

## LECTURE 14

### Content

Previously we have concerned ourselves with the energy states of an atom. In this lecture we will start to look at **transitions** between the states – transitions that are either *allowed* or *forbidden* by **selection rules**.

### Outcomes

At the end of this lecture you will:

- know that transitions between states are governed by selection rules
- know that selection rules for a transition may be obtained from Fermi's Golden Rule
- be able to explain how the electric dipole selection rules arise from the properties of the spherical harmonics
- be able to apply the electric dipole selection rules to transitions between states to determine which are allowed and which are forbidden

## 4 ATOMS AND ELECTROMAGNETIC FIELDS

### 4.1 ALLOWED AND FORBIDDEN TRANSITIONS

Transitions can occur between quantum states of atoms or molecules by emission or absorption of radiation. But not all are allowed: transitions are governed by **selection rules**.

The main ones we will concern ourselves with are the **electric dipole** selection rules.

Definition of electric dipole moment:  $\underline{P} = e\underline{r}$ .

The dipole of an *optically active electron* interacts with electromagnetic radiation.

Consider a one-electron atom exposed to an oscillating electric field:

$$\underline{E}(t) = \underline{E}_0 \exp[i\omega t] . \quad (1)$$

The Hamiltonian then will have an additional term:

$$H = H_0 - \underline{P} \cdot \underline{E} , \quad (2)$$

where  $H_0$  is the unperturbed Hamiltonian for the electron and  $\underline{P}$  is the dipole moment. It can be a permanent dipole moment, which persists when  $E = 0$ , or an induced dipole due to the field.

We will return to permanent and induced electric dipoles later when we discuss the Stark effect, so **remember them now!**

$V = -\underline{\mathbf{P}} \cdot \underline{\mathbf{E}}$  is a *time-dependent perturbation*, which has a small effect compared to  $H_0$ .

We can consider separately each component ( $x$ ,  $y$  and  $z$ ) of  $\underline{\mathbf{P}} = e\underline{\mathbf{r}} = er(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$ .

Looking at the  $z$  part first:  $V^{(z)} = er \cos \theta E_{0z} \exp[i\omega t]$ , where  $E_{0z}$  is the  $z$  component of  $\underline{\mathbf{E}}_0$  and we have used  $z = r \cos \theta$ .

From **time dependent perturbation theory** we can derive **Fermi's Golden Rule**:

Transitions occur between two quantum states  $i \rightarrow f$  with a probability,  $T_{if}$ , which is given by the square of the matrix element of the perturbation:

$$\begin{aligned} T_{if} &\propto \left| \int \Psi_f^* V \Psi_i d\tau \right|^2 \\ &\propto \left| \int \Psi_f^* r \cos \theta \Psi_i d\tau \right|^2. \end{aligned} \quad (3)$$

For the  $z$  component we are considering. Note: Integral is independent of  $e$  and  $E_z$ , and exponential terms vanish.

If:

- $T_{if} = 0$  the transition is **forbidden**.
- $T_{if} \neq 0$  the transition is **allowed**.

For an atomic state of a one-electron atom,

$$\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta, \phi), \quad (4)$$

(the product of radial and angular parts we had before) and we consider the transition  $nlm \rightarrow n'l'm'$ , where  $nlm$  ( $n'l'm'$ ) are the quantum numbers before (after) the transition.

$$T_{if} = \underbrace{\left| \int_0^\infty R_{nl}^*(r)rR_{n'l'}(r)r^2dr \right|^2}_{\text{radial} = \text{constant}} \times \underbrace{\left| \int_0^{2\pi} \int_0^\pi Y_{lm}^* \cos \theta Y_{l'm'} \sin \theta d\theta d\phi \right|^2}_{\text{angular}}. \quad (5)$$

We have a radial integral which equals some constant,  $C$  (non-zero). Hence the radial integral gives no selection rule.

However, the angular integrals (over  $\theta$  and  $\phi$ ), using properties of Spherical Harmonics, do yield selection rules:

$$\Delta l = \pm 1, \quad (6)$$

$$\Delta m = 0, \pm 1. \quad (7)$$

This result can be obtained using the fact the spherical harmonics are **orthogonal**, that is:

$$\int_0^{2\pi} \int_0^\pi Y_{lm}^*(\theta, \phi) Y_{l'm'}(\theta, \phi) \sin \theta d\theta d\phi = \delta_{ll'} \delta_{mm'}. \quad (8)$$

i.e. the integral is zero unless  $l = l'$  and  $m = m'$  and also that:

$$\cos \theta Y_{lm} = AY_{l+1m} + BY_{l-1m}, \quad (9)$$

where  $A$  and  $B$  are some constants.

So going back to the angular part of equation 5:

$$\int Y_{lm}^* \cos \theta Y_{l'm'} d\Omega = A \int Y_{lm}^* Y_{l'+1m} d\Omega + B \int Y_{lm}^* Y_{l'-1m} d\Omega \quad (10)$$

which, by orthogonality of the spherical harmonics, implies that  $l' = l \pm 1$  and  $m' = m$  for the integral to be non-zero.

A similar analysis, using for the  $x$  and  $y$  parts of the scalar product gives the  $\Delta m = \pm 1$  rule.

These are called the **electric dipole selection rules**:

$$\Delta l = \pm 1, \Delta m = 0, \pm 1$$

They are very important. *Learn them now.*

**Note:** The interaction,  $V$ , we have used to couple the initial and final states does not depend on  $\hat{S}$ , so the spin is not changed by the transition and  $\Delta s = 0$ .

**Remember also** that the  $V \propto \underline{r}$ . Now  $\underline{r}$  has **odd parity**. We know that the integrand in  $T_{if}$  must be **even** for  $T_{if}$  to be non-zero (you should have discussed this in Prof. Fisher's Quantum Course 2B22). Therefore we require the product  $\Psi_f^* \Psi_i$  to be **odd** and therefore the initial and final states have to be of **opposite** parity.

So recap of **electric dipole selection rules for one-electron atom**:

$$\Delta l = \pm 1, \Delta m = 0, \pm 1, \Delta s = 0,$$

and states are of **opposite** parity

Furthermore, if the *spin-orbit* interaction is significant then  $\Delta j = 0, \pm 1$  but not  $j = 0 \rightarrow j' = 0$  (which is forbidden by the change in parity rule).

Note that these are not strict selection rules. Other transitions can occur which would follow the magnetic dipole or electric quadrupole selection rules. These would be found by including further (higher order) perturbations into the Hamiltonian. However, the transition probabilities will be very small compared to those for electric dipole transitions, so that in our case they are in practice not present and we only consider electric dipole selection rules.

**Example:** Which of these transitions are allowed/forbidden ?

$$d \rightarrow s ?$$

$$p \rightarrow s ?$$

$$d \rightarrow p ?$$

### Transitions in multi-electrons atoms.

Similar dipole transition selection rules apply:

- $\Delta J = 0, \pm 1$  but not  $J = 0 \rightarrow J' = 0$ .
- $\Delta M_J = 0, \pm 1$ .
- $\Delta S = 0$ .
- If spin-orbit is weak,  $\Delta L = 0, \pm 1$  but not  $L = 0 \rightarrow L' = 0$ .
- States must have opposite parity.

See diagram of transitions in He.

## LECTURE 14 SUMMARY

- transitions between states are governed by selection rules
- selection rules for a transition may be obtained from Fermi's Golden Rule
- the properties of the spherical harmonics determine the selection rules
- for an electric dipole transition the selection rules are:  $\Delta l = \pm 1$ ,  $\Delta m = 0, \pm 1$ ,  $\Delta s = 0$ , and the states must be of opposite parity.  $\Delta j = 0, \pm 1$  (but not  $j = 0 \rightarrow j' = 0$ ) if spin-orbit interaction is significant

## LECTURE 15

### Content

In this lecture we will begin to examine the interaction between an atom (simplified to having just two energy levels) and a radiation field. We will introduce the processes of absorption, spontaneous emission and stimulated emission and derive the Einstein relations. We will discuss the lifetimes of excited states and the phenomenon of metastable states in preparation for a study of laser action.

### Outcomes

At the end of this lecture you will:

- know and be able to describe the processes by which an atom interacts with a radiation field
- be able to derive the Einstein relations between the coefficients for absorption, stimulated emission and spontaneous emission
- know that an excited state has a finite lifetime that leads to a finite energy width
- know that if selection rules inhibit spontaneous decay the lifetime is extended and the state is metastable

## 4.2 EINSTEIN A AND B COEFFICIENTS

Consider the following fundamental photon-atom processes that may occur when an atoms (simplified to a two-level system) is in equilibrium with a radiation field:

1. **Absorption:** the atom absorbs a photon from the radiation field and is excited to the higher energy state. The rate of absorption is proportional to the population of the ground state and the energy density, i.e.  $\propto N_1 U(\nu_{12})$
2. **Spontaneous emission:** the atoms decays from the excited state emitting a photon. The rate of decay is proportional to the excited state population, i.e.  $\propto N_2$
3. **Stimulated emission:** a photon from the radiation field causes the excited atom to decay, emitting a photon that is *coherent* with the stimulating photon. The rate of emission is proportional to the excited state population and the energy density, i.e.  $\propto N_2 U(\nu_{12})$

The two photons which result from stimulated emission have the same frequency,  $\nu_{12}$ , and are **coherent**, i.e., they are generated in phase. So from a single photon one can get two per stimulated transition. Each of these can go on to stimulate further transitions, leading to a cascade of photons which results in *monochromatic* waves with property of coherence on a large scale. This light-amplification is the basis for the operation of the laser.

**LASER** = **L**ight **A**mplification by **S**timulated **E**mission of **R**adiation

Consider an ensemble of atoms,  $N_1$  in a state with energy  $E_1$  and  $N_2$  in a state with energy,  $E_2$ .

When first exposed to a thermal radiation field (i.e., in which the photons have random orientation and polarization) of spectral energy density,  $U(\nu)$ , the population,  $N_1$  and  $N_2$  will be time-dependent.

The growth and decay of the upper and lower level populations can be expressed via the following *coupled first-order differential equations*:

$$\frac{dN_1}{dt} = \underbrace{CU(\nu_{12})N_1}_{\text{absorption}} - \underbrace{[A + BU(\nu_{12})]N_2}_{\text{spontaneous + stimulated emission}} \quad (11)$$

$$\frac{dN_2}{dt} = [A + BU(\nu_{12})]N_2 - CU(\nu_{12})N_1 . \quad (12)$$

Where  $A, B$  and  $C$  are the constants of proportionality implied previously.

After a sufficient amount of time, equilibrium is reached and

$$\frac{dN_1}{dt} = \frac{dN_2}{dt} = 0 . \quad (13)$$

i.e. in the *steady state* there is no change in the average populations  $N_1$  and  $N_2$ .

Then, from Eqs (11) and (12) we obtain:

$$CU(\nu_{12})N_1 = [A + BU(\nu_{12})]N_2 . \quad (14)$$

or for the ratio of populations:

$$\frac{N_1}{N_2} = \frac{[A + BU(\nu_{12})]}{CU(\nu_{12})} \quad (15)$$

Assuming the atoms to have a Maxwell-Boltzmann distribution (for a system in thermal equilibrium at temperature,  $T$ ) gives the ratio of populations as:

$$\frac{N_1}{N_2} = \frac{\exp[-E_1/kT]}{\exp[-E_2/kT]} = \exp[h\nu_{12}/kT] , \quad (16)$$

where  $h\nu_{12} = E_2 - E_1$ . Substituting Eq. (16) into (15) we obtain:

$$[A + BU(\nu_{12})] = CU(\nu_{12})e^{h\nu_{12}/kT}$$

from which

$$U(\nu_{12}) = \frac{A}{Ce^{h\nu_{12}/kT} - B} = \frac{A/B}{(C/B)e^{h\nu_{12}/kT} - 1} . \quad (17)$$

Comparing Eq. (17) with the spectral energy density characteristic of a black-body field (Planck's formula), i.e.,

$$U(\nu_{12}) = \frac{8\pi\nu_{12}^2}{c^3} \frac{h\nu_{12}}{e^{h\nu_{12}/kT} - 1} = \frac{8\pi h\nu_{12}^3}{c^3} \frac{1}{e^{h\nu_{12}/kT} - 1} ;$$

Hence we can identify

$$C = B \quad \text{and} \quad A = \frac{8\pi h\nu_{12}^3}{c^3} B . \quad (18)$$

These relations were first given by Einstein in 1917.

$A$  is known as the EINSTEIN COEFFICIENT for SPONTANEOUS EMISSION.

$B$  is the EINSTEIN COEFFICIENT for STIMULATED (INDUCED) EMISSION or ABSORPTION (we do not use  $C$  anymore).

These coefficients can be related to the transition probabilities evaluated using Fermi's Golden Rule (see Bransden and Joachain):

$$B = \frac{4\pi^2}{3\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right) |\langle \Psi_i | z | \Psi_f \rangle|^2 \quad (19)$$

### 4.2.1 LIFETIMES

So even an isolated excited atom (i.e., without radiation to stimulate it) will spontaneously decay to a lower state with a probability

$$P_{if} = A_{if} , \quad (20)$$

where  $A_{if}$  is the Einstein coefficient for *spontaneous emission* from state  $i$  to state  $f$ , which can be evaluated using equations (18) and (19).

An excited state,  $i$ , of an atom has a finite **lifetime** obtained by summing over the possible decay paths:

$$\Delta\tau_i = \frac{1}{\sum_f A_{if}} \sim 10^{-9} \text{ s for electric-dipole transitions .} \quad (21)$$

Where  $\Delta\tau_i$  here is obviously a *mean* lifetime.

By the Heisenberg uncertainty principle, there is an associated energy uncertainty:

$$\Delta\tau\Delta E \geq \hbar/2 \quad (22)$$

So, spectral lines are not perfectly sharp; even under the best experimental conditions they have an intrinsic energy width,  $\Delta E \approx \frac{\hbar}{2\Delta\tau}$ .

Therefore if we look at the spectra we have frequency width,  $\Delta\nu$ , the *natural line-width*.

**Remember:** time and energy (or equivalently frequency) are reciprocal variables, so *large* lifetime  $\Rightarrow$  *small* width.

### 4.2.2 METASTABLE LEVELS

If, for a level  $i$ , spontaneous decay is forbidden by electric dipole transitions, i.e.  $A_{if} = 0$  for **all**  $f$ , then the level is **metastable**. These levels are important for laser operation.

However, there are other possible transitions (magnetic dipole, electric quadrupole) but as the probability of them occurring is much smaller, they will lead to a longer lifetime.

E.g., for a 2s level in H, the transition 2s $\rightarrow$ 1s by electric dipole is forbidden as  $\Delta l = 0$ . The lifetime is  $\Delta\tau \sim 0.14$  s as compared to  $10^{-9}$  s for typical electric-dipole.

**LECTURE 15 SUMMARY**

- an atom interacts with a radiation field via absorption, spontaneous emission and stimulated emission of a photon
- the Einstein relations may be derived by considering the equilibrium of the atom with the radiation field
- the excited state has a finite lifetime and finite energy (frequency) width
- an electric dipole forbidden transition has a longer lifetime, producing a metastable state

## LECTURE 16

### Content

In this lecture we will outline the conditions needed to obtain laser action. We will then describe a scientific application of lasers (and an example of research at UCL) – the cooling of neutral atoms.

### Outcomes

At the end of this lecture you will:

- know that stimulated emission photons are coherent, and that this is the basis for laser action
- be able to describe the conditions necessary to achieve laser action in terms of a population inversion and metastable energy levels
- be able to explain how lasers may be used to cool atoms

### 4.3 LASER (Light Amplification by the Stimulated Emission of Radiation)

Stimulated emission means that an atom excited to level 2 can be prompted to decay to level 1 by a photon with energy  $E = E_2 - E_1 = h\nu_{12}$ . Two photons are emitted which are **in phase** or ‘**coherent**’ and have each  $E = h\nu_{12}$ .

The populations of both states will have a Boltzmann distribution, so that  $\frac{N_1}{N_2} = e^{(E_2 - E_1)/kT}$ , and there are many more atoms in state 1 than in state 2, i.e.,  $N_1 > N_2$ . Therefore an incoming photon with energy  $E = h\nu_{12}$  is more likely to be absorbed.

However, if we can make  $N_2 > N_1$ , we have **population inversion**, and an incoming photon is more likely to provoke stimulated emission. The two photons from stimulated emission can go on to stimulate another 2 atoms, then 4, then 8..., etc. A cascade builds up, resulting in an intense, coherent beam of monochromatic light.

**BUT:** we cannot produce a population inversion in a two-level system. If the population starts predominantly in state 1 ( $N_1 \gg N_2$ ) then absorption is most likely. The population of state 2 is increased until  $N_1 = N_2$  (the transition is *saturated*) when absorption and stimulated emission are equally likely. From here you can see that stimulated emission cannot become the dominant process that we need for laser action.

To get population inversion, we can use a three-level system including a *metastable level*.

1. The atoms are pumped with photons of frequency  $\nu_{13}$ .
2. Atoms accumulate in level (3) which decays spontaneously down to level (2).
3. Atoms accumulate in level (2) which is metastable.
4. Levels (2) and (1) now have population inversion.
5. A beam of  $\nu_{12}$  photons can result in laser light at frequency  $\nu_{12}$ .

Theodore Maiman (1960) is usually credited with being the first to demonstrate laser action, using Ruby (a 3 level system) as the gain medium, although his paper was rejected by the journal *Physical Review Letters* as the editor did not consider the content sufficiently different from Maiman's previous work. However Gordon Gould, who was the first to use the term laser, may also be considered to have a claim although he unfortunately delayed filing patents for his inventions.

Lasers are usually based on 3 or 4 level systems.

Lasers have many applications: surgical cutting and welding, precision surveying, communications in fibre optics, holography. . . Also, used by most of us on a daily basis, e.g bar-code readers, CD & DVD players. . . Lasers are also very important tools used in physics to study fundamental physical phenomena and to manipulate atoms, molecules and even micron-sized objects such as living cells.

#### 4.4 LASER COOLING (AN INTRODUCTION)

The 1997 Nobel Prize for Physics (Cohen-Tannoudji, Chu, Phillips) was awarded for this work, and the 2001 Prize (Cornell, Ketterle, Wiemann) for subsequent work on Bose-Einstein condensation of laser cooled neutral atoms.

At UCL two laser cooling experiments (one using caesium and one using rubidium) are being run by Dr Renzoni. Another (using rubidium) is being constructed by Professor Newell.

This technique is most usually applied to alkali atoms: Na, Rb, Cs etc.

At room temperature the rms velocity of an ensemble of atoms is several hundred metres per second. **Example:** caesium,  $m_{Cs} = 2.22 \times 10^{-25} \text{kg}$ ,  $v_{rms} = 137 \text{ms}^{-1}$  (1D), so  $p_{rms} = 3 \times 10^{-23} \text{kgms}^{-1}$ . The momentum carried by a photon of wavelength  $\lambda$  is  $p_\lambda = h/\lambda = 7.8 \times 10^{-28} \text{kgms}^{-1}$  for  $\lambda = 852 \text{nm}$ , relevant for Cs. As you can see a hit by a single photon will have very little effect, as  $p_\lambda \ll p_{rms}$ , but if very very many photons are scattered then the effect adds up and atoms can be slowed to  $\simeq 1 \text{cms}^{-1}$ , which would correspond to a temperature of a few micro-Kelvin.

Atoms are subjected to a pair of counterpropagating lasers of frequency  $\nu_L$ . The laser frequency,  $\nu_L$ , is slightly ‘detuned’ away from the resonant frequency  $\nu_{if}$  of a given atomic transition,  $i \rightarrow f$ .

If  $\nu_{if} > \nu_L$  then one has ‘red’ detuning - this is the case in laser cooling experiments. The detuning parameter is  $\delta = \nu_{if} - \nu_L$ . Importantly, the probability of scattering (that is, absorbing and re-emitting) a photon depends on how close the laser is tuned to resonance - remember that the excited state has a finite energy width.

Suppose that the lasers are aligned along  $\pm z$ . Consider an atom with component of velocity  $v$  along the  $z$  direction. Hence, the laser light, as ‘seen’ by the atom, is **Doppler-shifted**.

The laser light travelling in *same* direction as the atom, will be red-shifted:  $\nu' = \nu_L(1 - v/c)$ , i.e. *further* from resonance so the probability of scattering *decreases*.

The laser light travelling in the *opposite* direction to the atom, will be blue-shifted:  $\nu' = \nu_L(1 + v/c)$ , i.e. *closer* to resonance, so the probability of scattering *increases*.

Hence mainly photons travelling in the opposite direction to the atom’s velocity will be absorbed and there is a net transfer of momentum when a photon is absorbed of  $p = h\nu_L/c$  against the atoms momentum.

The atom will decay spontaneously and emit a photon and the atom will recoil (like a gun) in momentum by an amount  $p = h\nu_L/c$ . However, the direction of emission is *uncorrelated* with the direction of the laser beam, so if we average over many cycles of absorption and emission the effect of the recoil averages to zero, and there is a net momentum transfer from the laser beam to the atoms **against** the atoms original momentum.

As the rate of transfer of momentum (i.e. the *force*) depends on the rate of scattering photons, which depends on the *velocity*, it can be shown that the atom experiences a **net frictional force opposing the direction of motion**:

$$F_z = -\beta v . \quad (23)$$

The form of this force is familiar - it is a **viscous damping**. Faster atoms feel a larger force slowing them down. The result is a *narrowing* of the momentum distribution, as if the temperature was decreased - to as low as  $1\mu\text{K}$ !

An atom trap uses 3 pairs of lasers along  $x$ -,  $y$ - and  $z$ -axis to obtain so-called '*optical molasses*'. This name comes from the analogy of  $F_z$  with a viscous force - to the atoms it is like moving through a sticky viscous liquid.

An inhomogeneous magnetic field is added to confine the atoms. A typical trap may contain  $10^8$  atoms in a volume less than  $1\text{mm}^3$  at a temperature a few millionths of a degree above absolute zero.

A further technique called evaporative cooling (allowing hotter atoms to escape), can be used to cool down to  $10^{-7}$  -  $10^{-9}$  Kelvin (just a few nano-Kelvin!). At these temperatures a Bose-Einstein condensate can form – all the atoms occupy the same quantum state and are described by the same wavefunction.

Theoretical investigation and modelling of cold atom BECs are the interest of Dr Morgan and Professor Monteiro at UCL.

**LECTURE 16 SUMMARY**

- photons emitted in stimulated emission are coherent, which is the basis of the laser
- to achieve laser action needs a population inversion
- this is not possible in a two-level system, so usually a three- or four-level system is used
- lasers can be used to cool atoms by carefully choosing their frequency to exert a velocity dependent force

## LECTURE 17

### Content

In this lecture we will look at the X-ray spectra of atoms that arises as a result of bombarding with energetic electrons.

### Outcomes

At the end of this lecture you will:

- know that X-ray spectra are produced by the bombardment of a metal target by electrons
- be able to describe the principle feature of a typical X-ray spectrum
- know X-ray notation for the characteristic spectrum
- be able to calculate wavelengths of characteristic X-rays from atomic data

## 4.5 X-RAY SPECTRA OF ATOMS

So far we have been concerned with the outer (weakly-bound) electrons which yield optical (visible),  $\lambda \sim 10^{-6}\text{m}$ , or uv spectra,  $\lambda \sim 10^{-7} - 10^{-8}\text{m}$ .

But transitions of *inner* electrons yield X-rays of wavelength  $\lambda \sim 0.1\text{--}10.0\text{ \AA}$  ( $10^{-9}\text{ m}$ ) corresponding to energies 1–100 keV.

They may be produced by bombarding a high  $Z$  target (anode) with energetic electrons from a heated cathode. The kinetic energy of the electrons is determined by  $eV$  where  $V$  is the potential difference between the cathode and anode.

A typical X-ray spectrum consists of two parts:

1. *Continuous* X-rays are generated by fast moving electrons deflected and slowed down in the Coulomb field of heavy atoms. A charged particle emits radiation if accelerated in a field, giving rise to a continuous background of radiation, known as **Bremsstrahlung** (Braking radiation).

The electron initial and final energies,  $E_i$  and  $E_f$ , are *not quantized* (the electron is not confined by a potential) and a continuous spectrum is seen. The limiting case (shortest wavelength) occurs when an electron gives up all its energy, i.e.,  $\nu_{max} = E_i/h$  or  $\lambda_{min} = hc/E_i$ , and this is known as the **cut-off wavelength**.

2. *Characteristic X-ray spectra* are produced by transitions of **inner** electrons. If an electron is excited from an inner shell, it leaves a ‘hole’ which another electron from a higher state energy level can decay into by emission of an X-ray photon. This type of emission is characteristic of individual atoms.

If we assume a hydrogen-like  $1/n^2$  dependence of the energy, then the frequency of the X-rays is given by the energy difference

$$\nu_{if} = \frac{E_i - E_f}{h} = RZ_{\text{eff}}^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right), \quad (24)$$

where  $Z_{\text{eff}} = Z - S$  is the effective charge and  $S$  the screening constant ( $=\sigma_{nl}$  that we have seen in the previous chapter).

They form series (groups of lines):

Transitions to  $n_f = 1$  are called the K-series

Transitions to  $n_f = 2$  are called the L-series

Transitions to  $n_f = 3$  are called the M-series

Within each series,

$\Delta n (= n_i - n_f) = 1$  has subscript  $\alpha$

$\Delta n = 2$  has subscript  $\beta$ ,

$\Delta n = 3$  has subscript  $\gamma$ , etc.

So the lines are denoted e.g.,  $K_\alpha, K_\beta, K_\gamma \dots$

In 1913 Moseley found empirically that the frequencies for a given spectral line (e.g.  $K_\alpha$ ) for several atoms follow the relation:

$$\sqrt{\nu_{if}} = C_n(Z - S) \quad (25)$$

where  $C_n$  is independent of  $Z$  and  $S$  is different for different series. This work led Moseley to identify  $Z$  the atomic number with the nuclear charge and enabled him to predict unknown elements  $Z=43$  (Technetium), 61 (Promethium), and 75 (Rhenium).

Moseley's data gives empirical values for the screening constants of the  $K$  and  $L$  series as

$$S_K = 1; S_L = 7.4$$

**Example:** If 90keV electrons bombard a metal target, what is the shortest wavelength of X-rays ( $\lambda_0$ ) produced?

**Solution:** Energy,  $E = 90 \text{ keV} = 1.44 \times 10^{-14} \text{ J} = hc/\lambda_0$ .  
From this,  $\lambda_0 = 0.138 \text{ \AA}$ .

**Example:** Calcium has atomic number  $Z = 20$ . What is the wavelength of the  $K_\alpha$  line in the X-ray spectrum?

**Solution:**  $K_\alpha$  line has  $n_f = 1$  and  $\Delta n = 1$ , i.e.  $n_i = 2$ .  
So:

$$\begin{aligned} \frac{1}{\lambda} &= R(Z - 1)^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \\ &= 109737 \times 19^2 \times \frac{3}{4} \text{ cm}^{-1} \end{aligned} \quad (26)$$

So  $\lambda_{K_\alpha}^{-1} = 2.97 \times 10^7 \text{ cm}^{-1}$ , or  $\lambda_{K_\alpha} = 3.37 \text{ \AA}$ .

## LECTURE 17 SUMMARY

- X-rays are emitted when a target of heavy metal atoms is bombarded by energetic electrons
- The typical spectrum consists of a continuous background of Bremsstrahlung with characteristic peaks superimposed
- The Bremsstrahlung has a short wavelength cut-off determined by the energy of the electrons, independent of the target material
- The peaks are caused by the removal of an electron from an inner shell and higher energy electrons making a transition to the inner shell by emitting an X-ray photon
- The wavelength of the peaks is characteristic of the target and can be calculated from a Rydberg-type formula when a screening constant is included

## LECTURE 18

### Content

In this lecture we will start to examine the effect of applying an external field (electric or magnetic) on an atom. We will commence with a study of the **Zeeman effect** at low magnetic field, and distinguish between the ‘normal’ and ‘anomalous’ effects, depending on whether spin must be considered.

### Outcomes

At the end of this lecture you will:

- know that an atom interacts with a magnetic field through the magnetic dipole moment
- be able to treat this interaction in the perturbative limit
- be able to evaluate the effect in terms of a shift in energy levels and a splitting of spectral lines

## ATOMS IN EXTERNAL FIELDS

### 4.6 INTRODUCTION

We have studied in detail multi-electron *isolated* atoms using the Hamiltonian:

$$\hat{H} = \hat{H}_0(\underline{\mathbf{r}}_1, \underline{\mathbf{r}}_2, \dots, \underline{\mathbf{r}}_N) + \hat{H}_{\text{LS}} , \quad (27)$$

where  $\hat{H}_{\text{LS}}$  is the spin-orbit term due to **internal** magnetic fields in the atom.

We now consider the effects of **externally applied fields** (e.g. in the laboratory or a star, etc):

$$\hat{H} = \hat{H}_0(\underline{\mathbf{r}}_1, \underline{\mathbf{r}}_2, \dots, \underline{\mathbf{r}}_N) + \hat{H}_{\text{LS}} + V_B + V_E , \quad (28)$$

where

$V_B$  = Interaction with magnetic field (**Zeeman effect**)

and

$V_E$  = Interaction with electric field (**Stark effect**) .

External fields are very important in manipulating atoms - remember laser cooling - slowing atoms with light and trapping with a magnetic field.

We will restrict ourselves to the **perturbative** case:

$$\hat{H}_0 \gg V_B, \quad V_E, \quad \hat{H}_{\text{LS}}$$

This is OK provided the interactions are **small** and they produce only a small shift,  $\Delta E$ , in the energy levels.

For example, remember first-order perturbation theory (as we used for deriving the selection rules for electric dipole transitions from the Fermi Golden Rule) - the energy shift is given by the **matrix element**:

$$\begin{aligned} \Delta E &\simeq \int \psi^* V \psi d\tau \\ E^{\text{TOT}} &= E_0 + \Delta E \end{aligned} \tag{29}$$

where  $\hat{H}_0\psi = E_0\psi$  and  $E_0 \gg \Delta E$

## 4.7 ATOMS IN MAGNETIC FIELDS (ZEEMAN EFFECT)

The **Zeeman Effect** refers to the splitting of spectral lines in a magnetic field because of the change in energy of the levels associated with the magnetic dipole moment interacting with the magnetic field.

You will often see references to the so-called ‘normal’ and ‘anomalous’ Zeeman effects. The names are historical and refer to whether the concept of spin is needed to explain the number of spectral lines. In the days before the discovery of spin the ‘normal’ Zeeman effect fitted the theory, but the ‘anomalous’ zeeman effect could not be explained.

We will consider the Zeeman effect in the limiting cases of weak ( $V_B \ll \hat{H}_{LS}$ ) and strong ( $V_B \gg \hat{H}_{LS}$ ) fields and show how the normal and anomalous effects arise from considerations of spin.

Points to recall from previous lectures: the potential energy arising from a (general) magnetic moment,  $\underline{\mu}_X$ , is:

$$V_B = -\underline{\mu}_X \cdot \underline{B} . \quad (30)$$

Magnetic moments due to spin and orbital angular momentum are:

$$\underline{\mu}_S = -g_S \mu_B \frac{\underline{S}}{\hbar} \quad g_S = 2 , \quad (31)$$

and

$$\underline{\mu}_L = -g_L \mu_B \frac{\underline{L}}{\hbar} \quad g_L = 1 , \quad (32)$$

where  $g_S$  and  $g_L$  are the spin and orbital Landé g-factors.

4.7.1 WEAK FIELD (ZEEMAN) CASE:  $V_B \ll \hat{H}_{\text{SL}}$ **NORMAL ZEEMAN**

First consider an atoms with zero net spin, for example in a  $ns^2$  configuration. The magnetic moment is then due entirely to the *orbital* angular momentum, i.e.  $\underline{\mu} = \frac{-\mu_B}{\hbar} \underline{L}$ .

The interaction energy is  $\Delta E = -\underline{\mu} \cdot \underline{B}$ , so taking the magnetic field along the  $z$ -direction we have

$$\begin{aligned} V_B &= \frac{\mu_B}{\hbar} \underline{L} \cdot \underline{B} \\ &= \mu_B B_z m_l \end{aligned} \quad (33)$$

So a state with orbital angular momentum quantum number  $l$  is split into  $2l + 1$  **equally spaced** levels, with an energy shift that is proportional to  $m_l$ .

Remembering our **selection rules** for an electric dipole transition ( $\Delta m_l = 0, \pm 1$ ), we see that we can make a transition from a state  $(l, m_l)$  to a state  $(l', m_l)$  or  $(l', m_l \pm 1)$ , i.e. a single spectral line is split into **three**.

This is the so-called **normal** Zeeman effect in the weak field case. As you can see it is not widely applicable, as it only occurs for zero net spin. Most atoms with non-zero spin undergo the **anomalous** Zeeman effect.

## ANOMALOUS ZEEMAN

Remember we are in the regime where the external applied magnetic field is much smaller than the internal field of the atom. The spin-orbit interaction couples  $\underline{L}$  and  $\underline{S}$  into  $\underline{J} = \underline{L} + \underline{S}$ , and the external  $\underline{B}$ -field is too weak to uncouple them, so they precess rapidly around  $\underline{J}$ , which in turn precesses slowly around  $\underline{B}$ . As a result we find that  $m_l$  and  $m_s$  are not good quantum numbers.

The interaction energy is:

$$\begin{aligned} V_B &= -\underline{\mu} \cdot \underline{B} \\ &= (g_s \underline{S} + \underline{L}) \frac{\mu_B}{\hbar} \cdot \underline{B} \end{aligned} \quad (34)$$

where  $g_s = 2$ .

In order to evaluate this change in energy we need to use the good quantum numbers  $j$ ,  $l$ ,  $s$  and  $m_j$  and so we must express  $V_B$  in terms of the operators  $\hat{L}^2$ ,  $\hat{S}^2$ ,  $\hat{J}^2$  and  $\hat{J}_z$ .

The interaction is therefore :

$$V_B = \frac{\mu_B}{\hbar} \underline{B} \cdot (\underline{L} + 2\underline{S}) = \frac{\mu_B}{\hbar} \underline{B} \cdot (\underline{J} + \underline{S}) . \quad (35)$$

Taking the  $\underline{B}$ -field along the  $z$ -axis we directly find the contribution to  $\Delta E$  from the first part ( $\underline{B} \cdot \underline{J}$ ) as:

$$\Delta E_J = \int \psi^* \frac{\mu_B}{\hbar} B \hat{J}_z \psi d\tau = \mu_B B m_j. \quad (36)$$

For the second part ( $\underline{B} \cdot \underline{S}$ ):

$$\Delta E_S = \int \psi^* \frac{\mu_B}{\hbar} \underline{B} \cdot \underline{S} \psi d\tau \quad (37)$$

To solve this we note that  $\underline{S}$  precesses around  $\underline{J}$  with a constant projection on  $\underline{J}$  equal to  $S_J$ . All other components will average to zero and therefore we must find the component of  $\underline{S}$  in the direction of  $\underline{J}$ , i.e.

$$\left( \frac{\underline{S} \cdot \underline{J}}{J} \right) \left( \frac{\underline{J}}{J} \right) = \left( \frac{\underline{S} \cdot \underline{J}}{J^2} \right) \underline{J}.$$

Now re-introducing the quantum mechanical operators and using the relation  $\hat{J} = \hat{L} + \hat{S}$  (in a similar manner to what we did with the spin-orbit interaction) to write:

$$\hat{J} \cdot \hat{S} = \frac{1}{2} [\hat{J}^2 + \hat{S}^2 - \hat{L}^2] \quad (38)$$

we get:

$$\Delta E_S = \int \psi^* \frac{\mu_B}{\hbar} B \left[ \frac{\hat{J}^2 + \hat{S}^2 - \hat{L}^2}{2\hat{J}^2} \right] \hat{J}_z \psi d\tau, \quad (39)$$

which can be shown (see Brehm & Mullin or Bransden & Joachain) to be equal to

$$\Delta E_S = \mu_B B m_j \left( \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right) \quad (40)$$

(Note: As you can see in the text books, this results is not obtained by operating with  $\frac{1}{\hat{J}^2}$  to get the  $j(j+1)$  factor in the denominator)

Adding the two contributions, the total energy shift due to the anomalous Zeeman effect is:

$$\Delta E = \mu_B B m_j g_j \quad (41)$$

where  $g_j$  is the **Landé-factor** given by

$$g_j = 1 + \left( \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right). \quad (42)$$

For the many-electron atom case we get a similar result with

$$g_J = 1 + \left( \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right). \quad (43)$$

Note that by introducing another term into the Hamiltonian (i.e. the magnetic dipole interaction) we have lifted **another** degeneracy - that with respect to  $m_j$ .

## LECTURE 18 SUMMARY

- the interaction between an atom and a magnetic field is called the **Zeeman effect**
- the magnetic field interacts with the magnetic dipole moments of the atom that arise from the angular momenta (spin and orbital)
- the interaction can be evaluated in the limit where it is a small perturbation
- if the interaction is smaller than the spin-orbit interaction is is classed as ‘weak’
- the weak field Zeeman effect is classified as ‘normal’ or ‘anomalous’ depending on whether spin is needed to explain the effects
- the Zeeman effect splits a transition into a number of spectral lines

## LECTURE 19

### Content

In this lecture we will continue our study of atoms in external magnetic fields by examining the case of strong magnetic fields known as the **Paschen-Back** effect. We will investigate the effect of the transition from zero through weak to strong magnetic fields on the sodium Fraunhofer doublet.

We will then discuss an application of non-uniform magnetic fields in the **Stern-Gerlach experiment** which demonstrates the quantisation of spin. Lastly we will mention the magnetic moment that arises due to nuclear spin, and the **hyperfine splitting** due to its interaction with the magnetic field of the orbiting electron.

### Outcomes

At the end of this lecture you will:

- be able to explain the splitting of spectral lines in strong magnetic fields (the Paschen-Back effect)
- be able to calculate these splittings and identify allowed transitions
- be able to describe the Stern-Gerlach Experiment and the evidence for the quantisation of atomic angular momentum
- know that the nucleus also possesses spin and that this leads to further splitting of energy levels referred to as hyperfine structure

4.7.2 STRONG FIELD (PASCHEN-BACK) CASE:  $V_B \gg \hat{H}_{LS}$ 

We are now in the regime where  $V_B \gg \hat{H}_{LS}$  so that  $\underline{L}$  and  $\underline{S}$  decouple (**Paschen-Back limit**) and *both precess independently* about the  $\underline{B}$ -field direction, which we will define as the  $z$ -direction.

The precession arises from the **torque** due to the  $\underline{B}$ -field,  $\tau \propto \underline{L} \times \underline{B}$ .

Remember, we saw earlier that the potential energy arising from a (general) magnetic moment,  $\underline{\mu}_X$ , is:

$$V_B = -\underline{\mu}_X \cdot \underline{B}. \quad (44)$$

Remember we showed that

$$\underline{\mu}_S = -g_S \mu_B \frac{\underline{S}}{\hbar} \quad g_S = 2, \quad (45)$$

and

$$\underline{\mu}_L = -g_L \mu_B \frac{\underline{L}}{\hbar} \quad g_L = 1, \quad (46)$$

where  $g_S$  and  $g_L$  are the spin and orbital Landé g-factors.

In the present case the total magnetic moment arises from the orbital angular momentum and the spin angular momentum,  $\underline{\mu} = \underline{\mu}_L + \underline{\mu}_S$ .

In the strong field case we find that as  $\underline{L}$  and  $\underline{S}$  precess independently around  $\underline{B}$  they have constant components in that direction but the magnitude of the resultant,  $\underline{J}$ , is not constant. Taking the  $z$ -axis to lie along the direction of  $\underline{B}$  we find that  $l$ ,  $s$ ,  $m_l$  and  $m_s$  are good quantum numbers.

Again calculating the interaction energy:

$$\begin{aligned} V_B &= -\underline{\mu} \cdot \underline{B} \\ &= \frac{\mu_B}{\hbar} \underline{B} \cdot (\underline{L} + 2\underline{S}) \\ &= \frac{\mu_B}{\hbar} B (\hat{L}_z + 2\hat{S}_z) \end{aligned} \quad (47)$$

So that, in the case of a one-electron atom and taking  $\psi$  as being a normalised eigenfunction, we find:

$$\begin{aligned} \Delta E &= \int \psi^* V_B \psi d\tau \\ &= \int \psi^* \frac{\mu_B}{\hbar} B (\hat{L}_z + 2\hat{S}_z) \psi d\tau \\ &= \frac{\mu_B}{\hbar} B \int \psi^* \hbar (m_l + 2m_s) \psi d\tau \\ &= \mu_B B (m_l + 2m_s) \end{aligned} \quad (48)$$

because the projections of  $\underline{L}$  and  $\underline{S}$  onto the  $z$ -axis are constant and equal to  $m_l\hbar$  and  $m_s\hbar$ .

In the case of multi-electron atom we get:

$$\Delta E = \mu_B B (M_L + 2M_S) \quad (49)$$

What effect does this have on the spectral lines?

The initial and final states are shifted by amounts that depend on  $m_l$  and  $m_s$ . The change in frequency from the zero field case of a component of the line will be given by the difference in the Zeeman shifts of the two states, so

$$\begin{aligned}\Delta(h\nu) &= (m_l + 2m_s)\mu_B B - (m'_l + 2m'_s)\mu_B B \\ &= (m_l - m'_l)\mu_B B + 2(m_s - m'_s)\mu_B B \quad (50)\end{aligned}$$

But remembering our **electric dipole selection rules**  $\Delta m_l = 0, \pm 1$  and  $\Delta m_s = 0$  we see that  $\Delta(h\nu) = 0$  or  $\pm\mu_B B$  i.e. the line is split into **three**, just like in the ‘normal’ Zeeman effect at low field!

**EXAMPLE: SODIUM**

Consider the  $3^2P_{1/2,3/2} \rightarrow 3^2S_{1/2}$  transition.

- If the external magnetic field is **zero**,  $B = 0$ , then we have spin-orbit coupling only:

From your spin-orbit notes

$$\Delta E_{\text{LS}} = \frac{1}{2}A(L, S) [J(J+1) - L(L+1) - S(S+1)] \quad (51)$$

(in atomic units) giving the Landé Interval Rule:

$$\Delta E = \Delta E_{\text{LS}}(J) - \Delta E_{\text{LS}}(J-1) = A(L, S)J.$$

The possible values of  $J$  and energy shifts for the  $P$  levels are

$$\begin{aligned} J = 3/2 & \quad \Delta E_{\text{LS}}(3/2) = A/2 \\ J = 1/2 & \quad \Delta E_{\text{LS}}(1/2) = -A \end{aligned}$$

and then  $\Delta E_{\text{P}} = 3A/2$  as given by Landé Interval Rule. The Na  $3P$  state is split into two states by the spin-orbit interaction with  $\Delta E_{\text{P}} \simeq 17.2 \text{ cm}^{-1}$ .

For the S state  $J = 1/2$ , there is no spin-orbit splitting and  $\Delta E_{\text{S}} = 0$ .

From the selection rules we find two possible transitions,  $3^2P_{3/2} \rightarrow 3^2S_{1/2}$  and  $3^2P_{1/2} \rightarrow 3^2S_{1/2}$ , which gives rise to the famous doublet lines.

- If the external magnetic field is **weak** then we need to account for the spin orbit interaction.

$$\Delta E = \mu_B B M_J g_J \quad (52)$$

and the magnetic Landé g-factor can take the following values:

For the  $3^2S_{1/2}$  level we have  $M_J = \pm\frac{1}{2}$  and  $g_J = 2 \Rightarrow$  the level is split into 2, shifted by  $\pm\mu_B B$ .

For the  $3^2P$  levels we have  $M_J = \pm\frac{1}{2}$  (from  $J = \frac{1}{2}$  and  $\frac{3}{2}$ ) giving  $g_J = \frac{2}{3}$  and  $M_J = \pm\frac{3}{2}$  (from  $J = \frac{3}{2}$ ) giving  $g_J = \frac{4}{3}$ .

Allowed transitions have  $\Delta M_J = 0, \pm 1$ .

This means that the two  $P_{3/2}, P_{1/2} \longrightarrow S_{1/2}$  D-lines in a weak magnetic field split into 10 components. Without the selection rule we would obtain 12 lines (6 upper states  $\longrightarrow$  2 lower states)

- If the external magnetic field is **strong** then we can neglect the spin orbit interaction.

$$\Delta E = \mu_B B (M_L + 2M_S) \quad (53)$$

The  $3^2S$  and  $3^2P$  states split.

For the  $3^2S$ , we have  $M_L=0$  and  $M_S = \pm\frac{1}{2}$

giving  $(M_L + 2M_S) = \pm 1$ .

For the  $3^2P$ , we have  $M_L = 0, \pm 1$  and  $M_S = \pm\frac{1}{2}$

giving  $(M_L + 2M_S) = \pm 2, \pm 1, 0$ .

The selection rules require  $\Delta M_L = 0, \pm 1$  and  $\Delta M_S = 0$ . This gives rise to six possible transitions. However, only three lines are seen because pairs of the transitions have the same frequencies.

## 4.8 STERN-GERLACH EXPERIMENT

Stern and Gerlach (1921) demonstrated the quantization of spin. The experiment can be used to demonstrate the quantization of  $L$  and  $J$  too. Nowadays, this experiment is important in studies of what is called the *measurement problem* in quantum mechanics e.g., wavefunction collapse.

Stern and Gerlach placed Ag atoms  $^2S_{1/2}$  ( $L = 0$ ,  $S = 1/2$ ) in a non-uniform magnetic field, i.e.,  $B \equiv B(z)$ .

The atoms experience a force along  $z$ :

$$V_B = -\underline{\boldsymbol{\mu}}_S \cdot \underline{\mathbf{B}} = 2\mu_B \mathbf{S} \cdot \underline{\mathbf{B}}, \quad (54)$$

$$F_z = \frac{\partial V}{\partial z} = -2S_z \mu_B \frac{\partial B}{\partial z}. \quad (55)$$

Consider a beam along the  $x$ -direction:

Classically, the magnetic moment can point in any direction, so we would expect a uniform spread over the detector plate.

Stern and Gerlach found that for silver the beam splits into two; if  $\partial B/\partial z > 0$  then

Atoms with  $M_S = -1/2$  are ‘pushed’ in the  $+z$ -direction  
 Atoms with  $M_S = +1/2$  are ‘pushed’ in the  $-z$ -direction

This is evidence that the magnetic moment is quantised - it may only take particular values.

However a general angular momentum,  $X$  can take  $2X + 1$  values from  $+X$  to  $-X$  in integer steps, so the two beams observed by Stern & Gerlach imply that the angular momentum of the atom in their experiment is fractional.

The explanation was given by Goudsmit & Uhlenbeck in 1925 who showed that the splitting of spectral lines in a magnetic field (like that we have already discussed) could be explained by the electron possessing an intrinsic magnetic moment and hence an intrinsic angular momentum that we now call spin that can take only two values.

The deflection force will also be experienced by  $\underline{\mu}_L$  or  $\underline{\mu}_J$  as each is associated with an angular momentum.

A beam of atoms with orbital angular momentum,  $L$ , will split into  $(2L + 1) \times 2$  beams; the ‘ $\times 2$ ’ corresponds to the two possible spin states, spin-up and spin-down. Hence, for example,  $^2\text{P}$  atoms will give six beams.

A beam of atoms with total angular momentum,  $J$ , will split into  $(2J + 1)$  beams.

## 4.9 HYPERFINE STRUCTURE

Protons and neutrons are also fermions with a spin  $1/2$ . Hence, many nuclei have a net spin,  $I$ . This is associated with a magnetic moment,

$$\underline{\boldsymbol{\mu}}_I = g_N \mu_N \frac{\mathbf{I}}{\hbar}, \quad (56)$$

where  $\mu_N$  is the **nuclear** Bohr magneton which is very small:

$$\mu_N = \frac{m_e}{m_p} \mu_l \simeq \frac{\mu_B}{1836}. \quad (57)$$

The value taken by the  $g$ -factor,  $g_N$ , depends on the nucleus.

For hydrogen,  $g_N = 5.6$  and for  $^{12}\text{C}$ ,  $^{16}\text{O}$ ,  $g_N = 0$  (since  $I = 0$ ).

Hence,  $\underline{\boldsymbol{\mu}}_I$  produces an analogue of spin-orbit coupling with energy splittings proportional to  $\mathbf{I} \cdot \mathbf{J}$  and  $\mathbf{I} \cdot \mathbf{S}$ .

Thus, we have **hyperfine sub-levels** with total angular momentum:

$$\mathbf{F} = \mathbf{J} + \mathbf{I}, \quad (58)$$

e.g., ground state of hydrogen,  $1s$  ( $j = 1/2, s = 1/2$  and  $I = 1/2$ )) has now two levels labelled  $F=1$  and  $F=0$ .

For transitions between these levels,

$$\Delta E = \frac{hc}{\lambda} = 0.047 \text{ cm}^{-1} \quad (59)$$

which corresponds to  $\lambda = 21 \text{ cm}$  (radio line used to probe interstellar hydrogen clouds).

## LECTURE 19 SUMMARY

- in the limit of strong applied magnetic field spin and orbital angular momentum decouple and precess independently around the field direction
- $m_l$  and  $m_s$  are thus good quantum numbers
- due to the electric dipole selection rules a single spectral line is split into three
- the Stern-Gerlach Experiment provides evidence for the quantisation of angular momentum
- the nucleus of an atom also possesses a nuclear spin  $\underline{I}$ , and magnetic moment  $\underline{\mu}_I$
- $\underline{\mu}_I$  interacts with the magnetic field of the orbiting electron to split energy levels into hyperfine sublevels depending on their value of  $F = I + J$

## LECTURE 20

### Content

In this lecture we will look at the effect of an external electric field on atomic energy levels, i.e. the **Stark Effect**. We will see that for the majority of atoms that do not possess an intrinsic dipole moment there is no change in energy to first order, and it is the electric dipole *induced* by the electric field that produces a shift that is **quadratic** in the electric field. A special case arises for the degenerate (in  $l$  and  $m_l$ ) excited states of hydrogen which behave as though they have an electric dipole moment, and hence the energy change is **linear** in electric field.

### Outcomes

At the end of this lecture you will:

- know that most atoms do not possess an intrinsic dipole moment
- know that their interaction with an external electric field is thus limited to the second order effect of the induced dipole
- be able to describe the energy change in terms of the polarisability of the atom and evaluate it from given data
- know that a special case is the excited state of hydrogen which is degenerate in  $l$  and  $m_l$
- be able to compare and contrast linear and quadratic Stark effects

#### 4.10 ATOMS IN ELECTRIC FIELDS: THE STARK EFFECT

J. Stark (1913) carried out experimental measurements of the splitting of the energy levels of hydrogen in a static electric field (Nobel Prize 1919).

We treat the external electric field,  $\underline{E}_{ext}$ , as a small perturbation:

$$V_E \ll Z/r . \quad (60)$$

If we consider the effect of the field on two opposite charges separated by a distance  $z$ , we find that the extra small term in the Hamiltonian is:

$$V_E = -\underline{\mu} \cdot \underline{E}_{ext} , \quad (61)$$

where  $\underline{\mu} = -e\underline{r}$  is the **electric dipole moment**.

If the field is taken to be along the  $z$ -axis, then

$$V_E = -e\underline{r} \cdot \underline{E}_{ext} = +ezE_{ext} . \quad (62)$$

Note:  $V_E$  is positive, i.e. repulsive and it will decrease the binding energy.

This term gives rise to:

1. Quadratic Stark Effect (most atoms);
2. Linear Stark Effect (in the excited states of hydrogen)

### 4.10.1 QUADRATIC STARK EFFECT

The Quadratic Stark Effect arises in atoms which have no intrinsic dipole moment, which is the case for most atoms. A dipole implies some charge polarization along the  $z$ -direction.

Consider a distribution of charges, the total electric dipole moment will be:

$$\underline{\mu} = \sum_{i=1}^N e_i \underline{r}_i \quad (63)$$

Note that this operator is **odd** under the parity operation. A non-degenerate state (e.g. the hydrogen ground state) which has definite parity therefore cannot possess an intrinsic electric dipole moment as the expectation value  $\langle \psi_{100} | \underline{\mu} | \psi_{100} \rangle$  is zero.

Remember an atom in an s-state:

$\Psi = R(r)Y_{00}(\theta, \phi)$ , the charge distribution ( $\propto |\Psi|^2$ ) is spherically symmetric.

Alternatively,  $\langle V_E \rangle = eE_{\text{ext}} \langle \psi_{100} | z | \psi_{100} \rangle = 0$ .

**But**, the field itself **polarizes** the electron distribution, inducing a separation of charge and a dipole moment that is proportional to  $\underline{E}_{\text{ext}}$ :

The interaction energy is:

$$V_E = -\underline{\mu} \cdot \underline{E}_{\text{ext}} = \frac{1}{2} \alpha E_{\text{ext}}^2 \quad (64)$$

which is a term varying quadratically with the field, where  $\alpha$  is the dipole polarisability.

For the ground state of hydrogen,  $\alpha = 7.42 \times 10^{-41} \text{Fm}^{-1}$ .

The magnitude of the *induced* dipole moment is

$$\underline{\mu} = \frac{\partial V_E}{\partial \underline{E}_{\text{ext}}} = \alpha \underline{E}_{\text{ext}}; \quad (65)$$

This behaviour can be shown using *second order perturbation theory*.

For the ground state of H (1s) and a field  $E_{\text{ext}} \approx 10^8 \text{ V/m}$  we find  $\Delta E \approx 2.5 \times 10^{-6} \text{ eV}$ .

## 4.10.2 LINEAR STARK EFFECT

It occurs for atoms with an intrinsic dipole moment,  $\underline{\mu}_E$ , such as excited states of H and H-like atoms. For these atoms there is  $l$ -degeneracy: all of the s, p, d, ... levels have the same energy. The eigenstates are formed from superpositions of  $l$ -orbitals, e.g.  $n = 2, m = 0$ :

The applied electric field,  $\underline{E} = E_{\text{ext}}\hat{z}$  mixes the states and according to the electric dipole selection rules connects states with  $\Delta l = \pm 1$  and  $\Delta m_l = 0$  (because electric field in  $z$ -direction only).

$$\begin{aligned}\Psi &= R_{20}(r)Y_{00} + R_{21}(r)Y_{10} \\ &= \frac{1}{\sqrt{4\pi}} \left( R_{20}(r) + R_{21}(r)\sqrt{3}\cos\theta \right),\end{aligned}\quad (66)$$

$$(67)$$

which means that

$$|\Psi|^2 = \underbrace{a}_{\text{symmetric}} + \underbrace{b\cos\theta}_{\text{dipole}} + \underbrace{c\cos^2\theta}_{\text{symmetric}} \quad (68)$$

where  $a$ ,  $b$  and  $c$  are functions of  $r$  alone. This, therefore, has a dipole so that  $\Delta E \propto E_{\text{ext}}$ .

The new eigenstates of  $H = H_0 + eE_{\text{ext}}z$  are  $\psi_{2,1,\pm 1}$  and the combinations  $\psi_- = \frac{1}{\sqrt{2}}(\psi_{200} - \psi_{210})$  which is shifted higher in energy, and  $\psi_+ = \frac{1}{\sqrt{2}}(\psi_{200} + \psi_{210})$  which is shifted lower in energy, each by an amount  $V_E = \pm 3eE_{\text{ext}}a_0$ .

Note that  $\psi_{\pm}$  are also eigenstates of the unperturbed Hamiltonian  $H_0$  so no work is done in causing this splitting, and the energy is linear in  $E_{\text{ext}}$ .

The excited state behaves as though it had an electric dipole of magnitude  $3ea_0$ .

for comparison with the previous discussion, in an electric field of  $E_{\text{ext}} = 10^8 \text{Vm}^{-1}$  the change in energy is  $\pm 1.6 \times 10^{-3} \text{eV}$ .

For hydrogen:

$n = 1$  has only s-state  $\longrightarrow$  so Quadratic Stark Effect.

$n > 1$  has Linear Stark Effect.

Since  $E_{\text{ext}}$  is small:

QSE	$\propto F^2$	small splitting $\ll 1.0 \text{cm}^{-1}$ .
LSE	$\propto F$	larger splitting.

## LECTURE 20 SUMMARY

- most atoms (with non-degenerate energy levels) have zero electric dipole moment and so their interaction with an electric field is zero to first order
- however an electric field polarises the atom to induce a dipole moment proportional to the applied field
- the interaction energy is thus quadratic in electric field,  $\frac{1}{2}\alpha E_{ext}$
- an exception is the excited states of hydrogen that are degenerate in  $l$  and  $m_l$
- an electric field mixes these states to produce an energy shift linear in  $E_{ext}$