rightarrow 1s$ transition in atomic hydrogen was found to be a doublet). We will return to fine structure in a later lecture.

This led to the assignment of an additional quantum number to the electron, *spin*, s , associated with its *intrinsic* angular momentum, \hat{S} (remember these are operators), such that (in analogy with \hat{L}) we obtain the eigenvalue expressions for the simultaneous eigenfunctions of \hat{S}^2 and \hat{S}_z :

$$\hat{S}^2 \chi_{sm_s} = s(s+1)\hbar^2 \chi_{sm_s} \quad \text{with } s = \frac{1}{2} \quad (68)$$

$$\hat{S}_z \chi_{sm_s} = m_s \hbar \chi_{sm_s} \quad \text{with } m_s = \pm \frac{1}{2}. \quad (69)$$

and the spin eigenfunctions χ_{sm_s} are called **spinors**.

So, the **total** wavefunction of the H atom is:

$$\Psi_{nlm_l m_s}(\mathbf{r}) = \underbrace{R_{nl}(r)}_{\text{radial}} \underbrace{Y_{lm_l}(\theta, \phi)}_{\text{angular}} \underbrace{\chi_{m_s}}_{\text{spin}}. \quad (70)$$

The theoretical justification for spin eventually emerged through Dirac's relativistic theory of quantum mechanics. The same theory led to the prediction of antiparticles.

In order to make the Schrödinger equation consistent with the relativistic relation $E^2 = c^2p^2 + m^2c^4$ and to allow for the conservation of angular momentum in a central potential, $V(r)$, Dirac found that he had to allow the electron an *extra* angular momentum, the spin \hat{S} , such that the **total angular momentum**, $\hat{J} = \hat{L} + \hat{S}$, is a constant in a central field of force.

Dirac's theory (1930) also predicted that the allowed values of the total relativistic energy for a *free* electron are:

$$E = \pm\sqrt{c^2p^2 + m^2c^4}, \quad (71)$$

where c is the speed of light, p and m the momentum and rest mass of the electron, respectively.

While in classical theory, the negative energy solutions had been dismissed as unphysical, in quantum theory they could not (e.g., an electron can make a radiative transfer from a state of positive energy to one of negative energy when captured by a ion).

But, if these negative energy states do exist, what prevents ($E > 0$) electrons from jumping to such lower energy states? Dirac removed this difficulty by proposing that the negative energy states are usually full, so that the **Pauli Exclusion Principle** (see next section) prevents further transitions.

The normal state of the vacuum then consists of an infinite density of negative energy electrons. If an electron with $E < 0$ is excited to a state with $E > 0$, the *hole* left behind (or absence of a negatively charged electron with negative mass and negative kinetic energy) would manifest itself as a particle with $E > 0$, charge $+e$, and mass equal to the mass of an electron. This antiparticle of the electron — the **positron** — was observed a few years later (Anderson 1932, Blackett and Occhialini 1933).

The excitation of an electron from a state with $E < 0$ to one with $E > 0$ state is known as e^-e^+ *pair production*; it is an *endothermic* process requiring $E \geq 2mc^2$. The reverse is known as *annihilation*. This is an *exothermic* process releasing energy, most commonly through the emission of two γ -rays with $E \geq 511$ keV each.

LECTURE 6 SUMMARY

- The solutions to the radial part of the Schrödinger equation for the hydrogen atom, $R_{nl}(r)$, include an exponential decay and the associated Laguerre polynomials.
- unlike the Bohr model the electron does not have a fixed orbit, but there is a probability of finding the electron within a certain interval
- The quantity $r^2 R_{nl}^2$ is the radial probability density
- The energy eigenvalues, E_n , scale as n^{-2}
- In spectroscopic notation the angular momentum state is labelled with a letter, $s, p, d, f, g\dots$
- The total wavefunction for the hydrogen atom must include a spin component
- This arises from Dirac's relativistic theory of quantum mechanics, which also predicts the existence of antiparticles