- **Candidates should be able to** :

  - Explain how **spectral lines** are evidence for the existence of **discrete energy levels** in isolated atoms (i.e. in a gas discharge lamp).

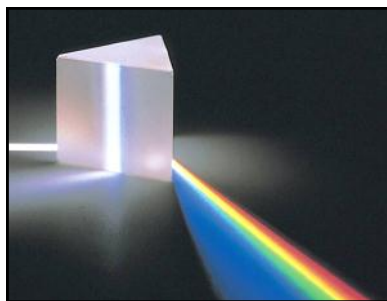 - Describe the origin of **emission and absorption line spectra**.

  - Use the relationships :
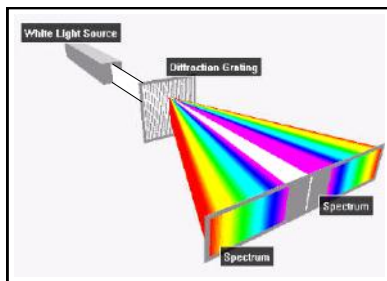
$$hf = E_1 - E_2$$

$$\frac{hc}{\lambda} = E_1 - E_2$$

- **SPECTRA**

We have already seen how a **visible light spectrum** can be formed by directing a narrow beam of white light at a triangular glass prism or at a diffraction grating.


The spectrum obtained is **CONTINUOUS** (i.e. there are no gaps in it) and contains light wavelengths in the range **~400 nm to ~700 nm**.

EMISSION LINE SPECTRA

When a gas discharge lamp is viewed through a narrow slit and a diffraction grating, an **emission line spectrum** is seen.
This consists of separate coloured lines (images of the slit) on a black background. Each coloured line has its own unique wavelength.

The line spectra shown below are those obtained using helium and mercury vapour lamps.

HELIUM — wavelength

MERCURY — wavelength
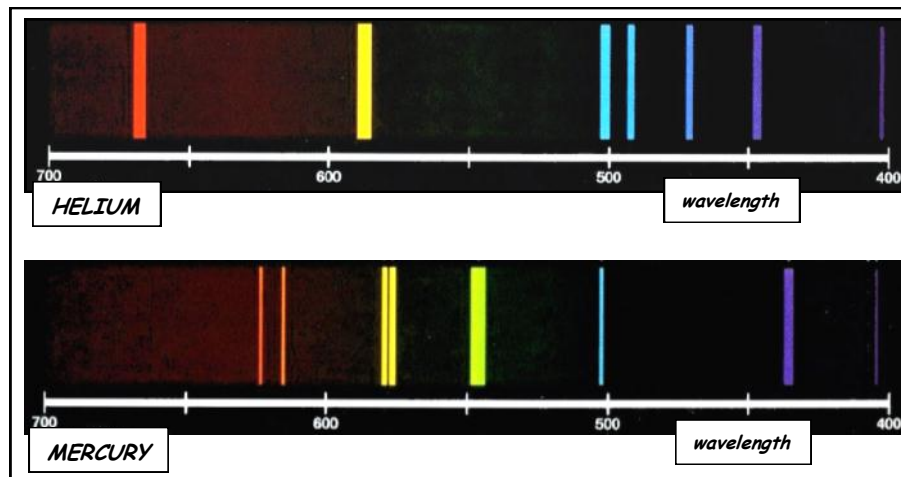
The line spectrum for any given element is unique and can therefore be used to identify the element.

The British astronomer William Huggins successfully identified the most common elements found in stars by studying the emission line spectra obtained from starlight.

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ABSORPTION LINE SPECTRA

Absorption line spectra are obtained when **white light** has passed through cool gases and they consist of **black lines** on a continuous white light spectrum background.

CONTINUOUS SPECTRUM

EMISSION LINE SPECTRUM

ABSORPTION LINE SPECTRUM

The black lines are formed because the elements present in the cool gas have absorbed certain discrete wavelengths of the white light passing through the gas.

A star emits white light containing all the wavelengths in the visible spectrum and when this light passes through the cooler outer layers of the star certain wavelengths will be absorbed to give an absorption line spectrum.
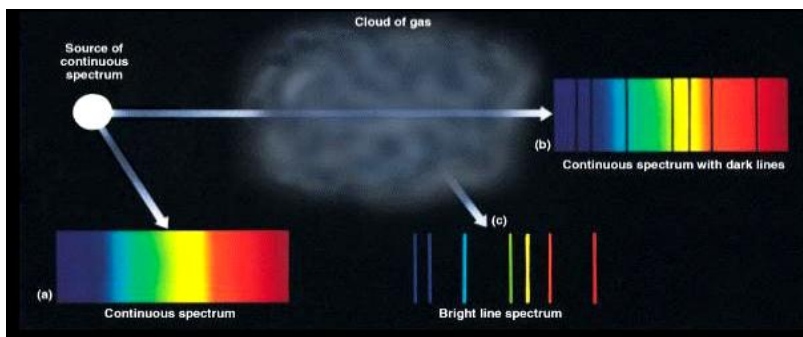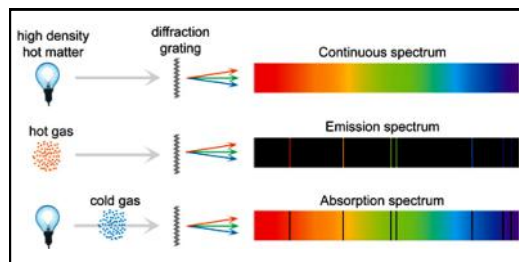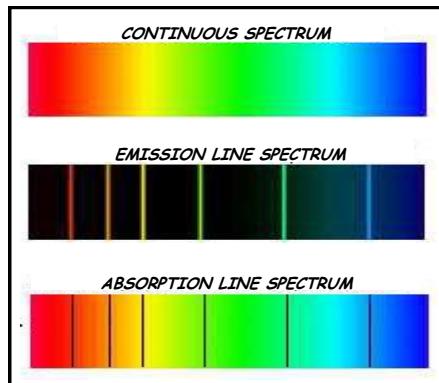

The Sun's spectrum (shown above) has many dark lines (absorption spectra) which are caused when light of specific wavelengths is absorbed by the cooler atmosphere around the Sun.

It should be noted that the dark lines correspond to the emission lines of the various elements contained in the atmosphere through which the Sun's light passes. This is because atoms can emit or absorb at the same wavelengths.

- **THE ORIGIN OF LINE SPECTRA**

- The appearance of line spectra (i.e. that the lines represent light of certain discrete wavelengths only) tells us that **the electrons in atoms can only absorb or emit photons of certain fixed energies**. This means that **the electrons in an atom can only have certain fixed values of energy**.

The diagram opposite shows the **permitted** or **allowed** energy levels for the simplest atom **(hydrogen)** consisting of a single proton and a single electron. The electron cannot have an energy which lies in between these levels.
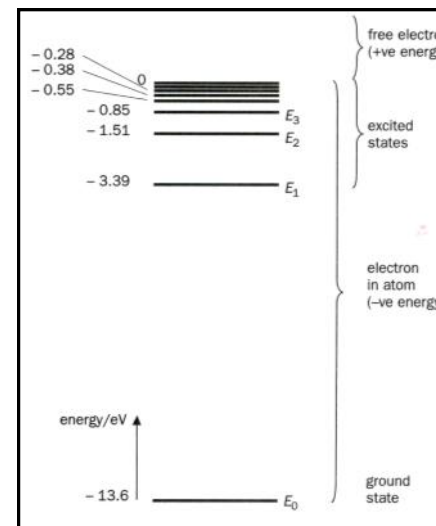
NOTE
The energy levels have **negative values**. This is because the electron is held within the atom by the electrostatic attraction of the nucleus and energy has to be supplied to remove it from the atom.

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- An atom **emits** light when one of its electrons falls from a higher to a lower energy level.
The movement of an electron from one energy level to another is called a **transition.**

Photon of frequency (f) and wavelength (λ) is emitted.
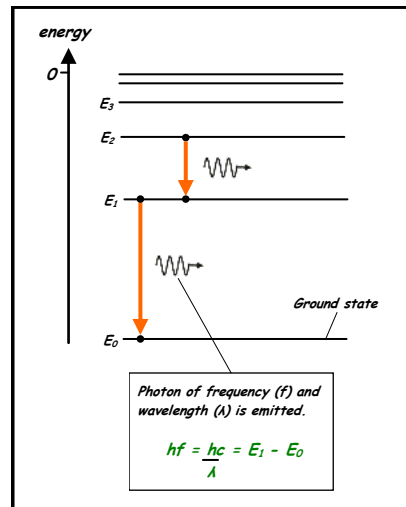
$$hf = \frac{hc}{\lambda} = E_1 - E_0$$

The energy of the emitted photon = The energy lost by the electron in the transition = The energy difference between the two levels involved.

$$hf = \frac{hc}{\lambda} = E_1 - E_0$$

The greater the energy difference between the energy levels involved in a given transition, the greater is the energy of the emitted photon.

Also, since $hf = hc/\lambda = E_1 - E_0$: The **greater the energy difference** of a transition, the **higher is the frequency (f)** and **the shorter is the wavelength (λ)** of the emitted photon.

The fact that the atoms of **different** elements have their own **unique** energy levels means that the wavelength of photons emitted are unique to the atom. For this reason, **different elements** produce distinct line spectra from which they can be identified.

- We can use similar reasoning to explain how **absorption line spectra** are produced when white light passes through a cool gas.

White light consists of photons having a continuous range of energies and wavelengths. So when white light passes through a particular gaseous element, the only photons absorbed are those whose energy is exactly equal to one of the energy jumps between the various energy levels of the element concerned.

Photon whose energy is NOT equal to the energy difference between any two levels is NOT ABSORBED.

Photon of frequency (f) having energy (hf) exactly equal to (E_1 - E_0) is ABSORBED and lifts an electron from E_0 to E_1.

The resultant observed spectrum is then continuous, except for those particular wavelengths which have been absorbed (i.e. black lines on a continuous spectrum background).
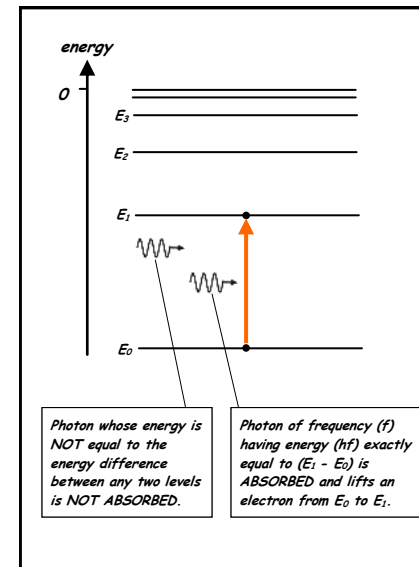
- **ISOLATED ATOMS**

The atoms in a gas are considered to be **ISOLATED** atoms because they are relatively far apart and so have minimal interaction with each other. As a result, discrete **LINE SPECTRA** obtained from hot gases.

In solids and liquids, the atoms are much closer together and so there is considerable interaction between the electrons from neighbouring atoms. This gives rise to a large number of closely spaced energy levels. As a result, the electromagnetic radiation emitted from solids and liquids forms spectra in which there are large numbers of lines which are so close together that they appear to be bands **(BAND SPECTRA).**

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- **PRACTICE QUESTIONS**

1   Complete the following :

- A **CONTINUOUS** visible light spectrum is one having all the wavelengths in the range ………………… nm to ………………… nm with no ……………… in between.

- An emission ……………… spectrum has only a few wavelengths, while the ………………………………… spectrum for the same element is a continuous spectrum with those same wavelengths missing.

- An emission ……………… spectrum is produced when electrons in an atom of a given element fall from …………………. to …………………. energy ……………….

- Emission ……………… spectra are obtained from hot gases because their atoms are relatively far apart and so do not …………………………… with each other.

- The **LINE** spectrum from any given element is ………………………… and can therefore be used to ……………………………… the element.

- ……………………………… **LINE** spectra are obtained when …………………… light has passed through cool gas and they consist of …………………… lines on a continuous white light spectrum background.

- At atom emits light when one of its ……………………………… falls from a ……………………………… to a ……………………………. energy level and this movement is called a ………………………………

- The greater the energy difference involved in a particular electron ……………………………… , the ……………………………… is the energy of the ……………………… emitted and the ……………………………… is its wavelength.

2   The diagram opposite shows a simplified energy level diagram for an atom.

The arrows represent three electron transitions between the energy levels. For **each transition** :

(a) Calculate the **energy** of the emitted or absorbed photon.

(b) Calculate the **frequency** and **wavelength** of the emitted or absorbed photon.

(c) State whether the transition contributes to an **EMISSION** or an **ABSORPTION** spectrum.
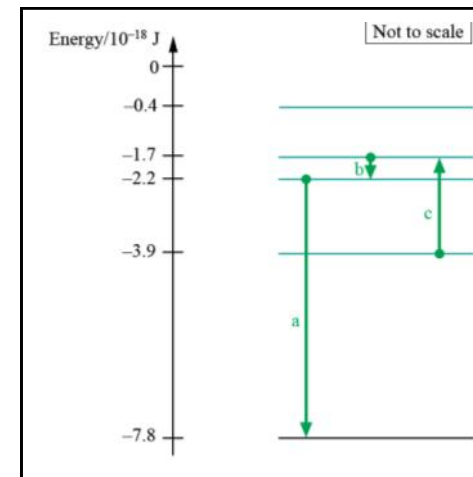
3   The emission spectrum from a particular element shows three lines of wavelength **445 nm, 586 nm** and **667 nm** respectively.

(a) Calculate the **energies** of the emitted photons which have produced the three lines in the spectrum (i) in **J** and (ii) in **eV.**
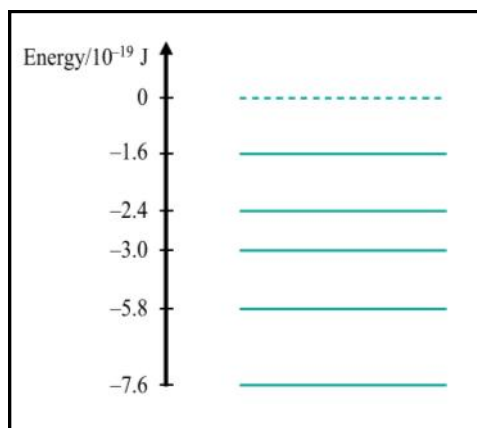
(b) Draw the **energy level** diagram for an atom of the element which has produced these photons and show the **electron transitions** which have given rise to the three spectral lines.
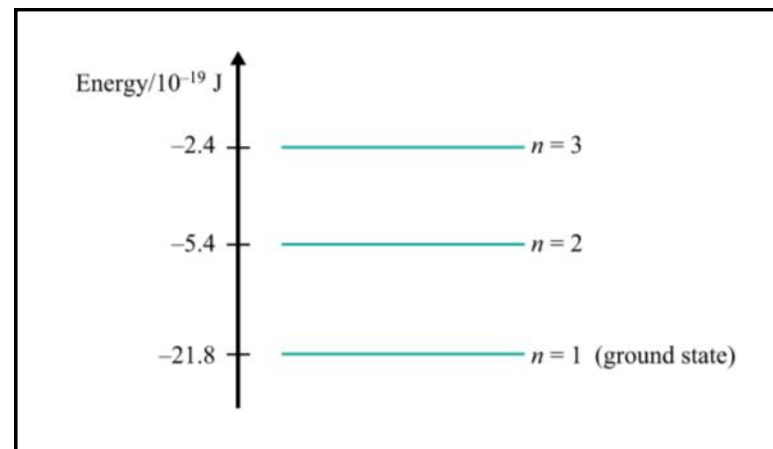
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| HOMEWORK QUESTIONS |

1 The spectrum of sunlight has **dark** lines. These dark lines are due to the absorption of certain wavelengths by the cooler gases in the atmosphere of the Sun.

(a) One particular dark spectral line has a wavelength of 590 nm. Calculate the energy of a photon with this wavelength.

(b) The diagram opposite shows some of the energy levels of an isolated atom of helium.

Energy/10^{-19} J

- 0
- −1.6
- −2.4
- −3.0
- −5.8
- −7.6

(i) **Explain** the significance of the energy levels having **negative values**.

(ii) **Explain**, with reference to the energy level diagram shown above, how a **dark** line in the spectrum may be due to the presence of helium in the atmosphere of the Sun.

(iii) All the light absorbed by the atoms in the Sun's atmosphere is **re-emitted**.
Suggest why a dark spectral line of wavelength **590 nm** is still observed from the Earth.

2 The diagram below shows some of the energy levels of an isolated hydrogen atom.

5

Energy/10^{-19} J

- −2.4 ——————— $n = 3$
- −5.4 ——————— $n = 2$
- −21.8 ——————— $n = 1$ (ground state)

The lowest energy level of the atom is known as its **ground state.** Each energy level is assigned an integer number n, known as the principal quantum number. The ground state has $n = 1$.

(a) **Explain** what happens to an electron in the ground state when it absorbs the energy from a photon of energy **21.8 $\times$ 10^{-19} J.**

(b) (i) **Explain** why a photon is emitted when an electron makes a transition between energy levels of $n = 3$ and $n = 2$.

(ii) Calculate the **wavelength** of electromagnetic radiation emitted when an electron makes a jump between energy levels of $n = 3$ and $n = 2$.

(iii) Use the energy level diagram above to show that the **energy E** of an energy level is **inversely proportional** to n^2.

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