

AN2

ATOMS

OBJECTIVES

Aims

In studying this chapter you should aim to understand the modern view of atomic structure in terms energy levels and transitions. You should view the sections on spectra and lasers as important illustrations of the principles of atomic physics. Try to relate this chapter to anything you may have learned about the structure of atoms from chemistry courses.

Minimum learning goals

When you have finished studying this chapter you should be able to do all of the following.

1. Explain, use and interpret the terms
state (of an atom), quantum number, energy level, energy band, principal quantum number, exclusion principle, excited state, ground state, shell, subshell, ionisation, ionisation energy, line spectrum, emission spectrum, absorption spectrum, radiative transition, spontaneous emission, stimulated emission, laser.
2. Describe and explain the composition and structure of atoms in terms of nuclei, electrons and energy levels.
3. (a) Describe and explain the emission and absorption of photons by atoms.
(b) State and apply the relations among energy levels, photon energy and frequency of radiation emitted or absorbed by atoms.
(c) Explain the origin of line spectra.
4. Describe and discuss how a helium-neon laser works.

TEXT

2-1 STRUCTURE AND STATE OF AN ATOM

The original idea of an atom was that it was the ultimate indivisible particle of matter. That picture was abandoned with the discovery of the electron, a constituent of matter, in the late nineteenth century. By 1913 the work of Ernest Rutherford and Niels Bohr had led to a new model in which an atom was considered to consist of a small, extremely dense, positively charged nucleus surrounded by negatively charged electrons (figure 2.1). The space occupied by the electrons, and hence the size of the atom, is very large compared with the size of the nucleus. A hydrogen atom (the simplest atom) would be pictured as a single electron orbiting around its nucleus, in this case a single proton, rather like a planet orbiting around the sun. The electron is negatively charged, the proton is positively charged and the attractive electrostatic interaction binds them together.

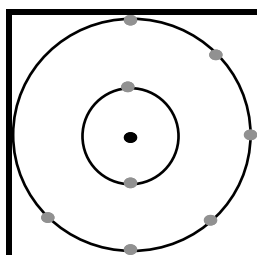


Figure 2.1 Rutherford-Bohr scheme for an atom

A central nucleus is surrounded by electrons. Diagrams like this do not represent the actual locations of electrons.

Although the original Rutherford-Bohr model pictured the electrons as particles in orbit around the nucleus, that view soon became untenable when it was realised that the wave nature of

electrons could not be ignored. According to the theory of quantum mechanics developed during the 1920s, it is not possible to know both the position and velocity (or momentum) of a particle, so the planetary model of the atom had to be abandoned. Although visual models of atoms can never be entirely correct, quantum mechanics gave a better visualisation of an electron in an atom as a fuzzy cloud which represents the probability of finding the electron in various parts of the space. Nevertheless the nucleus of an atom, where most of the atom's mass is located, can be thought of as being confined to a very small fraction of the atom's total volume, while the electrons occupy the remaining space. Figure 2.2 shows some possible "maps" of the single electron cloud in a free hydrogen atom. The most heavily shaded areas show where the amplitude of the wave associated with the proton-electron system has its greatest value. These areas also indicate where the electron is more likely to be found.

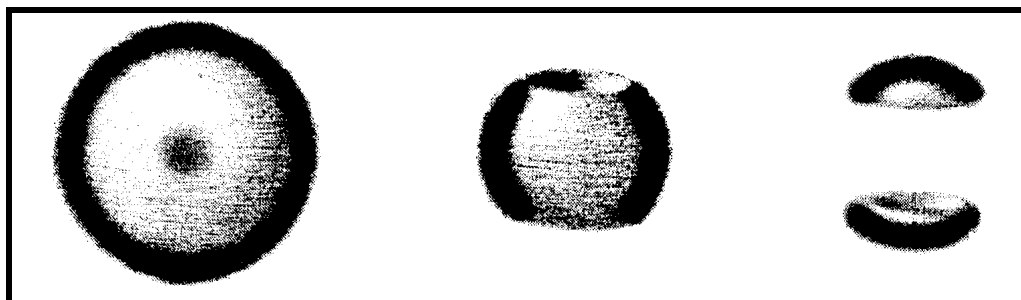


Figure 2.2 Electron density maps for a hydrogen atom - schematic

The single electron is represented as a fuzzy cloud which is related to the probability of finding the particle in a particular region of space. These perspective sketches show three different possibilities for a hydrogen atom with $n = 2$.

Even though atomic electrons do not have definite positions and velocities, the physical **state** of an atom can be specified by quoting values of physical quantities such as energy and the components of a quantity called angular momentum, associated with each of its electrons. For each electron in an isolated atom each of four quantities can take only certain restricted values; the quantities are said to be **quantised**. Those allowed values can be described by quoting the values of four distinct **quantum numbers** for each electron in the atom. So the state of each electron is completely determined by a total of four quantum numbers.

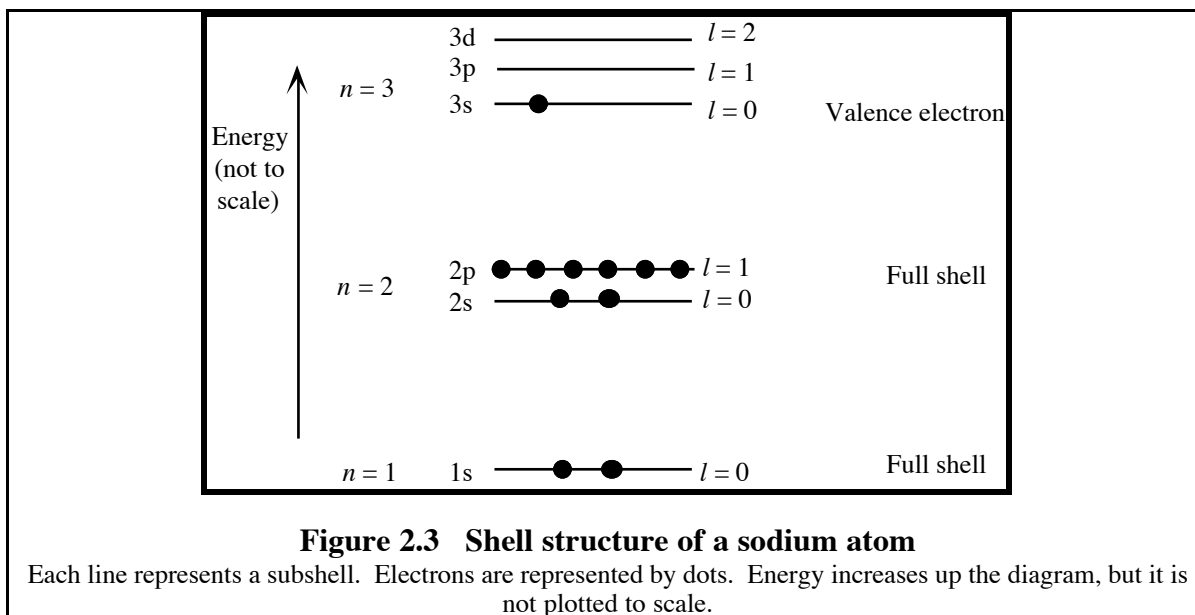
Many important properties of electrons in atoms can be described in terms of just two of the four quantum numbers. These are the **principal quantum number** n which must be a positive integer ($n = 1, 2, 3, \dots$) and the orbital angular momentum quantum number l which can take integer values between 0 and $n - 1$.

Shell label	n	Subshell label	l	Capacity of subshell	Capacity of shell
K	1	s	0	2	2
L	2	s	0	2	8
		p	1	6	
M	3	s	0	2	18
		p	1	6	
		d	2	10	
N	4	s	0	2	32
		p	1	6	
		d	2	10	
		f	3	14	
etc.					

Table 2.1 The shell structure of atoms

Electron states can be grouped, according to their quantum numbers, into shells and subshells. All states with the same value of n constitute a **shell**, while all those states with the same pair of values for n and l make a **subshell**.

A fundamental principle of quantum mechanics, the **exclusion principle**, says that there cannot be more than one electron in any state. This principle limits the number of electrons which can occupy any subshell to the number of available states in the subshell. There is also a simple numerical rule which says that the number of states in a subshell with quantum number l is equal to $2(2l + 1)$. Table 2.1 and figure 2.3 show how the electron states are organised into shells and subshells.



Shells are often specified by capital-letter labels rather than the principal quantum number. The K shell has $n = 1$, L means $n = 2$ and so on. Similarly a set of lower case letters s, p, d, f, .. is used to label the value of l . A common way of specifying a subshell is to combine the value of n with the label for l . For example the 3p subshell contains all the states with $n = 3$ and $l = 1$.

The way that electrons are distributed among the shells and subshells depends on the energies associated with the electron states, as described below, but the general idea is that the configuration with the lowest energy is the most stable one.

Many properties of atoms can be understood in terms of their shell structure. For example, atoms with completely filled shells are particularly stable and chemically unreactive, whereas atoms with unfilled shells bond readily to other atoms.

2-2 ENERGY LEVELS

Many atomic processes can be understood in terms of the energies associated with the binding of each electron to the whole atom. Associated with each electron in a stable atom there is a definite value of energy. That value depends in a complex way on the quantum state occupied by the electron, the charge of the nucleus and on the distribution of the other electrons in the atom.

By convention, the energy of every bound electron is negative. This is simply a consequence of taking the reference point for the potential energy of two interacting particles at infinite separation. For two particles which attract, such as a positively charged nucleus and a negatively charged electron, the potential energy at any finite separation must, therefore, be negative. (See also, for instance, the example of a diatomic molecule in §5-10 of *Forces and Energy*.) Although each electron also has kinetic energy, which must be positive, it turns out that as long as the electron remains bound in the atom the sum of its potential and kinetic energies is always negative. In practice, it is not feasible to distinguish between the internal kinetic energy and potential energy while an electron is bound in an atom. The important quantity is their sum, which we refer to simply

as the energy, E , of the electron state. Although it is common practice to refer to the energies of individual electrons, you should remember that since the potential energy arises from the interaction between each electron and the rest of the atom (including the other electrons), the energy is really a property of the whole atom. The energy, E , of an electron state does not include kinetic energy associated with the motion of the whole atom.

Atoms, like other natural systems, have a tendency to go to a state of minimum potential energy. So the lowest energy for an isolated atom which contains Z electrons is that for which the lowest Z electron-energy states have been filled and all the higher energy states are empty. This situation is called the **ground state** of the atom - the lowest possible energy state. Any atom which contains an electron whose energy is higher than that of an unoccupied state is said to be **excited** and it cannot be expected to remain in that state for long. In general, an excited atom is unstable and will return to its ground state by losing energy somehow.

In the simplest atoms, which have only a few electrons, the energies of the electron states increase with increasing values of the principal quantum number n , so that the higher shells have higher energies. In more complex atoms, however, that simple trend breaks down and the energies are more usefully associated with subshells, which generally contain electrons with similar, but not absolutely identical, energies. (For example in atoms with high atomic number the electrons in the 3d subshell have higher energies than those in the 4s subshell.)

The minimum energy required to remove an electron from an atom is called the **ionisation energy**. The ionisation energy is equal to the minus the energy of the electron state within the atom: $-E$. Note that since E is always negative, ionisation energy is positive. A related idea is the **atomic binding energy**, which is the amount of energy you would have to supply to remove *all* the electrons from the atom.

The allowed energies associated with the electrons within an atom can be shown on a one-dimensional plot called an **energy-level diagram**, such as figure 2.3 or 2.4, in which each allowed energy (or group of closely-spaced energies) is represented by a line. Electrons occupying the energy levels can be shown on the diagrams as dots.

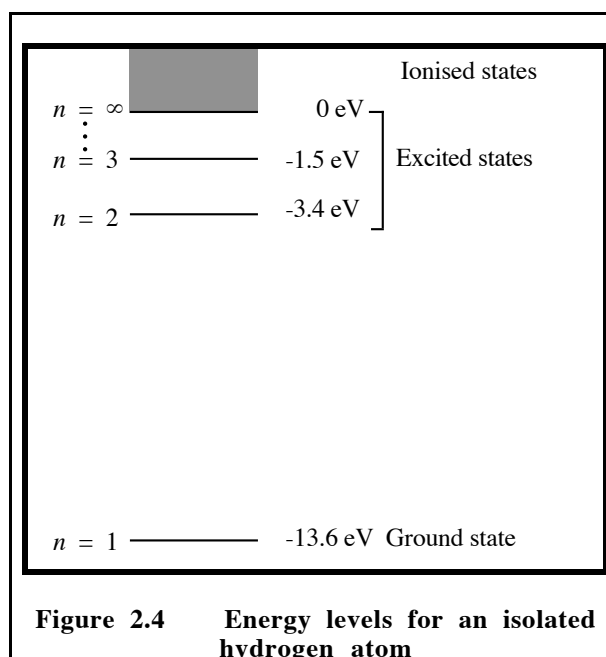
Example: a hydrogen atom

Figure 2.4 shows some of the allowed energy levels for an isolated hydrogen atom. The lowest energy level, the ground state, has principal quantum number $n = 1$, and $E = -13.6$ eV. Since a hydrogen atom contains a single electron, only one of the allowed states can be occupied at one time.

Fairly accurate values of the energy levels, E , of an isolated hydrogen atom can be calculated from the value of the principal quantum number, n :

$$E = -\frac{E_0}{n^2}$$

where $E_0 = 13.6$ eV, the ionisation energy for the ground state. Thus the energy for the first excited state, $n = 2$, has $E = -3.4$ eV. Other levels have higher energies. The principal quantum number can take any positive integer value, but as n increases, the energy levels get much closer together, and the energies of all bound states remain less than zero.

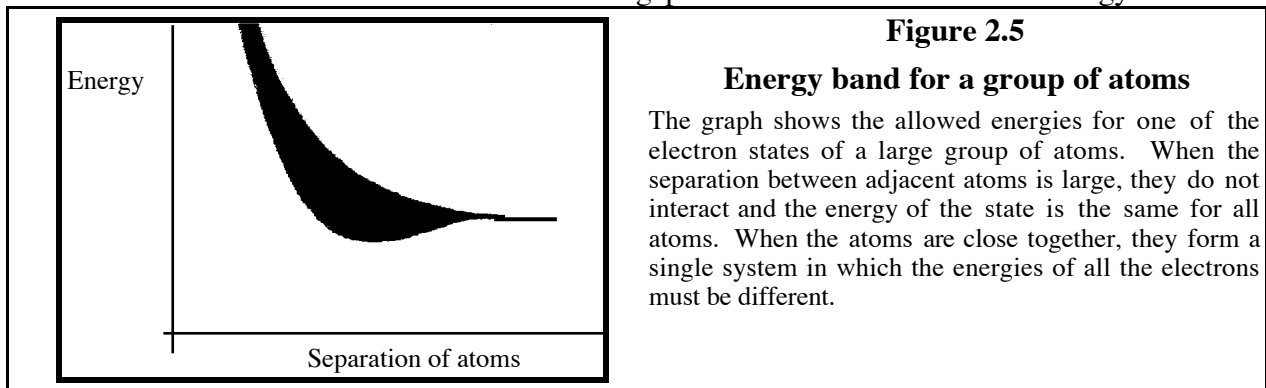


Molecular energy levels

A molecule consists of several atoms bound together. A proper treatment of molecular energies regards all atoms and all their electrons as one system. A typical molecule has many more possible energy states than a single atom. Consequently, since every electron in a molecule must occupy a different state, many molecules have sets of very closely spaced energy levels.

Energy bands in crystals

In a system of many interacting atoms, such as a crystal, the exclusion principle, that no two electrons can have exactly the same state, applies to the whole system. Since the system contains a huge number of electrons there must also be a huge number of different states. As a consequence there must be a very large number of different allowed energies. These energy states form groups of very closely spaced levels, called **energy bands**. Within each band the energy levels are so close together that in practice they seem to be continuous. The bands correspond roughly to the subshells in an isolated atom. Between the bands there are gaps where there are no allowed energy states.



In the usual state of a crystalline solid the lowest energy levels are filled before the higher levels. So the lower energy bands are normally completely filled, with only the uppermost band (subshell) having any vacancies. Those electrons involved in chemical bonding occupy a high energy band, called the **valence band** and can be considered to be shared among neighbouring atoms in the crystal. Some crystals, particularly metals, may have a partly filled band, called the **conduction band**, in which the electrons can move to another state without the need to acquire much energy, because the energy levels are so close together. These electrons are essentially mobile, being able to go anywhere in the crystal, so they are called **conduction electrons**. Conduction electrons contribute to both electrical conduction and the conduction of heat through solids. In metals, the conduction band is identical with the valence band.

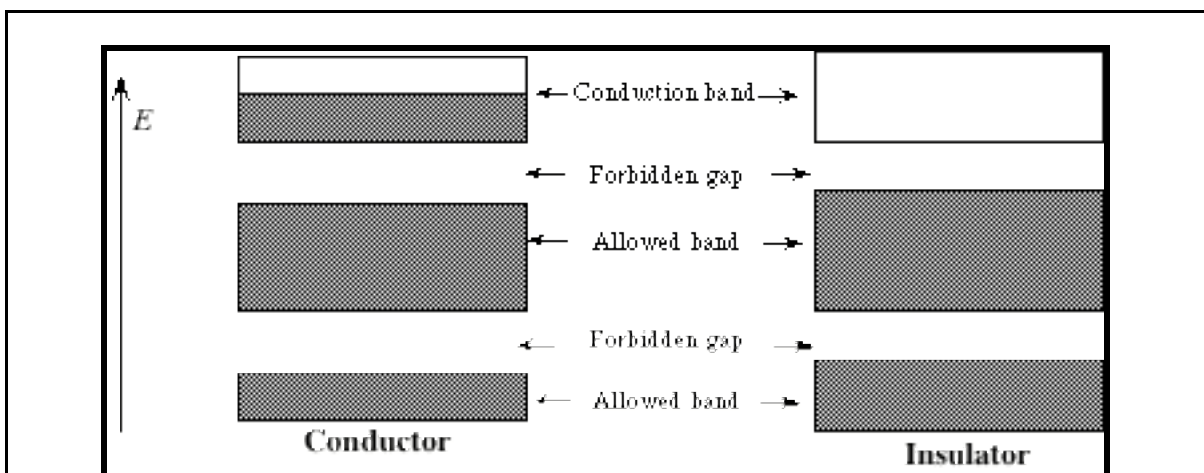


Figure 2.6 Energy level bands in crystals

Shaded areas indicate occupied states. In a conductor electrons already in the conduction band need only a tiny amount of energy to reach an unoccupied state. In an insulator there is a forbidden energy gap between the top of the highest filled band and the conduction band, so very few electrons get enough energy to move up.

2-3 IONISATION

Normally an atom is electrically neutral, having a total of Z negatively charged electrons and a nucleus with a positive charge of Ze . However, it is possible for an atom to absorb enough energy (the ionisation energy) to remove one or more of its electrons completely. The atom is then **ionised** and the remaining positively charged atom is a positive **ion**. It is also possible to form negative ions by adding extra electrons to some kinds of atom. To ionise an atom by the removal of an electron requires the absorption of energy by the atom. If the electron is removed from a ground state, the energy absorbed by the atom must be at least as great as the ionisation energy of that electron.

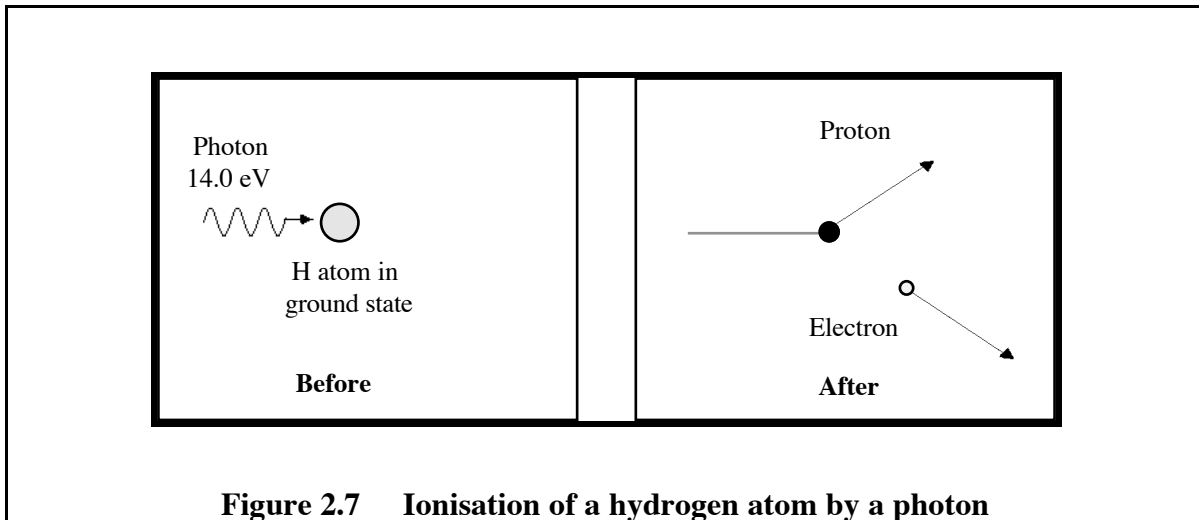


Figure 2.7 Ionisation of a hydrogen atom by a photon

Thus, for example, if a hydrogen atom in its ground state, -13.6 eV, absorbs a 14.0 eV photon it will be ionised. The remaining 0.4 eV of energy supplied will become additional kinetic energy shared between the ion and the electron.

Ionisation can also be caused by collisions with charged particles such as electrons, other ions or energetic neutral atoms.

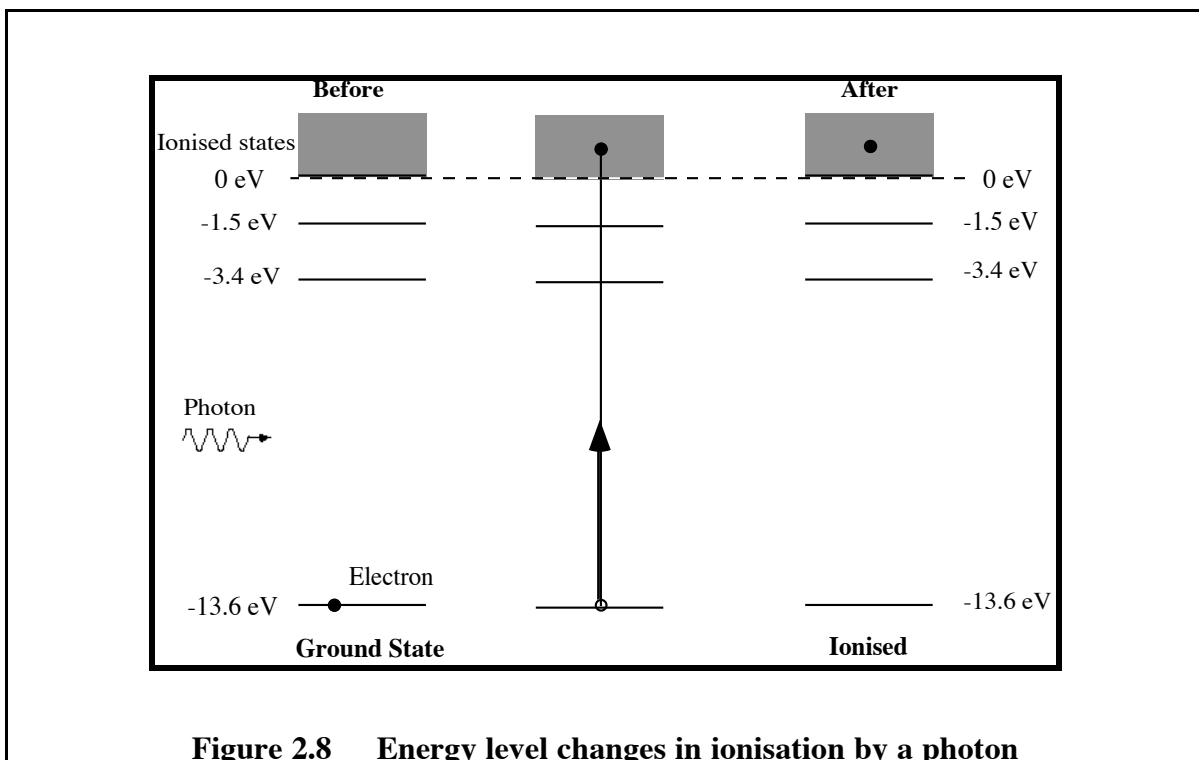


Figure 2.8 Energy level changes in ionisation by a photon

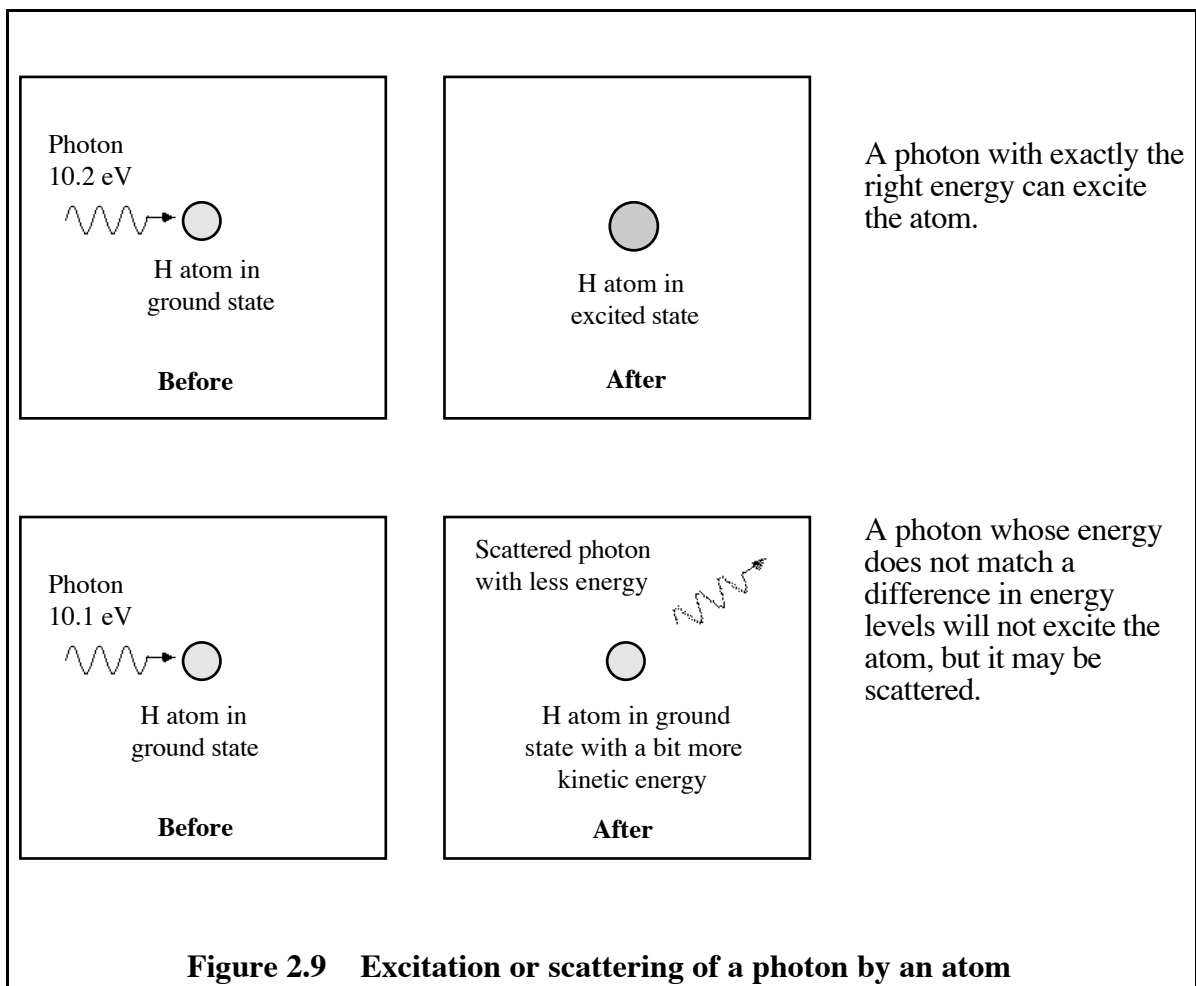
2-4 RADIATIVE TRANSITIONS

One of the ways in which an atom can change its internal energy state is by the emission or absorption of a photon. Such changes are called **radiative transitions**. However a radiative transition between bound states can occur only if the photon energy is exactly equal to the difference in energies between the two states.

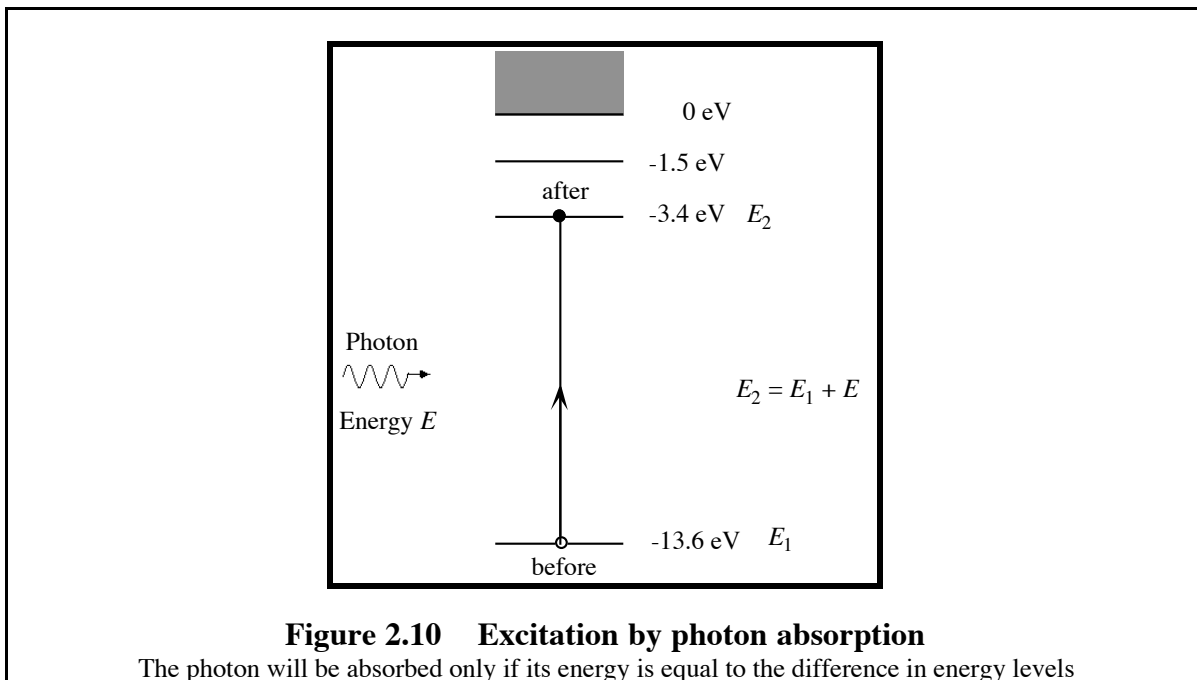
An atom can absorb a photon only if the photon's energy is equal to the energy difference between an occupied state and a higher, unoccupied state. In that case, the photon can be completely destroyed and its energy transferred to the atom by raising the electron to the higher energy level. See figure 2.8.

The energy E of the photon and the frequency f of its associated electromagnetic wave must be related to the initial atomic energy level E_i and the final level E_f :

$$E = hf = E_f - E_i$$



For example if a 10.2 eV photon strikes a hydrogen atom which is in its ground state ($E_i = -13.6$ eV), the atom may be raised into its first excited state ($E_f = -3.4$ eV). On the other hand a 10.1 eV photon or a 10.3 eV photon cannot be absorbed by the atom (figure 2.9).

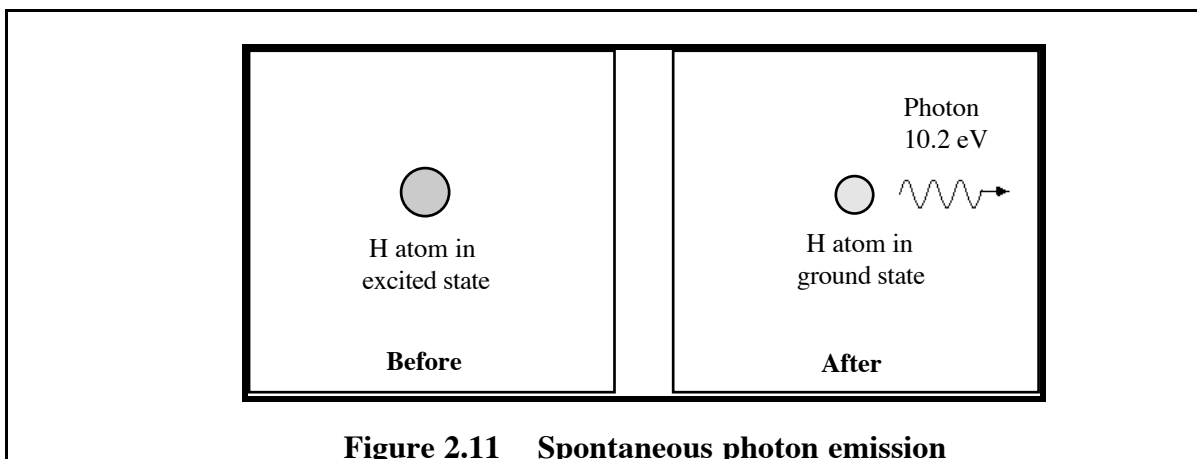


As already mentioned, if the photon's energy is greater than the ionisation energy of an atomic electron, that electron can be completely ejected to become a free electron, leaving the ionised atom behind.

Whenever an atom absorbs a photon it ends up either ionised or in an excited state. An atom in an excited state is unstable and will soon lose energy. One way of losing that energy is by successive **spontaneous emission** of one or more photons. Again, the only possible radiative transitions for the excited neutral atom are those between allowed energy levels. In this case the photon energy, wave frequency and atomic energy levels are related by:

$$E = hf = E_i - E_f.$$

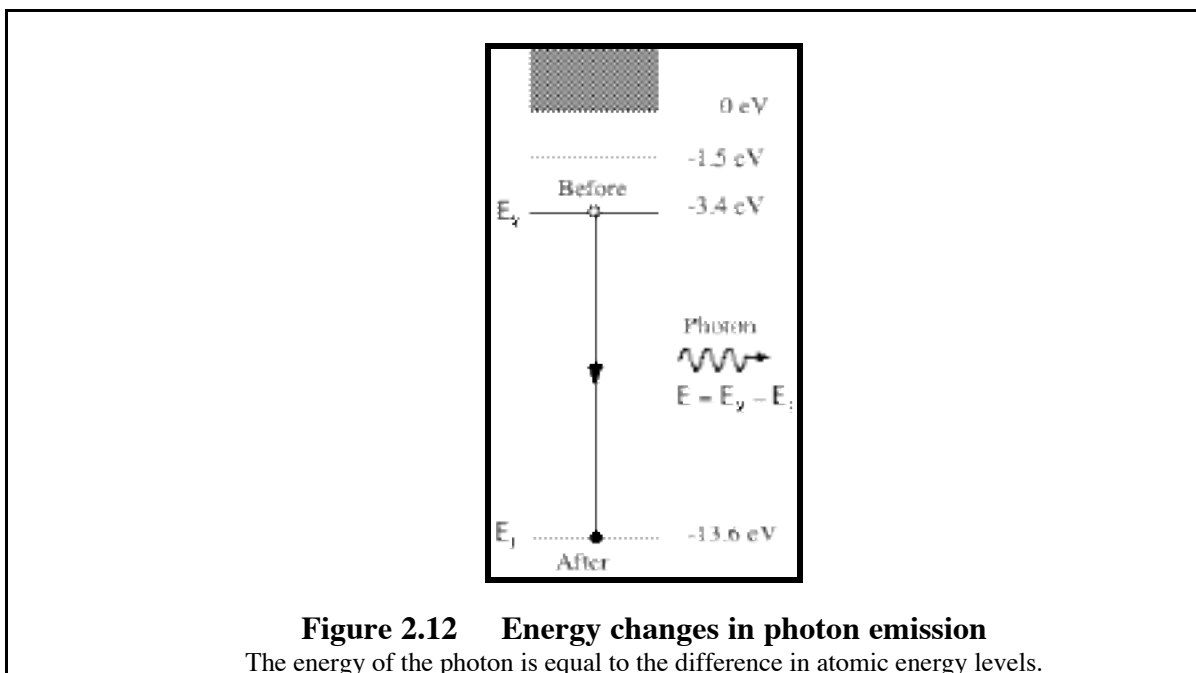
A highly excited atom can often return to its ground state either directly or by a sequence of transitions between energy levels. Each photon energy is equal to the difference in energy levels for the transition.



2-5 OTHER MECHANISMS OF CHANGING ENERGY STATES

Radiative transitions are not the only way that an atom can change its internal energy state. Collisions with other atoms, ions or charged particles can also alter an atom's internal energy.

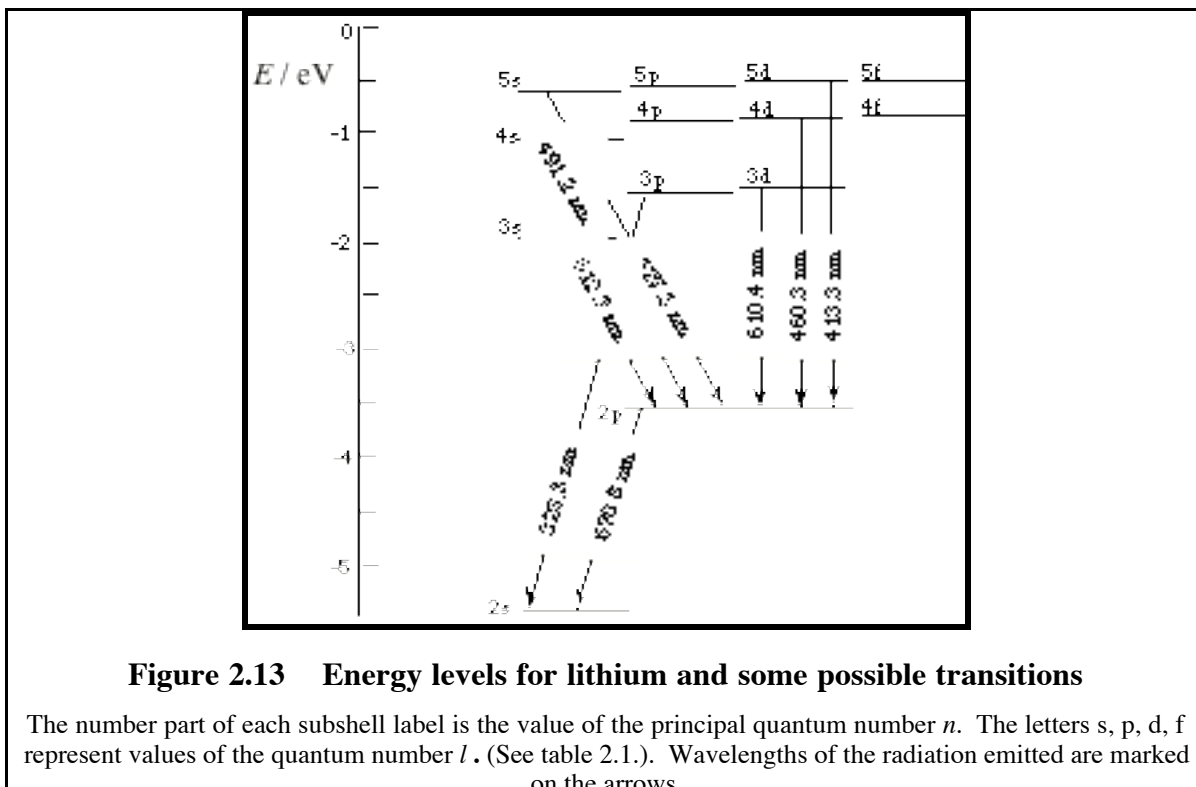
For example if an electron whose kinetic energy is 10.8 eV collides with a hydrogen atom which is in its ground state (-13.6 eV), the atom can be raised into its first excited state (-3.4 eV). This requires only 10.2 eV so the remaining 0.6 eV would appear as kinetic energy, shared between the scattered electron and the motion of the atom as a whole.



2-6 ATOMIC AND MOLECULAR SPECTRA

Radiative transitions between energy levels within atoms and molecules account for the existence of line spectra in both visible light and invisible electromagnetic radiation. Radiative transitions between atomic energy levels produce spectra characteristic of the atoms of each element. Similarly the spectra of molecules are made up of groups of many lines close together, giving the appearance of bands.

The principles can be illustrated by considering the spectra formed by free atoms. Each spectral line corresponds to one type of transition between energy levels. An electron in an excited state can move into another state at lower energy, emitting a photon with a well defined energy. For a typical atom there are many possible excited states and a large number of possible transitions. Figure 2.13 shows a few of the possible transitions which give rise to the characteristic spectrum of lithium - a comparatively simple atom.



There are two kinds of complementary atomic spectra: emission spectra and absorption spectra. Emission spectra are formed when excited atoms emit photons with well-defined energies. Absorption spectra are due to the selective removal of photons from a beam of radiation that has a continuous distribution of wave frequencies and photon energies.

An atomic **emission spectrum** can be produced by any mechanism which supplies energy to excite free atoms. Common examples are electrical discharges in gases and the action of flames. When solid matter is introduced into a flame, some of its molecules can be split into individual excited atoms or ions. (This is an instance of excitation by collisions.) The atoms then radiate at definite frequencies as they return to their ground states.

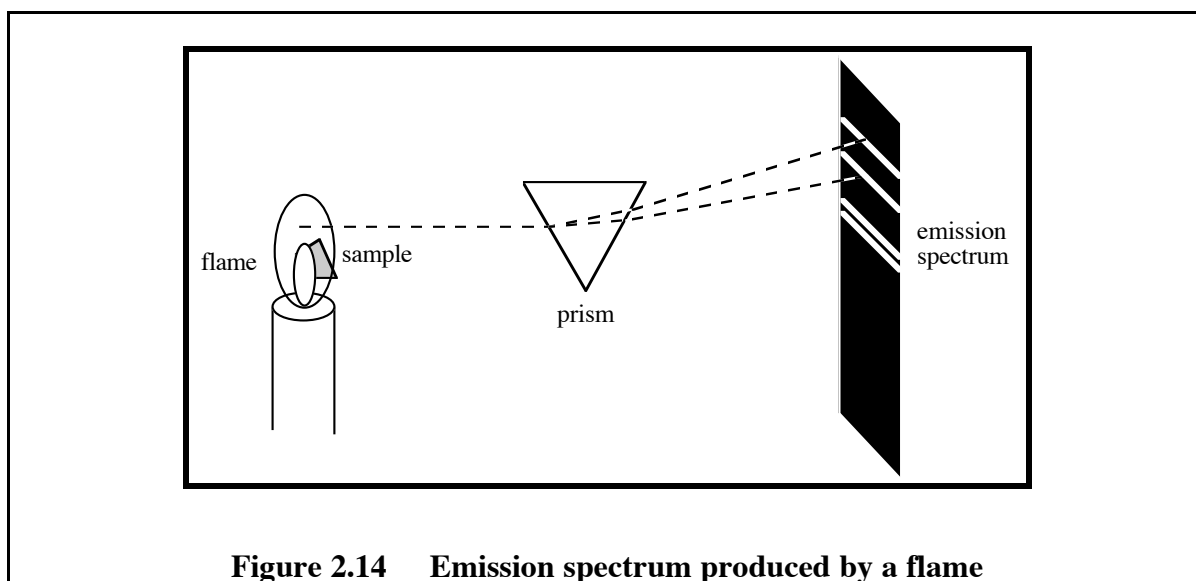


Figure 2.14 Emission spectrum produced by a flame

Since atoms of a particular element have a unique set of energy levels, each element gives a characteristic emission spectrum of bright lines, which can be used to identify the element.

An atomic **absorption spectrum** can be produced by sending an intense beam of radiation through a sample of material containing free atoms. Again the free atoms could be produced in a flame. The spectrum appears as a set of dark lines corresponding to the frequencies of radiation absorbed when the absorbing atoms are raised to higher energy states. Many molecular absorption spectra can be produced by sending white light through solutions of the compounds under study.

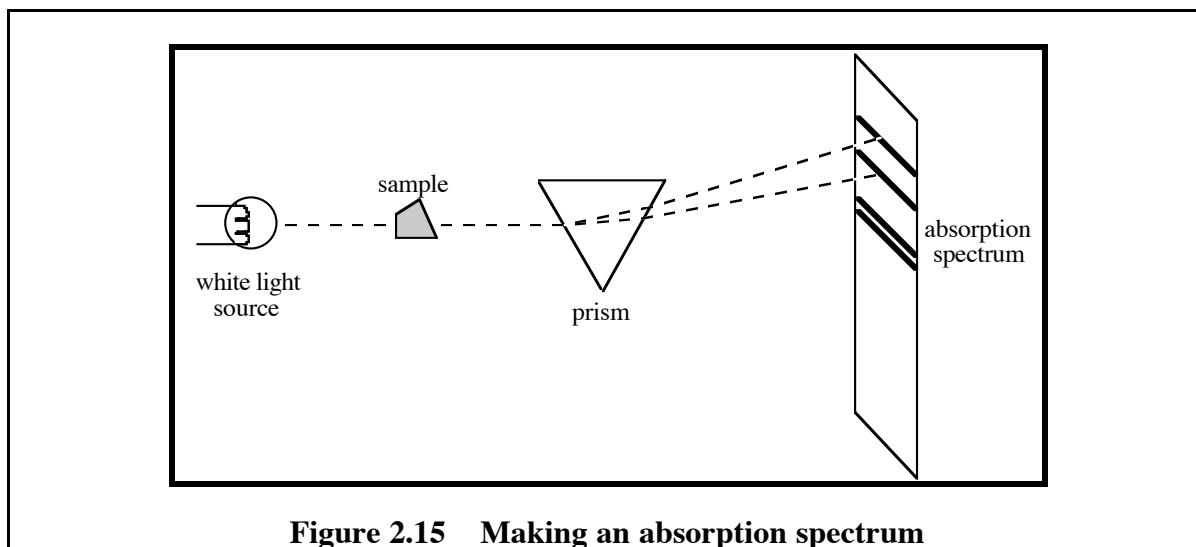


Figure 2.15 Making an absorption spectrum

Most of the light passes through the sample. Only those elementary waves with frequencies corresponding to differences in energy levels for free atoms or molecules in the sample are absorbed. This gives an absorption spectrum of characteristic dark lines or bands in the otherwise continuous spectrum.

An accessible example of an atomic absorption spectrum is found in sunlight. When it is examined closely the continuous spectrum of light is seen to be interrupted by numerous dark lines, called Fraunhofer lines. These lines can be grouped into sets which are characteristic of various light elements that are present in the outer layers of the Sun's atmosphere. These elements absorb parts of the continuous spectrum produced in deeper layers of the Sun. The element helium was identified from absorption lines in the solar spectrum before it was discovered on Earth.

2-7 STIMULATED EMISSION AND LASERS

Stimulated emission

An excited atom left alone will lose energy by spontaneously emitting a photon. Since spontaneous emission is fundamentally a random process it is not possible to predict when an individual excited atom will decay. Some atoms will remain in their excited states longer than others. On the other hand, a collection of excited atoms will remain excited for a statistically predictable average time. There is another emission process called **stimulated emission** in which an excited atom is triggered to emit its photon instead of decaying randomly. The stimulus must be a photon whose energy is exactly equal to the energy of the emitted photon. As we have already seen the value of this energy is determined by the difference in the energy levels of the atom. Stimulated emission will occur whenever a suitable photon passes close enough to an excited atom. Since the stimulating and emitted photons have equal energies, the frequencies of their associated elementary wavelets are also identical. Furthermore the two waves are exactly in phase and they travel in the same direction as the incident photon. In short, the stimulating photon and the emitted photon are identical in every respect. Stimulated emission is the key process in the operation of lasers.

The helium-neon laser

The word 'laser' is an acronym derived from **L**ight **A**mplification by **S**timulated **E**mission of **R**adiation. Laser light is very monochromatic and highly coherent. Those properties are achieved using the process of stimulated emission to create an avalanche of identical photons. As more and more photons are released by stimulated emission from excited atoms each new photon can stimulate more atoms to emit their photons. In order to maintain this process there are two essential requirements. Firstly there must be a plentiful supply of suitably excited atoms and secondly the avalanche of photons must be confined sufficiently so that further stimulated emissions can occur. We will consider these requirements below.

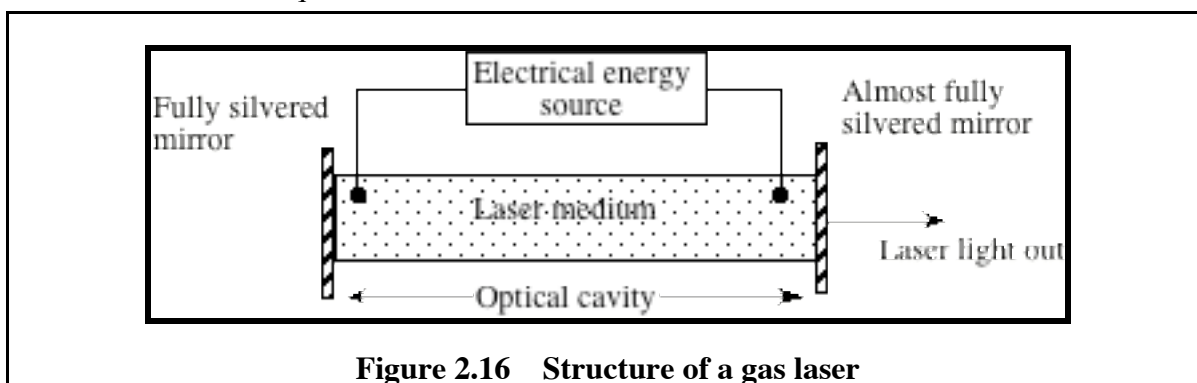
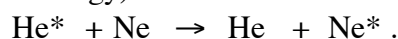


Figure 2.16 Structure of a gas laser

A helium-neon laser contains a mixture of helium and neon gases in a container which is fitted with a pair of parallel mirrors. Energy is supplied to the gas mixture by passing an electrical current through it. The current ionises the gas and, by a sequence of collision processes, excites the neon atoms. The energy required to lift a neon atom to its excited state is obtained by collision with an excited helium atom, whose excitation energy is just below the energy required by the neon (the extra energy comes from kinetic energy) and the helium atom returns to its ground state.



(The asterisk indicates an excited state.) This process is indicated on the left side of figure 2.17.

The helium atoms, in turn, get their excitation energy in collisions with electrons produced in the electrical discharge. These collision processes must occur quickly enough to keep most of the neon atoms in their excited state.

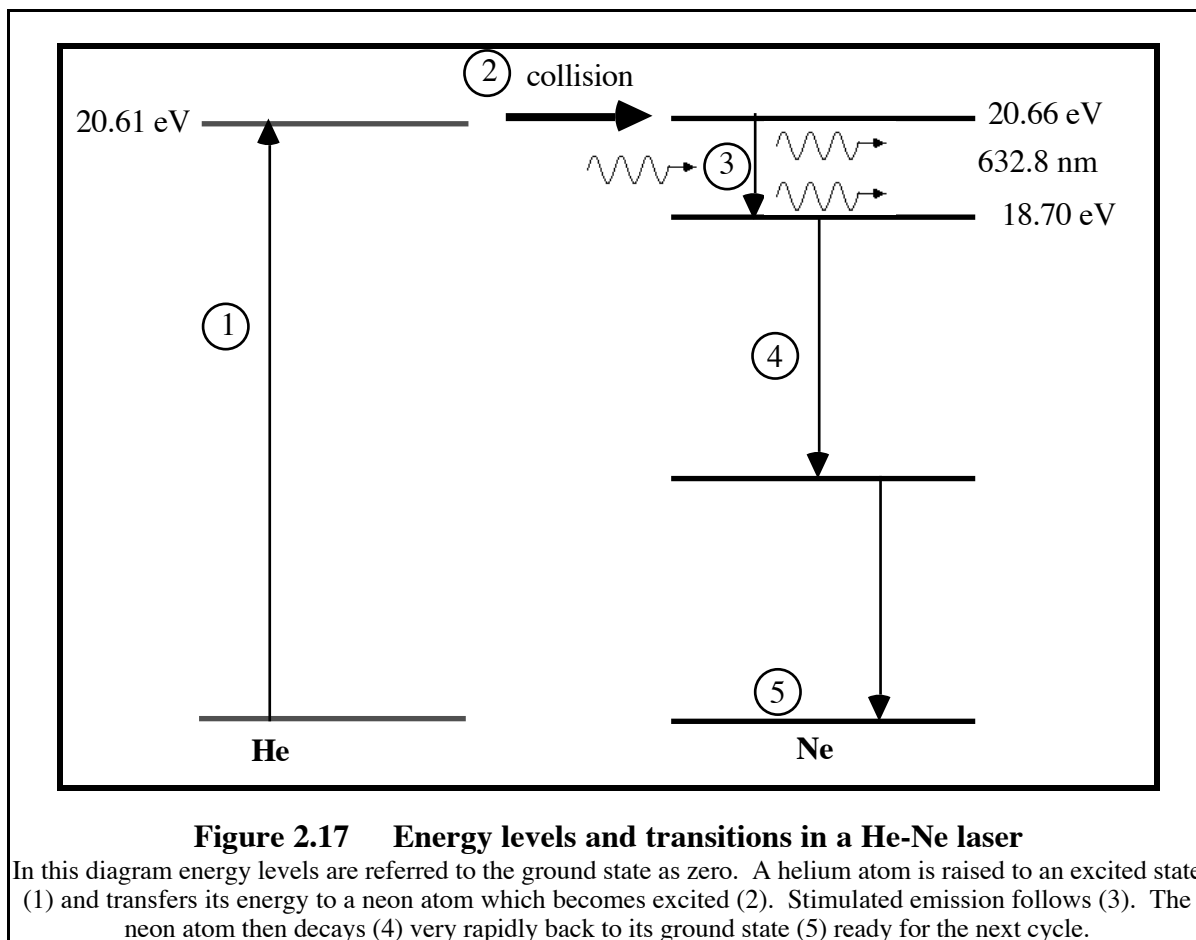
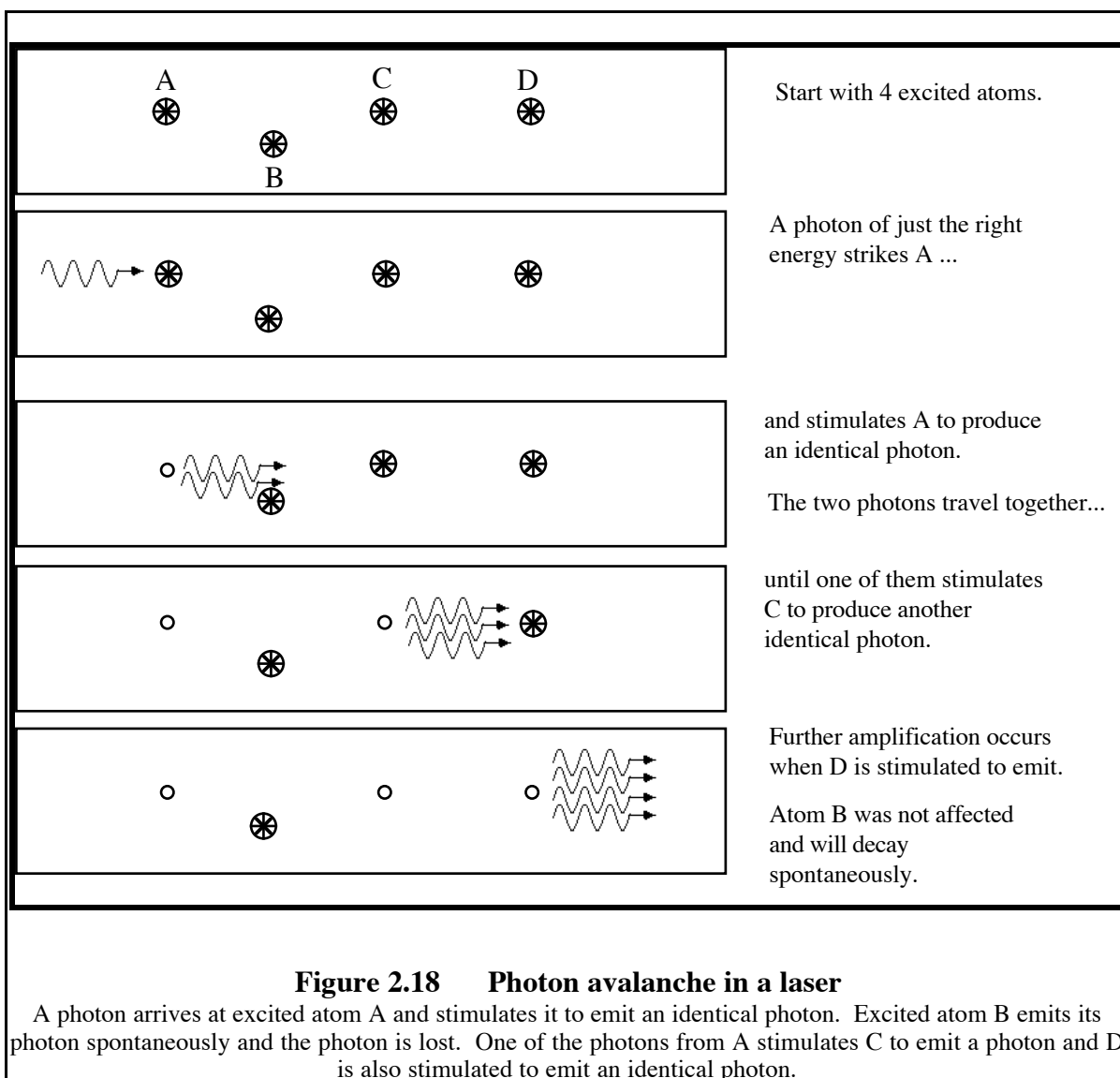


Figure 2.17 Energy levels and transitions in a He-Ne laser

In this diagram energy levels are referred to the ground state as zero. A helium atom is raised to an excited state (1) and transfers its energy to a neon atom which becomes excited (2). Stimulated emission follows (3). The neon atom then decays (4) very rapidly back to its ground state (5) ready for the next cycle.

Once the neon atoms have been excited they are stimulated to emit laser light. Initially the stimulating photons come from spontaneous decays, but once the laser process has been started, most of them will come from previously stimulated transitions. Since each photon released can stimulate more transitions, the number of photons can build up very rapidly. To keep the laser process going, the beam of photons is confined by two accurately parallel, highly reflective, mirrors at opposite ends of the discharge chamber. Since each stimulated photon travels in the same direction as the photon which triggered it, the number of photons bouncing back and forth along the axis of the laser cavity soon builds up to produce a very intense beam of light inside the laser. Those photons which do not travel parallel to the axis are lost from the beam and take no further part in the laser action. A small part of the intense beam between the mirrors is let out of the laser by having one of the mirrors not quite perfectly reflecting (say 99.9% reflectivity). Even the small fraction of the beam which comes out is still very intense.

The radiative transition which produces the laser light from the neon atom does not leave the atom in its ground state - if it did there would be many neon atoms able to re-absorb the photons in the laser light. So any neon atoms in a state which could remove laser photons need to be got rid of very quickly. The lower state of the lasing transition is another unstable state which then decays very rapidly in two stages back to its ground state as shown in figure 2.17. (The two photons emitted in these transitions have no role in the laser action.)



The laser action is sustained by returning neon atoms from their ground state back to the excited state, through further collisions with excited helium atoms.

Properties of laser light

The important features of laser light are as follows.

- It is spectrally very pure, being much closer to the ideal of pure monochromatic light than light from spectral lamps. For example, the sodium D line from an ordinary sodium vapour lamp has a bandwidth (or frequency spread) of 1 GHz but a gas laser can easily attain a bandwidth of only 1 MHz.
- The light is highly **coherent**. Whereas coherent light produced by splitting waves (as in Young's experiment or in thin films) loses its coherence as the path difference between the beams is increased, laser light maintains its coherence much longer.
- Because of its coherence laser light can be made highly collimated, i.e. a parallel beam remains parallel to a much greater degree than a conventional light beam.
- Very high power concentrations can be achieved, i.e. the irradiance of laser light can be made very large.

FURTHER READING

Steven S. Zumdahl, *Chemistry*, 2nd edition, Chapter 7.

QUESTIONS

- Q2.1** A hydrogen atom is in the -3.4 eV excited state.
- (i) Calculate the energy a photon must have to excite the atom into the -1.5 eV excited state.
 - (ii) What is the wavelength of this photon?
 - (iii) What part of the electromagnetic spectrum does this correspond to?
- Q2.2** A hydrogen atom in the -1.5 eV excited state falls to the ground state. Calculate the wavelength of the photon emitted.
- Q2.3** A laser is powered by a discharge lamp running from a capacitor bank that stores 4 kJ. The conversion to laser light is 0.2% efficient and the laser pulse length is 50 ns. What is the power in the laser pulse? What is the irradiance if the area of the beam is $2 \times 10^{-6} \text{ m}^2$?
- Q2.4** The emission spectrum of sodium has two closely spaced lines at wavelengths of 588.995 nm and 589.592 nm. Both lines are due to transitions which end up at the same level. Calculate the difference in the energies of the upper levels.
- Q2.5** Describe the sequence of energy level transitions of a neon atom in a helium-neon laser. Why is it important that should be more than one radiative transition?
- Q2.6** Some lasers operate at wavelengths outside the visible range. For example a methyl fluoride laser involves stimulated emission between molecular energy levels about 3 meV apart. Estimate the wavelength of the radiation. What part of the spectrum does it lie in?

Discussion questions

- Q2.7** Absorption and emission spectra of the same element do not usually contain the same prominent spectral lines. Why not?
- Q2.8** The materials on the inside of fluorescent light tubes absorb ultraviolet light and subsequently emit visible light. What do you think of a claim from an inventor who says he has found a material that absorbs visible light and emits ultraviolet?
- Q2.9** Atoms in the gaseous state emit line spectra but in solids they emit continuous spectra. How do you account for the difference?
- Q2.10** In black and white photographic film, the latent images are formed when light splits some atomic bonds between silver and chloride ions. The film is more sensitive to blue light than red light, and hardly reacts at all to infrared. Can you explain that?
- Q2.11** At a distance of 1 km the light from a 1 mW laser is much brighter than that from a 1 kW flood lamp. Explain why.