Session 11

Atoms and Light

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Contents

Welcome

Welcome to session 11. In this session we shall look at how light interacts with atoms. This will enable us to determine the internal structure of atoms and also the quantum behaviour of light.

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Learning Objectives

- Give the experimental basis for the nuclear atom and the Bohr model, including the photoelectric effect as evidence for light quanta
- Show a knowledge of the limitations of the Bohr model
- Account in principle for the periodic table from electronic structure and the Pauli principle
- Distinguish between spontaneous and stimulated emission and explain in principle how a laser works
- Give an account of the thermal equilibrium of radiation and matter including the Planck spectrum

The Problem

The problem statement for this session is a bit different from usual: we've given you an equation. Once you understand this equation you should understand the major issues in radiation physics.

$$h\nu = kT$$

Let's begin by defining the symbols:

h is a fundamental constant of physics called Planck's constant with the dimensions of energy times time. h = $6.62\text{x}10^{-34}$ Js or $4.14\text{x}10^{-15}$eVs

ν is the frequency of radiation in the system. In the optical region we can think of this as the colour of light.

k is another constant of nature called Boltzmann's constant. It has the units of energy per degree so we can think of it as a conversion factor from temperature to energy units. We'll meet it again when we study thermodynamics. k =$1.38\text{x}10^{-23}$ JK^{-1}

T is the temperature of matter in thermal equilibrium with the radiation field. We'll explain this more fully later.

What do the symbols mean?

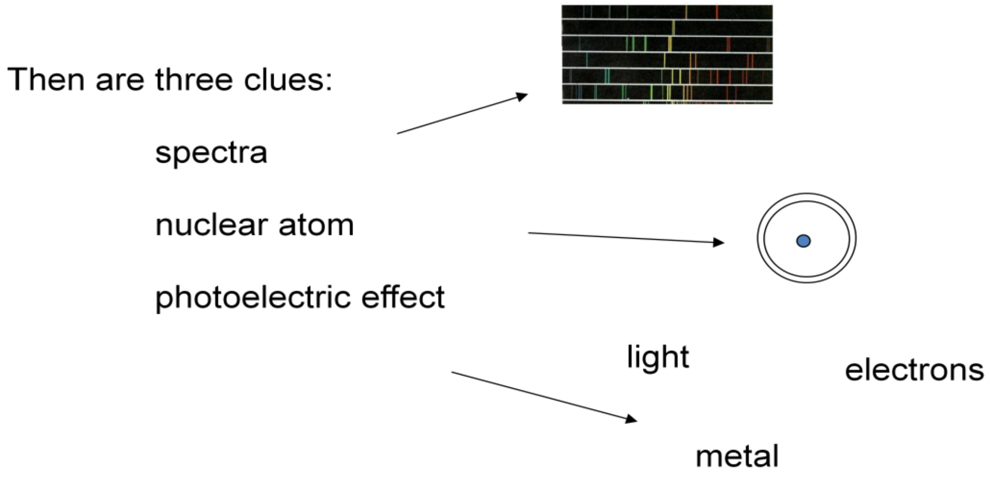
Learning Issues

$h\nu$ and kT are energies. What are they the energies of?

Systems with temperature are in thermal equilibrium - what is in equilibrium here?

Structure of the Atom

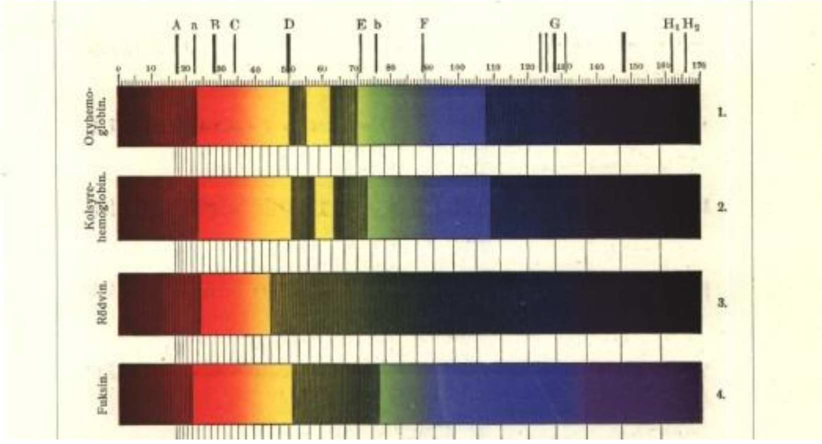
We shall investigate three clues:



1. Atoms emit and absorb radiation in narrow ranges of frequency called spectral lines. The spectral lines together make up a spectrum. These spectra have complicated patterns, which must reflect the internal structures of the atoms to which they belong. This is our first clue. The illustration shows the emission of light from various elements spatially dispersed into a spectrum.
2. Our second clue is evidence that the positive charge in the atom is concentrated at its centre: most of the atom is empty space, which is itself a problem to which we shall return in session 13. The illustration is a cartoon of an atom with a central nucleus and a surrounding distribution of electrons.
3. Finally, the emission of electrons from metals illuminated by ultraviolet light gives us evidence of the structure of light. Why is this an essential clue to the structure of atoms? Because, as we'll see, in showing how light must interact with atoms, it provides a vital step in the solution to the problem of atomic structure.

Clue 1: Spectra

Here’s what some emission spectra look like.



Image[1]

The emitted light has been dispersed in wavelength (or frequency) to show the different emission lines spatially separated. Atoms emit radiation at these wavelengths when excited, for example by collisions with other atoms, or with electrons. This can be achieved by heating the gas, or passing an electric current through it. Also, atoms absorb at just these same wavelengths any light that falls on them.

Why do atoms when excited, emit radiation at just these characteristic wavelengths? In other words, what is it that happens in the excited atom that causes it to emit light? And conversely, what happens in the atom when it absorbs light?

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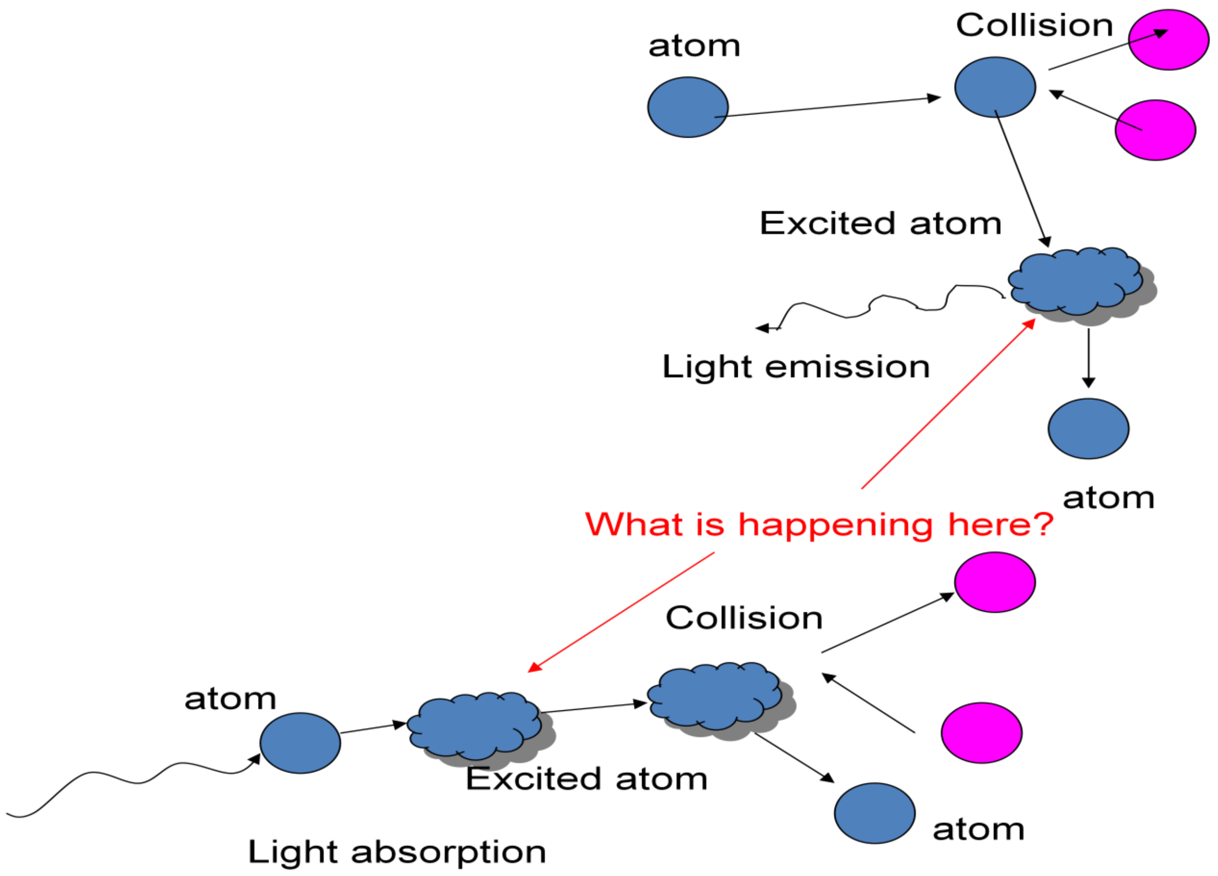
[1] Ugglan_spektrum2, Nordisk Familjebok, as posted on www.commons.wikimedia.org. Creative Commons Licensed



Let’s simplify the problem a bit by concentrating on the spectrum of the simplest atom, namely hydrogen. Here the line spectrum divides into several separate series, named after the researchers who first investigated them in detail. Figure 1 shows some of these series.

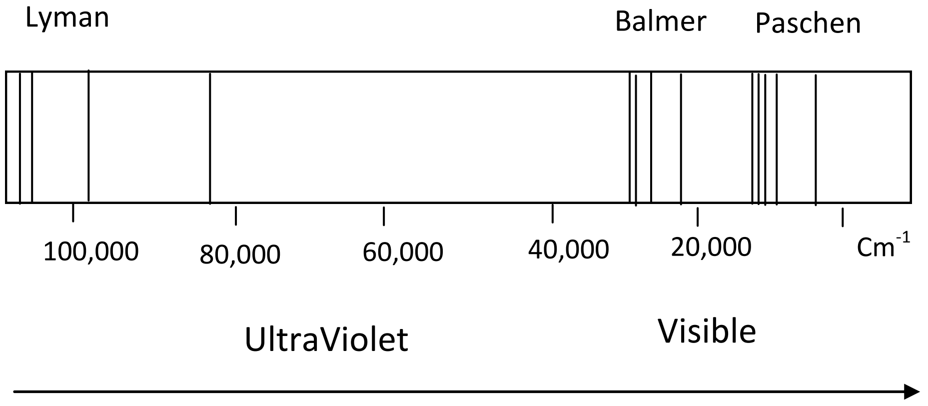


Figure 1: Emission spectrum of heated hydrogen

Figure 2 shows the Balmer series in detail, with the lowest frequency line labelled Hα.

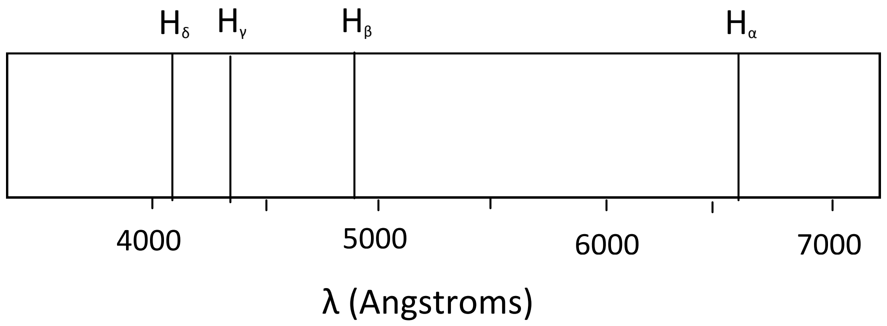


Figure 2: The Balmer Series

Remarkably, the frequencies of the lines in each series can be represented by a simple formula - they are proportional to the difference of the reciprocals of the squares of integers, equation (1). Any acceptable theory of atomic structure will have to provide an explanation of these oscillation frequencies.

$$\nu = cR\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad (1)$$

or: $$h\nu = 13.6\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ eV}$$

Where R (the Rydberg Constant) = 10 973 731.6 m^{-1}

Balmer: $n_1=2$, $n_2=3, 4\ldots$

Lyman: $n_1 = 1$, $n_2 = 2,3\ldots$

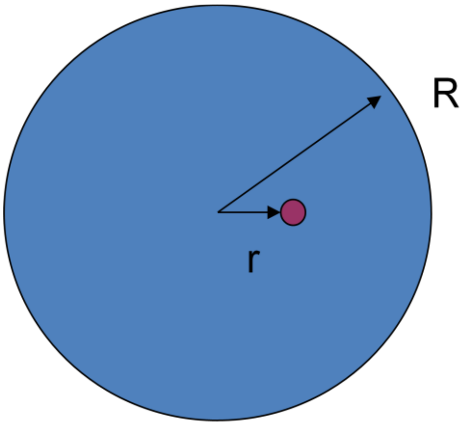
The largest wavelength (lowest frequency) in the Brackett series in hydrogen is 4053 nm. Work out a formula (ie gives the values of n_1 and n_2) for the Brackett series

Clue 2: Nuclear Atom

Our second clue comes from evidence of the internal structure of the atom itself. To set this in context let's begin by looking at an attempt by J. J Thomson to produce a picture of the inside of an atom. Recall that even up to the beginning of the 20th century atoms were regarded as indivisible. Thompson was led to a different conclusion by his discovery of the electron as a constituent of atoms. Thomson's model distributed the positive and negative charge uniformly through the atom in what looked like a plum pudding, with the electrons as the plums, and the positive charge as the pudding. This arrangement of changes is stable.

We can get some Idea of the frequencies of oscillation associated with this model by looking at the motion of an electron disturbed from its equilibrium position.

An electron at radius r will be attracted by the charge within a sphere of radius r, and unaffected by the charge beyond r.



Assuming that the charge q is uniformly distributed within r -and ignoring the influence of the other electrons - the force on the electron is $qe/4\pi\varepsilon_0 r^2$. Equating the force to mass times acceleration gives us equation (1).

$$m\ddot{r} = -\frac{\frac{4}{3}\pi r^3 \rho e}{4\pi\varepsilon_0 r^2} \quad (1)$$

$$\ddot{r} = -\frac{Ne^2}{4\pi\varepsilon_0 m R^3} r \quad (2)$$

Now, the positive charge within the atom of radius R is just N e. So the charge density $\rho = Ne/(4/3\ \pi R^3)$. Inserting this in equation (1) gives us equation (2). This is the equation for simple harmonic motion. Before continuing, see if you can determine the frequency of oscillation and work out a rough order of magnitude. We can assume that this atom would emit radiation with a frequency equal to its frequency of oscillation. Was Thomson in the right area?

This is SHM – what is the frequency?

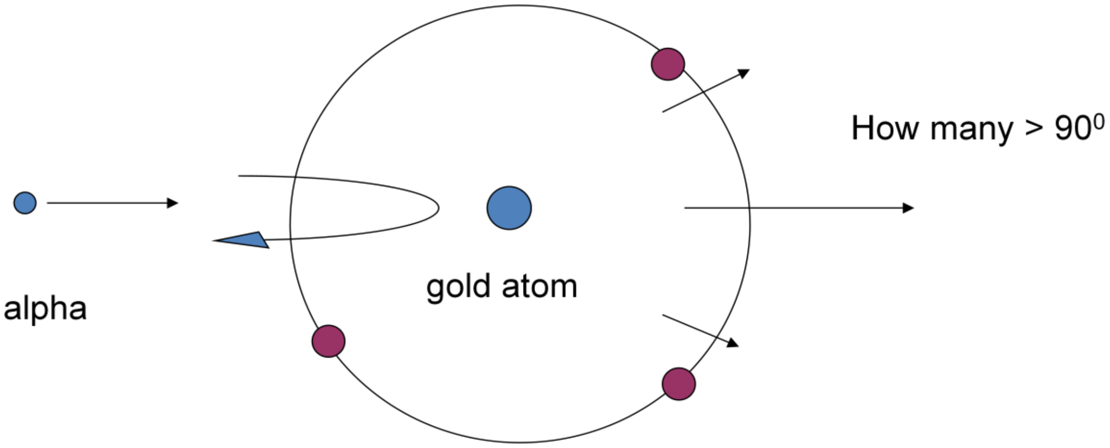
Giving a frequency of oscillation $\frac{1}{2\pi}\sqrt{\frac{Ne^2}{4\pi\varepsilon_0 mR^3}}$. Put in the constants to get the order of magnitude.

For N=1, that is a hydrogen atom, we get a wavelength of about 250 nm in the UV – but of course this is the only line!

Structure of the atom: Rutherford Nuclear Atom

Thomson's model failed in detail, but a plum pudding type of picture was generally accepted prior to Rutherford's experiments of 1911. In these experiments alpha particles were fired at a thin film of gold foil. Gold was used because it can be rolled to a thickness of only a few atoms thereby ensuring that the alpha particles would hit at most one target atom.

The results were a death blow to the plum pudding picture. Instead of passing straight through the diffuse charge, occasionally an alpha partite would be tuned through 180, back to the source. Rutherford realised that this could happen only if the positive change were concentrated at the centre of each atom. This is the Rutherford nuclear model of the atom. He assumed that the force was electrostatic, so only a very compact nucleus would generate a high enough field to reverse the motion of an alpha particle.



Rutherford was able to obtain a formula for the number of alpha particles scattered through an angle greater or equal to θ, by assuming that there was no transfer of momentum from the alpha particle to the atom. We have given you the way in which one version of Rutherford's formula depends on θ in equation (1).

Rutherford formula: The fraction of particles scattered through an angle θ or greater is:

$$f = \pi n t \left(\frac{Ze^2}{4\pi\varepsilon_0 T} \right)^2 \cot^2 \theta / 2 \qquad (1)$$

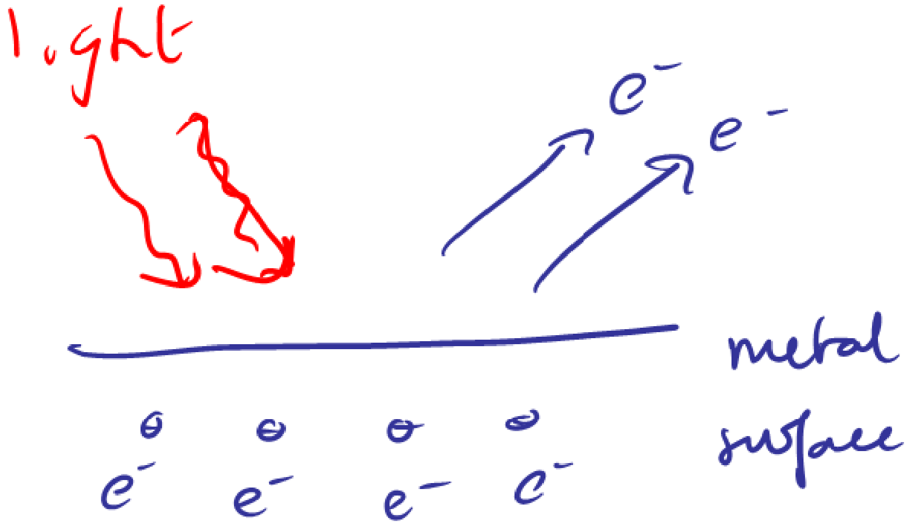
We can use this to work out the fraction of particles scattered through more than 90^0.

The result is not very large – only a few times 10^{-5}; (The result is $f = 3.8\text{x}10^{-5}$) but the Thomson model predicts zero and the appearance of energetic particles turned back on themselves by a thin sheet of gold foil came as a shock when it was first discovered.

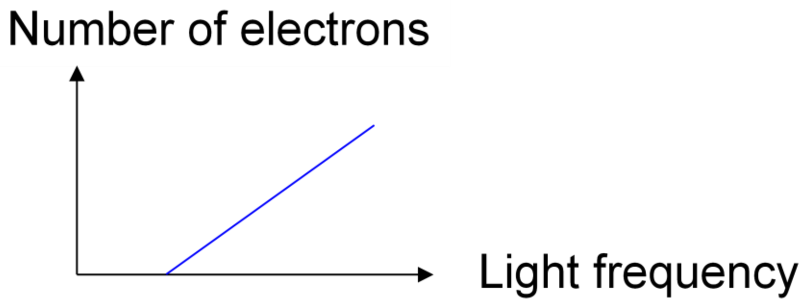
Clue 3: The Photoelectric Effect

Our final clue to the structure of the atom comes from an unlikely source, namely the photoelectric effect. The importance of the clue was that it enabled Einstein to deduce the particle nature of light, which was crucial to an understanding of how light and atoms interact, and hence to how spectra are formed.

Before we explain the effect let's look at what we might expect. Imagine shaking a dusty carpet. The amount of dust coming out will depend on the frequency with which you shake the capet, and the energy of the dust will depend on how hard you shake it. The photoelectric effect is quite different.



When ultraviolet light is shone on to a metal surface electrons are ejected from the surface. We might expect that the more intense the light beam the more energetic the electrons would be. In fact, increasing the intensity increases the number of electrons emitted. We might also expect that the higher the frequency of the light the higher the rate of ejection of electrons – think perhaps of each cycle of a wave ejecting an electron. In fact, raising the frequency raises the energy of the emitted electrons. There's one complication, namely that below a certain frequency of light no electrons at all are ejected.



Incidentally, the experiment is quite difficult to perform: it requires that the clean metal surface is held in a good vacuum.

Expect:	More intense light implies faster electrons	Higher frequency light implies more electrons
Observe:	More intense light implies more electrons	Higher frequency, above a certain threshold, implies higher speed electrons

There's one very serious problem that any classical picture of the photoelectric effect has to face. Classically a wave impinging on a metal would take time to supply an electron with the few electron volts of energy it needs to escape. For an incident flux of 1000 W m^{-2}, an electron, which has an effective size of 6.65 x 10^{-29} m^2 interacting with radiation, would take a few months to collect the energy it requires to escape. In practice however, the electrons are ejected in less than 10^{-9} seconds –immediately in effect. How is this possible?

Einstein's Solution

The explanation of the photoelectric effect was given by Einstein in 1905, for which he won the Nobel prize in 1922. Einstein's solution was to postulate that light consisted of particles, now called photons. How this could be compatible with the wave theory of light that we studied in session 10 was for a long time a matter of debate. But before we worry about that in session 13 let's see how Einstein's solution works.

Einstein assumed that in a light beam at frequency υ each photon had energy $E = h\upsilon$, where h is a Universal constant, now called Planck's constant.

This energy either is or is not enough to eject an electron from the metal surface. Since work has to be done in separating a negatively charged electron from the positively charged lattice, electrons will be ejected only if E is greater than this work, say E > ϕ. Any energy in excess of ϕ appears as kinetic energy of the electron. So above the threshold the kinetic energy grows linearly with frequency. This was verified by Millikan in 1915.

On the other hand, each photon ejects precisely one electron: thus the more intense the beam of light, the larger the number of photons, and hence the larger the number of electrons ejected. The energy is supplied as a whole to the electron once it has absorbed a photon, so there is no time delay in the appearance of the electrons.

The important clue to the structure of the atom is that when it interacts with matter, light behaves as discrete entities, the photons.

The light particles are called photons

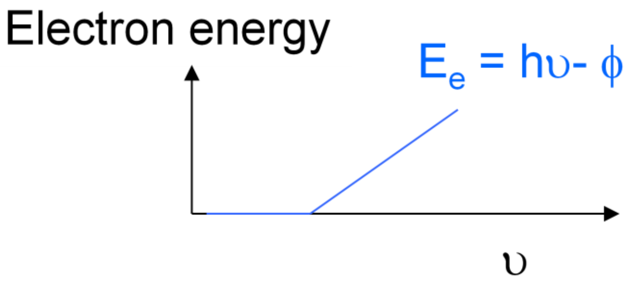
Light frequency

$E = h\nu$

Photon energy

Planck's constant

Predict energy linear in ν above threshold



So returning for a moment to our initial problem: we now know that the quantity hυ refers to the energy of a photon.

Summary

- Spectra of atoms show regular, if complex patterns.
- The spectrum of hydrogen can be described by a simple formula. The atom consists of a small positively charged nucleus surrounded by a cloud of negative electrons.
- The photoelectric effect shows light to be composed of quanta of energy, called photons.

SAQs

1. Photoelectric effect: light of wavelength 400nm shining on a layer of sodium ejects electrons from the surface. The intensity of the light is then doubled. How does this affect (i) the energy of the electrons (ii) the number of electrons?

   (i) (a)The energy doubles (b) the energy is unchanged

   (ii) (a) The number of electrons is unchanged (b)The number of electrons doubles

2. Electrons are emitted from a certain metal only once the wavelength has reached a threshold value of 500nm. What does this tell you about the work required to liberate an electron from the metal surface?

   a) Nothing

   b) It equals hc/λ where $\lambda = 500$ nm

   c) c) It lies between 0 and hc/λ

3. Rutherford atom: how close can an alpha particle of energy 5 MeV come to the nucleus of a gold atom?

   a) 5×10^{-14} m

   b) 6×10^{-16} m

   c) 7×10^{-33} m

   d) 5×10^{-8} m

   e) 2.4×10^{-14} m

The answers appear on the following page

Answers

1. i) a) Incorrect: if the frequency of the light is unchanged then the intensity is a measure of the number of photons, each of which will eject an electron with a fixed energy.

   b) Correct: The intensity of the light gives the number of photons hence the number of electrons per unit time. The energy of the electrons is unchanged

   ii) a) Incorrect: If the frequency is fixed then the intensity of the light is directly related to the number of photons per unit time each of which ejects an electron

   b) Correct: If the frequency is fixed then the intensity of the light is directly related to the number of photons per unit time each of which ejects an electron

2. a) Incorrect: the cut-off photon energy equals the work function of the metal surface

   b) Correct. The work function equals the minimum photon energy $h\nu=hc/\lambda$

   c) Incorrect: if this were so, longer wavelength radiation would also eject electrons.

3. a) correct: use alpha particle energy = $Ze^2/4\pi\varepsilon_0 r$ because all the KE is converted to PE at the closest approach

   b) Incorrect – you've omitted the charge on the gold nucleus which is 79e

   c) Incorrect: you've forgotten to convert eV to Joules.

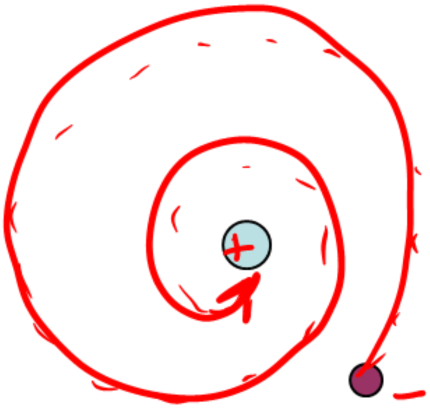
   d) Incorrect: you've taken a 5 eV alpha particle, not a 5 MeV one

   e) Incorrect: you've forgotten that the charge on the alpha particle is 2e.

The Quantum Atom

The Rutherford Atom

First let's look at what's wrong with Rutherford's picture of the atom. Recall that this described the atom as a concentrated central region of positive charge, the nucleus, and an extended region of negative charge, the electrons. This arrangement is unfortunately unstable: the problem with the Rutherford atom is that an electron in orbit will according to classical electromagnetic theory radiate energy and spiral into the nucleus.



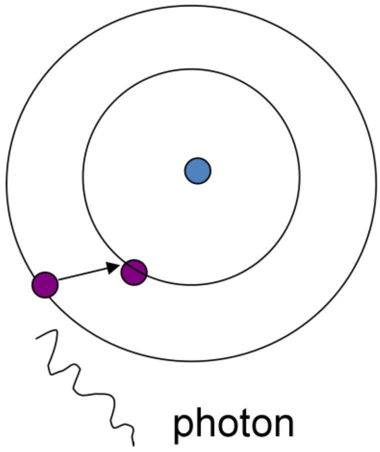
The electron spirals into the nucleus (positive charge attracts' negative).

Where does the energy go?

Show that *h* is a both a unit of energy (per unit frequency) and a unit of angular momentum

Bohr did not solve the problem of stability – he simple postulated that it was not there, but in a rather cunning way: he assumed that the electrons orbiting the central nucleus could populate only certain discrete orbits. He also assumed that the electrons could jump between orbits rather rapidly. When an electron gained some energy it could jump up to a higher orbit. It could later jump down again, emitting the energy difference between the orbits as a single photon.

Bohr postulated that the orbits that could be occupied had an integer number of units of angular momentum (equation 1). This forces the orbits to be discrete. Note that Planck's constant has the units of angular momentum. The quantity on the left side of equation (1) is the angular momentum of the electron. When an electron jumps down between discrete orbits it emits quanta of definite energy – the spectral lines.



$$(1)\quad mvr = nh/2\pi$$

$$(2)\quad \frac{mv^2}{r} = \frac{Ze^2}{4\pi\varepsilon_0 r^2}$$

Eliminate r

$$\frac{Ze^2 mv}{2\varepsilon_0 nh} = mv^2$$

$$(3)\quad \Delta E = h\nu = \Delta\left(\frac{mv^2}{2}\right)$$

$$\frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{Ze^2}{2\varepsilon_0 nh}\right)^2$$

$$\nu = \frac{1}{2}\left(\frac{Ze^2}{2\varepsilon_0}\right)^2 \frac{m}{h^3}\left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right)$$

or $\lambda^{-1} = \frac{\nu}{c} = Z^2 R\left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right)$ where $R = \frac{me^4}{8\varepsilon_0{}^2 h^3 c}$

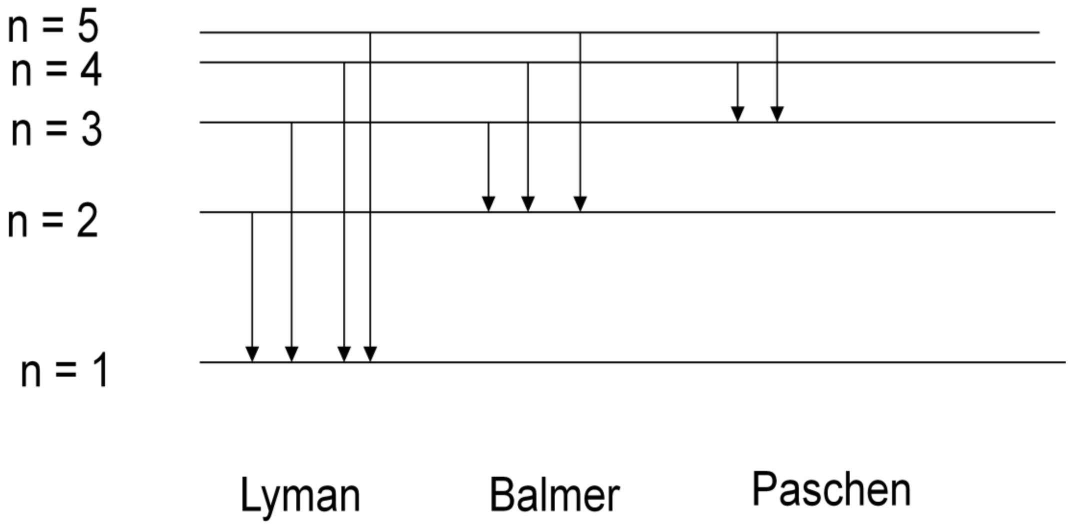
In this section we've put this together with two other ideas to get the Bohr model of the hydrogen or hydrogen-like atom with just one orbiting electron. The first idea (equation 2) is that the electron orbits the nucleus like a classical charged particle acted on by the electrostatic inverse square law force of the nucleus, and satisfying Newton's equations of motion.

The second idea is that the electron can jump between orbits, and when it does so it emits or absorbs a photon with an energy equal to the energy difference between the orbits. This is expressed in equation 3. Note that the energy difference between the orbits contains both the Kinetic and Potential Energy – the electron speeds up in a closer orbit but this increase in kinetic energy uses up only half the change in potential energy.

We can now rearrange these equations and use Einstein's relation $E = h\upsilon$ to get the frequencies of the spectral lines of one electron atoms. Specifically for hydrogen they agree with observation almost exactly! For other ions, with only one electron, there is also agreement between this theory and observation. The next section shows the energy level scheme in more detail. Nevertheless, it is as well to bear in mind that this model is unsatisfactory in several respects: we'll return to this in a moment.

Energy Level Scheme

This section summarises the transitions giving rise to three of the series of emission lines in hydrogen. The Lyman series arises from photons jumping down to level 1 from higher levels; the Balmer series arises from transitions to level 2 and the Paschen series from transitions to level 3. There is infinite sequence of levels above the ones shown.



How many problems can you find with the Bohr model?

Here are some of the problems we think we've found with the Bohr model:

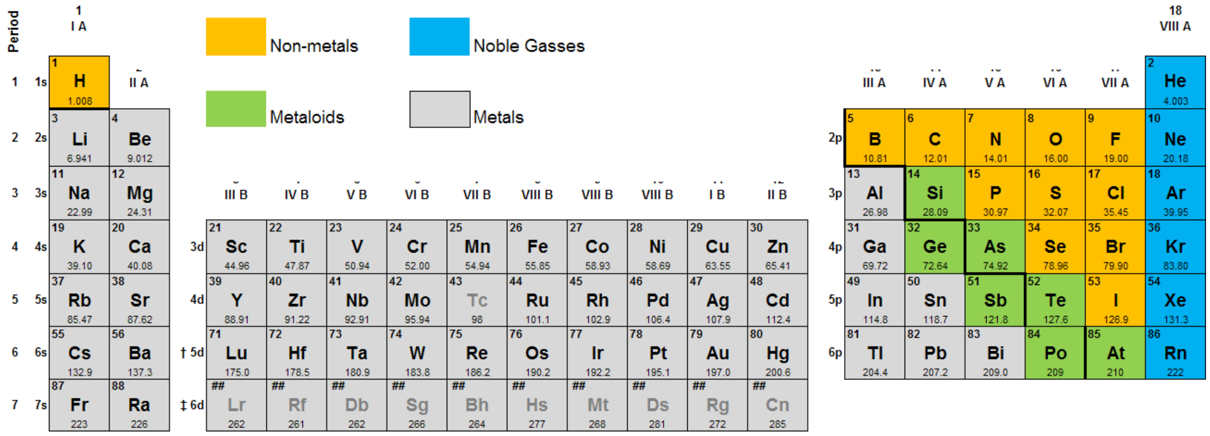
- Integer quantisation of angular momentum is arbitrary. Energy would be the natural choice
- Stability of innermost orbit --why not r=0?
- The ground state is given non-zero angular momentum to hold the electron out of the nucleus
- Jumps are postulated – no reason given
- Classical electromagnetism is suspended to make the ground state stable
- It is a mixture of classical and quantum ideas
- Only works for one-electron systems

The Bohr atom is just what we would now call a toy model. It gives the right answers but it's not clear that it's for the right reasons.

Can we extend the Bohr model to more complicated atoms? It works for atoms with single electrons, such as once ionised helium provided we put in the correct nuclear charge. But not for anything more complicated. Nevertheless, we can use the idea of electron orbits to build up a picture of more complex atoms that will allow us to understand the periodic table of elements.

Periodic Table

The Bohr model can account for the spectrum of hydrogen, but that is what it was set up to do. Can we extend the idea of quantised atomic energy levels to account for any other aspects of atoms? It turns out that the notion of electron orbits can be extended to account for the chemical behaviour of the elements, specifically their arrangement in the periodic table. The section shows all the elements arranged according to their chemical similarities. Without going into the chemical details, the next section shows how some of the main features of this pattern come about.



🟨 Non-metals
🟦 Noble Gasses
🟩 Metaloids
⬜ Metals

Period		1 I A	II A		III B	IV B	V B	VI B	VII B	VIII B	VIII B	VIII B	I B	II B		III A	IV A	V A	VI A	VII A	18 VIII A
1	1s	1 **H** 1.008																			2 **He** 4.003
2	2s	3 **Li** 6.941	4 **Be** 9.012												2p	5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
3	3s	11 **Na** 22.99	12 **Mg** 24.31												3p	13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
4	4s	19 **K** 39.10	20 **Ca** 40.08	3d	21 **Sc** 44.96	22 **Ti** 47.87	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.41	4p	31 **Ga** 69.72	32 **Ge** 72.64	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
5	5s	37 **Rb** 85.47	38 **Sr** 87.62	4d	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** 98	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	5p	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
6	6s	55 **Cs** 132.9	56 **Ba** 137.3	† 5d	71 **Lu** 175.0	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	6p	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** 209	85 **At** 210	86 **Rn** 222
7	7s	87 **Fr** 223	88 **Ra** 226	‡ 6d	## **Lr** 262	## **Rf** 261	## **Db** 262	## **Sg** 266	## **Bh** 264	## **Hs** 277	## **Mt** 268	## **Ds** 281	## **Rg** 272	## **Cn** 285							

To construct a periodic table of elements

Label each electron state with a principle quantum number $n = 1, 2, 3, \ldots$.

For each n, label a state by its angular momentum quantum number $l = 0, 1, 2, \ldots (n - 1)$

For each value of l, label a state by its magnetic quantum number $m = -l, -l + 1, \ldots, l$

For each value of m, label a state by its spin quantum number +1/2 or -1/2

The key to forming the electron distribution of the elements is the Pauli exclusion principle, which states that no two electrons can be in the same state. This tells us how to fill up the electron shells, starting with the lowest energy and proceeding.

n	l	m	s	total
1	0	0	+1/2, -1/2	2
2	0; 1	0; -1, 0, 1	+1/2, -1/2	2; 6
3	0; 1; 2	0; -1, 0, 1; -2, -1, 0, 2, 1	+1/2, -1/2	2; 6; 10

This gives shells with: 2, 8, 18, … electrons ($=2n^2$)

The second element is helium; with 2 electrons. These both go into n=1,l=0, with s=-1/2 and s=+1/2. This fills up the first shell. The other noble gases, Neon, Argon and so on down the right hand column of the periodic table, also have filled shells, so we expect their chemical behaviour to be similar to that of helium. In fact, in all cases they are chemically relatively inert. Lithium, sodium, potassium and so on down the first column have one electron in their outer shell, so again we expect them to be chemically similar.

Unfortunately, there are a few complications as we get to atoms of higher atomic number: the orbital energies are such that electrons can go into an outer shell before the shell below it has been filled up.

Our conclusion is that we can have confidence in the quantisation of electron orbits in atoms.

For complex atoms:

Rearrangements of the outer electrons gives rise to optical lines.

Rearrangements of the inner electrons gives rise to X-rays.

Summary

- The Bohr model provides a picture of the nuclear atom consistent with spectral features
- An extension of the model can account for the period table of the elements
- Nevertheless the model has several unsatisfactory features which are addressed in a proper quantum theory treatment. We shall return to this is session 13.

As a result of this section we have enough information about the structure of atoms to begin to look at how atoms and radiation interact. In particular, for our overall problem, we shall want to consider a system of matter and radiation in thermal equilibrium so that we can assign a common temperature to the system. We shall turn to this in the next section.

SAQs

1. The wavelength of the first line in the Lyman series of H is 121.5 nm. What is the wavelength of the corresponding line in He^+?

   (a) 60.5 nm (b) 243 nm (c) 486 nm (d) 30 nm

2. What is the ionisation energy of Hydrogen (from the ground state)?

   (a) 0 (b) 13.6 eV (c) 91.2 nm

3. Which Balmer line has a frequency higher than the first Lyman line (if any)?

   (a) $n_2 = \infty$ (i.e the last line of the series) (b) $n_2 = 3$ (i.e. the first line of the series)

   (c) none

4. How many electrons in the energy level $n = 4$?

   a) 18 (b) 14 (c) 7 (d) 32

The answers appear on the following page

Answers

1. (a), (b), (c) incorrect: according to the Bohr theory the frequency depends on Z^2, hence the wavelength Z^2. Here Z = 4

   (d) correct: use the Bohr theory for a one-electron atom with nuclear charge 2e

2. (a) incorrect: the zero of energy can be put anywhere, but physically measurable quantities are energy differences which are independent of the choice of zero.

   (b) correct – use the Bohr theory with n_1=1 and n_2 = infinity.

   (c) incorrect – this is the right value of the wavelength but you need to convert it to an energy using E = hc/λ

3. (a), (b) incorrect – the series do not overlap (this can be proved from the Bohr formula)

   (c) correct – the series do not overlap

4. (a) Incorrect: this is the total in levels n=1,2,3.

   (b) Incorrect; for n = 4 and l=3 we have m = -3, -2 ,-1, 0, 1, 2, 3 giving 7 states, hence 14 possible sates taking spin into account, but we also need to include the states with l=2 and l=1.

   (c) This is the same error as (b) plus the omission of spin

   (d) Correct. We have 1=3 giving 10 states with m = -3, -2, -1, 0, 1, 2 (each with spin + 1/2 or-1/2) and l=2 and 1 with 10 and 6 states respectively

Radiation and Matter

Matter in Thermal Equilibrium

A gas contains atoms in motion constantly undergoing collisions. In these collisions energy is exchanged. If the atoms were structure-less particles this would imply only a sharing of kinetic energy. But atoms, as we have seen, have an internal structure, which allows an exchange of energy between the translational motion and the internal motion of the electrons. Thus, as a result of collisions we expect some atoms to become excited, that is we expect one of the electrons to jump into a higher energy level. We want to know how many are in each excited state, because this will affect the interaction with radiation - it will give the frequencies that can be absorbed and emitted.

The relative numbers of atoms in each excited state is given by a general result called the Boltzmann law. Consider a system of atoms at temperature T. Let No be the number of atoms in the lower of two states, and N_E be the number in a state with an energy E relative to the lower state. Then the occupancies of the states are given by N_E/N_0=e to the power (-E/kT).

Boltzmann's Law:

For matter in equilibrium at temperature T:

$$\frac{N_E}{N_0} = \frac{g_E}{g_0} e^{-E/kT}$$

k = **8.617×10^{-5} eV K^{-1}**

We've simplified this result slightly from the one in the section for clarity by assuming that there is only one state at zero energy and one at energy E. If there are go and g_E states respectively then the law becomes N_0 /N_E =g_E/g_0 e to the power $^{-E/kT,}$ as shown in the section.

The law is very general - we shall come across it again later as the barometer formula. But I know of no simple proof, so we shall content ourselves with stating the law and asking you to commit it to memory.

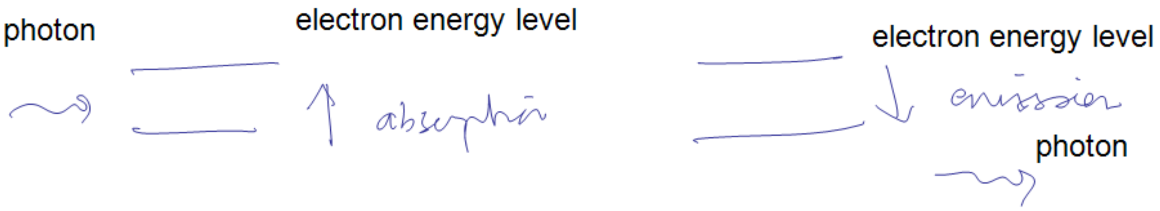
Note that it is useful to have Boltzmann's constant k in eV per degree for use in order of magnitude estimates.

The ionisation energy of hydrogen is 13.6 eV. What fraction of hydrogen atoms are ionised at room temperature?

Radiation and Equilibrium

Consider an enclosure heated to some temperature T say. The enclosure will contain radiation interacting with the atoms in the walls of the container. Radiation absorbed by an in the wall will excite the atom; excited atoms will emit radiation back to the interior. A detector inside the container would measure radiation across a range of frequencies. At room temperature this would be mainly infrared or heat radiation. At higher temperatures the container might glow red hot. Whatever the apparent colour to the eye, radiation in equilibrium is called blackbody radiation. This is because it is also the radiation from a surface that is absorbs any radiation falling on it – like a small hole in a container with blackened interior walls.

What then can we say about the radiation in equilibrium with a system of atoms at some temperature T? What do we mean by equilibrium? Clearly, we mean that in equilibrium there should we no overall change of state. Therefore, the rate at which radiation is being emitted by electrons that drop down from higher levels must be balanced by those that are raised by absorption. So we begin by writing down the various rates.



Let us restrict our discussion to atoms which we suppose to have only two levels, a lower one labelled l, and an upper one labelled u. Consider first emission, equation (1) below. This will depend on the number of atoms in the higher state N_u. We don't know the coefficient of proportionality, so call it A. It will depend on the inner workings of the atom but not on the temperature.

Consider next absorption, equation (2). This will depend both on the number of atoms in the lower state, but also on how much energy is present in the radiation field at the energy of the spectral line. Let the energy per unit volume be $u_{ph}(E)$. Then the rate of absorption is proportional to $N_l\ u_{ph}(E)$. We don't know the coefficient of proportionality, so call it B_{lu}.

Equating the rates of emission and absorption gives us equation (3) from which we obtain a prediction for the intensity of radiation that must be present at each energy if the matter and radiation are to be in equilibrium at temperature T. This is equation (4).

Emission: $N_u A_u$ (1)

Absorption: $N_l B_{lu} u_{ph}(E)$ (2)

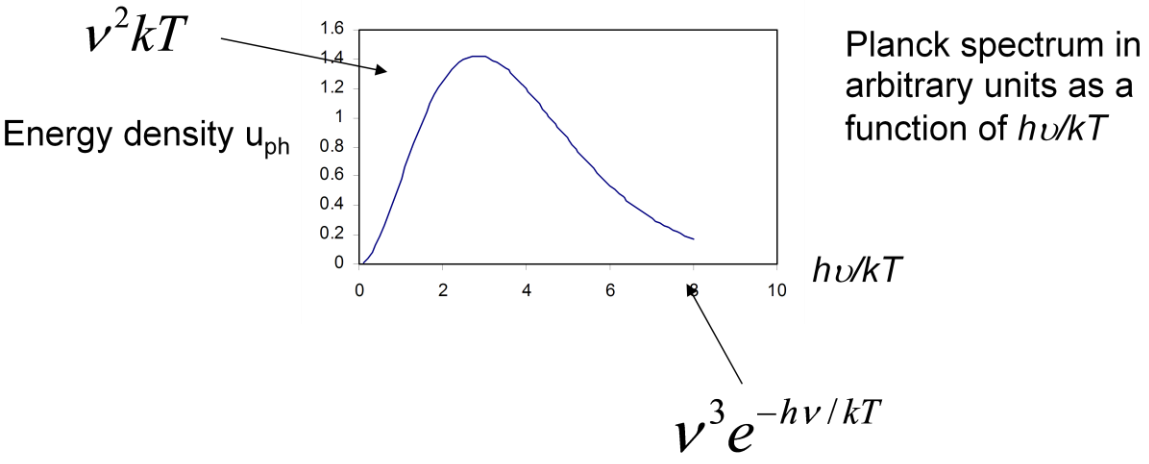
Equilibrium: (3)

$$u_{ph}(E)=\frac{A_u}{B_{lu}}e^{-E/kT} \quad \text{or} \quad u_{ph}(\nu)=\frac{A_u}{B_{lu}}e^{-h\nu/kT} \qquad (4)$$

How does this predication compare with observation? It disagrees!

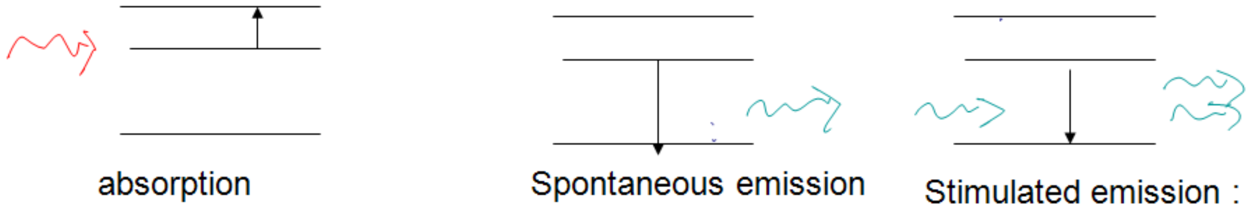
Plank Spectrum

To compare with observation we need to know the energy dependence of A/B. This can be obtained theoretically, but we shall get it from observation. The figure shows the observed form of the spectrum from a body in thermal equilibrium. The energy per unit volume per unit frequency is plotted against hυ/kT to give the universal Planck curve. From the figure we see that we can get approximate agreement between theory and experiment for high frequency if $A/B \propto v^3$. But theory and experiment then disagree at low frequency. The solution to this problem was given by Einstein. We'll look at it in the next section.



At low frequency the Planck spectrum departs from exponential form

Einstein proposed that if an atom in an excited state is struck by a photon of the right energy or, equivalently, the right frequency, then it may be stimulated to emit a photon. When this happens the emitted photon has exactly the same energy and momentum as the incident photon.



$$B_{ul} N_u u_{ph}(\nu)$$

We must add this process into the equilibrium rate in equation (1).

$$AN_u + B_{ul} N_u u_{ph} = B_{lu} N_l u_{ph} \qquad (1)$$

$$\frac{N_l}{N_u} = e^{E/kT} \qquad (2)$$

We now use the Boltzmann law, equation (2), to eliminate the occupation numbers of the lower and upper states from (1), and re-arrange to get equation (3).

$$A = \left(e^{E/kT} B_{lu} - B_{ul}\right) u_{ph} \qquad (3)$$

$$B_{lu} = B_{ul} = B$$

This must hold for all temperatures. There is only one way to achieve this: the B coefficient must be symmetric, that is we must have $B_{ul} = B_{lu}$, and the radiation intensity must be given by equation (4). Thus we arrive at an equilibrium distribution of photons given by the Planck formula, equation (4).

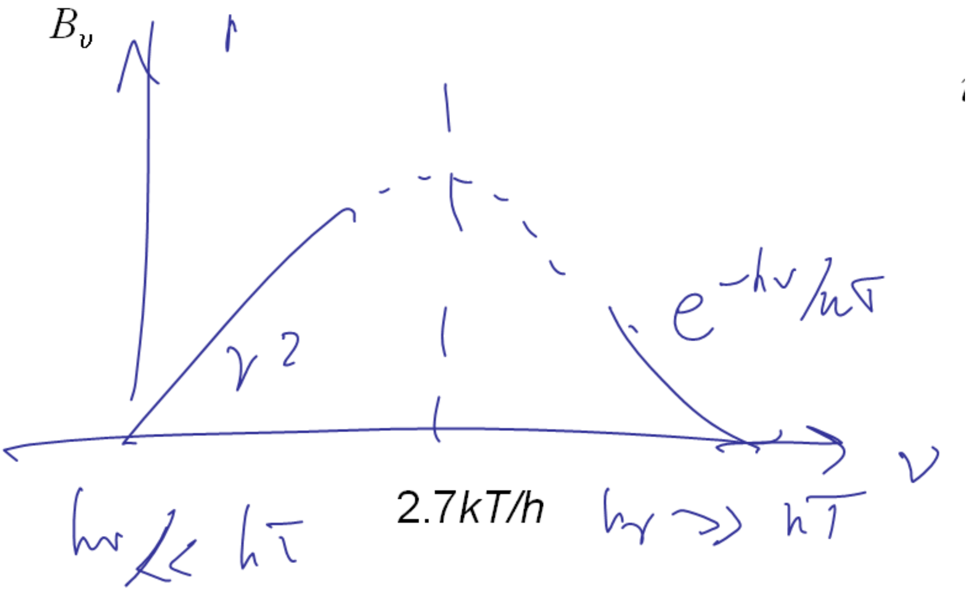
$$u_{ph}(E) = \frac{A}{B\left(e^{E/kT} - 1\right)} \qquad (4)$$

With:

$$E = h\nu$$

The Plank Distribution B_ν

In this section we've plotted the form of the Planck distribution for the energy per unit volume of a radiation field in thermal equilibrium. The Planck function is often called B_ν. . We see that the photon spectrum decays exponentially at high frequency, but is also correctly proportional to ν^2 at low frequency.



Note the exact form is: $u_\nu = B_\nu \equiv \frac{8\pi h^3}{c^3}\frac{\nu^3}{e^{h\nu/kT} - 1}$

Where u_ν is: energy per unit volume per unit frequency ($\mathrm{Jm^{-3}Hz^{-1}}$)

Where then is the maximum of this curve? Clearly, somewhere between hν> kT and hν < kT, hence around hν =kT. We have reached an explanation of the equation in our problem! In the next section we'll summarise this.

Before we do so however, one thing to note: we've looked at a graph of the energy density per unit frequency interval u_υ against υ. A more exact value for the frequency at which this graph peaks is given by hυ = 2.7 kT. We could have looked at a graph of the energy density per unit wavelength against wavelength. Then:

$$u_\lambda = B_\lambda \equiv \frac{8\pi h^3}{c^3}\frac{\lambda^{-5}}{e^{hc/\lambda kT}-1}$$

Both of these graphs are called the Planck or blackbody spectrum. But the peak of this wavelength graph cannot be found by substituting υ = c/λ. This is because the energy per unit wavelength is a different chunk of energy from the energy per unit frequency. A uniform set of intervals in frequency δυ corresponds to a non-uniform set of intervals $c/\lambda^2\ \delta\lambda$ in wavelength. The upshot of this is that the peak of a graph of the spectrum plotted in wavelength occurs at around hc/λ = 4.8 kT. This is Wien's law.

$$\lambda T = b \text{ (Wien's Law) where } b = 2.89\times10^{-3}\ \mathrm{m\,K} \approx 4.8hc/k$$

Summary

- The internal electron states of an atom in equilibrium at a temperature T are populated according to the Boltzmann law

$$\frac{n_u}{n_l} = e^{-E/kT}$$

- The energy per unit volume of radiation as a function of frequency in equilibrium with matter at a temperature T is given by the Planck distribution

$$u_\nu = B_\nu \equiv \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1}$$

- The peak of the Planck distribution occurs for frequencies around $\upsilon \sim kT/h$. This is therefore the "colour" of a system in equilibrium at a temperature T.
- More precisely the peak of the Planck spectrum occurs at $\upsilon \sim 2.7kT/h$
- The peak of B_ν, the Planck spectrum plotted as a function of wavelength occurs around $\lambda T = 4.8hc/k$

SAQs

1. What temperature is required to populate n=2 to half of n=1 in Hydrogen? Give your answer in the form m,n where $T = m\ 10^n$ and m and n are integers.

2. The Solar spectrum peaks in wavelength around yellow light: assuming that the Sun radiates as a blackbody with a Planck spectrum, what is its approximate temperature?

   (a) 6000 K (b) 7000 K (c) 8000 K (d) 9000 K

3. At what wavelength (approximately) is the peak of the radiation from a human body ?

   (a) 100 nm (b) 1000 nm (c) 10000nm (d) 100000 nm

4. For a typical atomic level of hydrogen, $A = 10^{-8}$ $sec^{-1.}$.what does this tell us about the average lifetime of an excited state?

   (a) nothing (b) it is around 10^8 s (c) it is much longer than 10^8 s (d) it is much less than 10^8 s.

5. As the temperature of a gas in equilibrium with radiation increases the peak of the emission moves to

   (a), longer, b) shorter wavelengths or (c) is unchanged

The answers appear on the following page

Answers

1. Correct: 7×10^5K. Use $n_2/n_1 = \exp(-E/kT) = ½$, so $T = E/(k\log_e 2)$ where $E=13.6(1/n_1^2 – 1/n_2^2) = 13.6\ (1-1/4) = 10.2$ eV and hence $T=10^5 \times 10.2/(8.6 \log_e 2)=7\times10^5$ K

2. (a) correct: Use $h\lambda/c = 4.8\ kT$ with υ = 580nm for yellow light to get T = 6000 K approximately.

   (b), (c) Incorrect: You appear to be guessing - see (a) for the correct answer

   (d) Incorrect – you've used the peak in the energy as a function of frequency rather than wavelength, which is not the given data.

3. $\lambda = hc/4.8\ kT$ gives λ = 8500 nm so (c) is the nearest, hence correct. Alternatively you can argue that the body emits predominantly infrared radiation, which is around 10 μm or 10^4 nm

4. (a), (c), (d) incorrect:

   (b) Correct: A is the rate of transition from the excited state in other words the number of transitions per unit time. Thus 1/A is the time per transition hence the average lifetime of the state.

5. (a) incorrect: the energy of the gas and the radiation increase together so the frequency gets higher or the wavelength shorter.

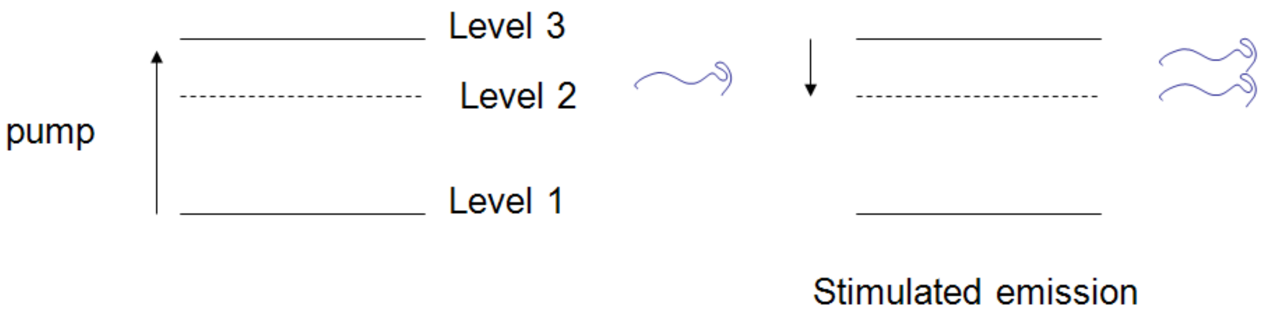
   (b) correct: this follows from Wien's law, λT = constant

   (c) incorrect: the radiation is assumed here to be in equilibrium with the gas so the energies must increase together.

Additional Problems

Problem 1: How can stimulate emission be used to make monochromatic light?

In stimulated emission the emitted photon has exactly the same properties as the stimulating photon – the same wavelength, polarisation and phase. Our first question is how can you use stimulated emission to make monochromatic light?



A "model" three level atom

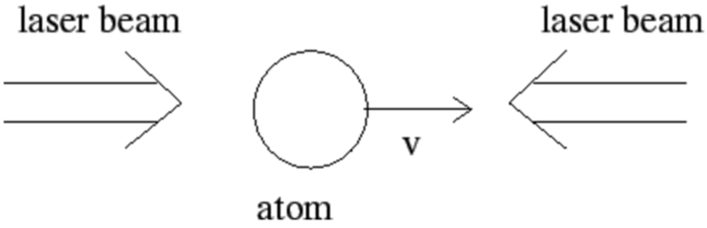
There are two requirements: to enhance the numbers of photons from stimulated emission (these will all be the same colour) and to loose any other photons. To achieve this we arrange to "pump" our atoms into an excited state from which we stimulate the required decay. We then trap these photons between mirrors sending them back and forth to enhance the radiation field at the required frequency. The pumping is achieved by absorption of external radiation from the lowest level of the three here to the highest. This creates a population inversion between levels 2 and 3 relative to that in thermal equilibrium: instead of the population of electrons in level 3 being less than in level 2 by the Boltzmann exponential factor, it is higher. This is how a laser achieves amplification, because there will be more stimulated emissions from level 3 than absorptions from level 2. Of course, we are restricted to frequencies corresponding to available atomic transitions.

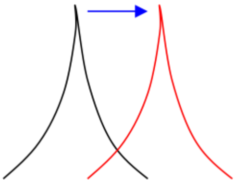
The light cannot be exactly monochromatic because the atoms are in motion, hence emitting at slightly different frequencies as a result of the Doppler effect. Even if we could get rid of this, an emission line form an atom has a natural width – we'll explain this in section 13.

Problem 2: Laser Cooling

The 1997 Nobel prize in physics was awarded for methods of cooling atoms by using laser light. Shining light on a material usually heats it – how can it be used to cool it?

The atom receives light from two laser beams arranged so that it absorbs more light from the one it is moving towards and emits isotropically by spontaneous emission – there is therefore a net transfer of momentum opposing the motion. How are the laser beams arranged to ensure this?





Doppler Cooling

They are tuned just to the red side of an absorption line in the atom, so the Doppler shift of the laser in front moves the laser beam towards the line frequency and is absorbed.

The momentum of a photon of energy E is $p=E/c$. Show that $p = h/\lambda$.

If an atom of mass m emits a photon of energy E show that (by conservation of momentum) it must recoil with energy $\frac{h^2}{2m\lambda^2}$

According to kinetic theory the atoms in a gas at temperature T have average energy of order $3/2\ kT$. Show that the lowest temperature that can be attained by Doppler cooling of sodium ions is around 20 μK. (You will need to look up, or guess, the wavelength of the sodium line in the visible.)

Overall Summary

- Line Spectra and Rutherford Scattering show the atom to consist of a positive nucleus surrounded by electron shells. This picture is supported by the periodic table
- The photoelectric effect shows that in interactions with atoms light behaves as photons with energy $E = h\upsilon$
- The Bohr model provides an incomplete picture of atom-light interactions
- The distribution of electrons amongst energy levels in thermal equilibrium follows the Boltzmann law
- The distribution of radiation as a function of frequency from a body in thermal equilibrium at temperature T follows a Planck curve with a peak around $\upsilon \sim KT/h$
- The spectrum of radiation in equilibrium with matter can be accounted for by including stimulated emission

Meta tags

Author: Derek Raine.

Owner: University of Leicester

Title: Enhancing Physics Knowledge for Teaching – Atoms and Light

Keywords: Atomic structure; Quantum Physics; Radiation; Optics; Light; sfsoer; ukoer

Description: In this session we shall look at how light interacts with atoms. This will enable us to determine the internal structure of atoms and also the quantum behaviour of light.

Language: English

Version: 1.0

Additional Information

This pack is the Version 1.0 release of the module. Additional information can be obtained by contacting the Centre for Interdisciplinary Science at the University of Leicester. http://www.le.ac.uk/iscience