Practical 1P9
Energy Levels and Band Gaps

What you should learn from this practical

Science
This practical illustrates some of the points from the lecture course on Elementary Quantum Mechanics and Bonding and also the second year lecture course on Semiconductor Materials. It will help you to understand:

1. The spectrum of hydrogen, which provides evidence for discrete (quantised) energy levels.
2. The emission and absorption of light by a semiconductor. This will provide evidence for the bands of allowed energy levels which are found in solids.

However, the practical is designed to be self-contained and you should be able to complete it satisfactorily using only this sheet and the attached appendix.

Practical skills
- Good practice for data collection and manipulation.
- Treatment of errors.
- Fine adjustment of delicate optical equipment.
Overview

Note

Marking: A written report is submitted in the usual way, but in this case the marker will read the report in advance of an individual 15-minute oral marking session over MS Teams. Student speaks to their report and discusses it with the SD at this mini-tutorial style marking session. Most students would be unable to do this well if they had not prepared thoroughly by writing the report. The final mark is based primarily on this discussion.

The practical consists of three separate parts. The first investigates the optical emission spectrum of atomic hydrogen whilst the second investigates the emission and absorption of light by a semiconductor. In this case a blue, light-emitting diode (LED) is studied. The absorption of light by the semiconductor is measured indirectly by monitoring the photocurrent produced when the LED is illuminated with different wavelength light. The final stage of the practical is to investigate the emission and absorption of a “white LED” and deduce the way in which the device produces white light.

1. You will set up and align the optical monochromator. You will use the monochromator to measure the wavelength of the four visible lines in the spectrum of hydrogen. You will verify that the wavelengths obey the simple formula given in the Quantum Mechanics course and you will estimate the ionisation energy of a hydrogen atom.

2. You will use a tungsten halogen bulb emitting white light, a photodetector, the monochromator and the blue LED to investigate, as a function of wavelength, the absorption and emission of light by a semiconductor. The characteristics of the halogen bulb and
monochromator will be measured using the photodetector, and the data will be used to correct the absorption measurements obtained from the LED to give an accurate absorption spectrum.

3. You will measure and then use the emission and absorption spectrum of the “white LED” to deduce how the device produces white light.
Safety

Do not touch the lamp tube as it gets hot enough to burn. Do not look directly into the tungsten halogen bulb.

Experimental details

1. The hydrogen spectrum

There are four visible lines in the hydrogen spectrum. These lines should be observed directly by eye using the spectrometer which is set up in the laboratory. Two are blue-violet, quite close to each other, and the third one, a blue-green one, is not far away. The blue-green line is the brightest. These three lines appear over a fairly bright background. The fourth line is red, and it appears at a larger angle over a dark background.

The hydrogen lamp may also contain small quantities of impurities which can emit light, such as sodium (\(\lambda \sim 589\) nm), caesium (452 nm, 583 nm, 612 nm), chlorine (546 nm) and mercury (546 nm).

Note: You are provided with an optical monochromator. This is an expensive and delicate item of equipment. Treat it with care and never apply more than the gentlest force to the wavelength selecting handle. Never allow the digital read out to exceed a reading of 800 nm. Be careful not to knock the slit assemblies. When adjusting the slit width only turn the micrometers very gently and do not use slit widths greater than 2 mm.

The monochromator is set up so that the digital read out on the instrument is equivalent to the wavelength of the transmitted light measured in
nanometers. The spread in wavelength of the light transmitted through the monochromator is dependent on the slit width selected. The width of the entrance and exit slits should always be selected to be the same. A larger slit width results in more light being transmitted through the monochromator, but with less spectral resolution. For example with a slit width of 120 \( \mu \text{m} \) the spectral resolution is approximately 1 nm, whilst with 1.5 mm slit width the spectral resolution is approximately 10 nm.

It is a feature of this type of monochromator that the digital read out of wavelength may show a slightly different value to the actual wavelength transmitted through the instrument. This offset in reading compared to the actual value is constant irrespective of the wavelength selected on the monochromator. The size of the offset can be measured by noting the precise value, close to zero, at which the light transmitted through the monochromator is a maximum. The difference between this reading and zero gives the magnitude of the offset. This offset should be taken into account when you measure the position of the four lines in the hydrogen spectrum and you should explain the corrections you have made to the measured values in your write-up.

1. Position the left edge of the carrier supporting the monochromator 25 cm from the end of the optical rail.
2. Set the widths of the entrance and exit slits of the monochromator to 120 \( \mu \text{m} \). Ensure that the horizontal sliders, which control the vertical extent of the light transmitted through the slits, are in the open position. This is when the round knob is pushed up against the side of the slit holder.
3. Position the hydrogen lamp on the bench to the left of the monochromator and place the lens on the optical rail to focus (approximately) an image of the hydrogen lamp onto the entrance slit of the monochromator.

4. Position the silicon photodetector over the exit slit of the monochromator and connect it to the digital meter, which should be set to measure voltage. Ensure that the side of the connector marked white is inserted in the positive (red) terminal of the digital meter.

5. Adjust the monochromator so that the wavelength reading is zero (for this setting all wavelengths of light are transmitted through the monochromator) and fine position the lens and the hydrogen lamp to maximise the signal produced by the detector. You should aim to achieve a signal greater than 90 mV and you should record in your write-up the value that you obtain.

6. Adjust the widths of the entrance and exit slits of the monochromator to be 1.5 mm and record the position of four hydrogen lines. They have wavelengths within the range 700 to 400 nm.

7. Repeat step 6, but with a narrower slit width to improve the resolution of your measurements. Record the values of the slit width you use and the values of the wavelengths you measure. Since the measurement is made in air, the wavelengths you obtain are shorter than they would be in vacuum. The differences are 0.181 nm for the red line, 0.136 nm for the blue-green, 0.122 nm for the first blue-violet, and 0.116 nm for the second blue-violet.

8. Record the shape of the peak produced by this optical set up for the longest wavelength hydrogen line. Do this by measuring the
photodetector output as a function of wavelength. Use the best resolution you can obtain.

According to the Bohr theory, the wavelengths emitted by the hydrogen atom are given by the formula:

\[
\frac{1}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)
\]

where \( R_H \) is the Rydberg constant for hydrogen and \( n_1 \) and \( n_2 \) are integers with \( n_2 \geq n_1 + 1 \). Plot graphs with \( 1/\lambda \) on the y-axis and \( \left(1/n_1^2 - 1/n_2^2\right) \) on the x-axis. Use values of \( n_1 = 1, 2 \) and 3 to plot three graphs with \( n_2 = n_1 + 1, n_2 = n_1 + 2, n_2 = n_1 + 3, n_2 = n_1 + 4 \) for each graph. You should plot your measured values for the wavelengths of the red, blue-green, first blue-violet and second blue-violet lines to correspond to the points with \( n_2 = n_1 + 1, n_2 = n_1 + 2, n_2 = n_1 + 3, n_2 = n_1 + 4 \) respectively. By inspection of these graphs and by considering the equation given above deduce which atomic transitions are responsible for each spectral line you have measured. (Hint: only one of the graphs you have plotted represents the physical processes taking place.) Calculate the value of \( R_H \) from your graph and estimate the error. (Hint: consider the largest and smallest values for \( R_H \) which are consistent with your data. How did you arrive at these values?) Compare your value with the tabulated value, which is

\[
R_H = (1.096775854\pm0.000000082) \times 10^7 \text{ m}^{-1}
\]
Deduce the ionisation energy for a hydrogen atom. Give your answer in electron volts (eV) where 1 eV = 1.6022 × 10⁻¹⁹ J.

2. Emission and absorption of light by a semiconductor
   a) Emission spectrum of the blue LED

1. Position the silicon photodetector over the exit slit of the monochromator and connect it to the digital meter.
2. Connect the LED to the LED power supply ensuring correct polarity of connections.
3. Mount the LED in the LED holder provided and secure in place using the grub screw.
4. Mount the LED holder onto the optical rail and by sliding the holder along the optical rail move the LED to within ~1mm of the monochromator slit.

CAUTION: The monochromator’s slits are fragile. On no account should the LED be brought into contact with a slit. On no account should the slit width (adjusted by the micrometer) be set greater than 2mm.

5. Optimise the position of the LED by adjusting the fine positioning stages on the LED holder to maximise the signal produced.
6. Obtain the emission spectrum of the LED by measuring the potential produced by the photodetector as a function of the wavelength setting of the monochromator. You may assume that the output of the photodetector is proportional to the photon flux incident on it and that it
is independent of wavelength for the range of wavelengths investigated in this experiment. Select the appropriate slit width so that your measurements have sufficient signal and good spectral resolution.

b) **Absorption: the photocurrent spectrum of the blue LED**

**Note:** In this section you will be measuring very small currents and any movement near the input leads to the digital meter will cause electrical noise to be generated. This may make your readings unstable.

1. Set the monochromator slit width to be 250 $\mu$m.
2. Align the LED at the exit slit of the monochromator by sliding the holder along the optical rail, move the LED to within ~1 mm of the monochromator slit. Connect the LED to the digital meter to measure voltage.
3. Place the tungsten halogen light source and lens on the optical rail. Adjust the heights of the source and the lens so that their centres coincide with the centre of the monochromator slit. Position the monochromator and source so that the slit and filament are separated by ~20 cm and move the lens so that an image of the bulb is produced on the monochromator slit.
4. Set the monochromator to 430 nm and carefully re-adjust the source, lens and LED to maximise signal. You may have to adjust the height of the LED slightly. You should aim to achieve a reading of greater than 20 mV.
5. Measure the photocurrent produced by the LED as a function of the wavelength of light incident on it. **(Note:** This measurement is performed by using the voltage reading mode of the meter and works
because the input impedance of the meter is 10 MΩ. Thus, for example, a photocurrent of $10^{-9}$ A produces a voltage reading of 10 mV).

6. Replace the LED with the silicon photodetector and measure, as a function of wavelength, the intensity of light produced by the halogen bulb at the exit slit of the monochromator. Do this for the same range of wavelengths used to characterise the behaviour of the LED.

7. Use the data obtained in step 6 above, concerning the wavelength dependence of the intensity of light at the exit slit, to produce an accurate absorption spectrum of the LED.

**Note:** In the absorption spectrum you may detect small oscillations in the photocurrent reading as a function of wavelength. The period of these oscillations is approximately 3 nm. They are not due to the fundamental processes of light emission and absorption in semiconductors, but arise from the way in which the LED is fabricated. You need not include an explanation of these in your write-up.

3. **Emission and absorption of light by a “white LED”**
Repeat Section 2 for the “white LED” obtaining both emission and absorption spectra. (You do not need to repeat step 6.)

**Rough timetable**

**Day 1:**
Measure the emission spectrum of hydrogen.
Observe the hydrogen emission spectrum directly using spectrometer.
Measure the emission spectrum of the blue LED.
Day 2:
Measure the absorption of light by the blue LED.
Measure the emission and absorption spectra of the “white LED”.

What should be in the lab notebook:
1. You should provide answers to the questions asked in these Guide Notes and should deduce $R_H$ and the ionisation energy of hydrogen. Include estimates of the error in each. Include in your write-up the plot you obtained of the shape of the longest wavelength hydrogen peak. Discuss to what extent the shape of the peak might represent the width of the energy levels you are measuring and the characteristics of the monochromator you are using.

2. You should plot emission and photocurrent (absorption) spectra for the blue LED as a function of energy (in eV). You should comment on the shape of the photocurrent and emission spectra and describe how these provide evidence for bands of energy levels and also for a band gap in the distribution of allowed energy levels. In particular you should consider the following:

Photocurrent spectrum:
- Why is there no photocurrent produced for photon energies less than ~2.65 eV?
- Which transitions occur to produce a photocurrent for photons with energies greater than the band gap?

You may like to answer these points with the help of arrows marking the electron transitions on band diagrams.
Emission spectrum:
- Why is very little emission observed for energies more than a few kT greater than the band gap energy?
- Why is there a “tail” in the emission spectrum towards lower energies?
- Why is there no emission at energies much less than the band gap?

3. Use the emission and absorption spectra of the “white LED” to deduce by what means the white light is generated. In doing this you should consider the following:
- Inspect the emission spectrum to deduce how many different emitting materials are used in the manufacture of the “white LED”. Estimate the peak emission wavelength of each material.
- Use the absorption spectrum to deduce which one(s) of these produce a photocurrent in the leads connected to the device.
- Try to think of methods by which each of the materials in the device may be excited to emit light which are consistent with what you have deduced above.

(The relation between the energy of a photon $E$, and its wavelength $\lambda$, is given by $E = hc / \lambda$, where $h$ and $c$ are respectively Planck’s constant and the speed of light. The band gap energy for this GaN based LED at 300 K is $\sim 2.67$ eV, and 1 eV is equivalent to $1.6 \times 10^{-19}$ J).
Appendix: Optoelectronic properties of semiconductors.

A very brief summary of features relevant to this practical.

In a perfect crystalline semiconductor the allowed energy levels are arranged into bands with a gap in electron energy separating the highest energy band full of electrons from the lowest energy band empty of electrons. These bands are termed the valence and conduction bands respectively. When such material is excited, either thermally or by photons of sufficient energy, electrons are promoted from the full valence band into the conduction band. This process leaves a “hole”, that is an allowed energy level in the valence band which is not now occupied by an electron, and also an electron in the conduction band. The hole, which represents the absence of an electron in an otherwise full or nearly full band can be thought of as a positively charged particle similar to an electron but with opposite sign charge, see Figure 1. Both the hole in the valence band and the electron in the conduction band are free to move and so are able to conduct electrical current. Once created they may move off in different directions through the semiconductor. It is a good approximation that any photon, which has energy greater than or equal to the band gap, will produce an electron hole pair when absorbed by a semiconductor.
Figure 1. Valence and conduction bands for a perfect semiconductor crystal showing an electron in the conduction band and a positively charged hole in the valence band. If the electron and hole recombine an energy $E_g$ will be liberated.

If an electron in the conduction band subsequently comes to the same position in the crystal as a hole in the valence band, a process termed recombination can take place. This is a process whereby the electron “falls” into the hole and annihilates it. That is to say the electron makes the transition from the conduction band to the empty state in the valence band and liberates the energy difference between the two states. This energy may be given off in the form of a photon which will have an energy equal to the difference between the two states, which for an electron close to the bottom of the conduction band and a hole close to the top of the valence band will be approximately equal to the band gap energy. In practice, at room temperature, one or more phonons (a phonon is a quantised lattice vibration) are normally also produced and hence the photon energy is less than otherwise expected by an amount equal to the energy of the phonons produced. In GaN a typical phonon energy is $\sim 0.05$ eV. Thus, in summary, when an electron and hole meet they may recombine and a photon may be
emitted, the energy of the photon depending on the energy difference between the two states and also on the number of phonons also produced.

In light emitting diodes (LEDs), semiconducting material is used which contains very small quantities of impurities which have the effect of acting as doping atoms. Depending on the nature of the impurity this generates material which contains either an excess of holes or an excess of electrons in the conduction band, over the concentrations that would otherwise be present. Such material is termed p-type or n-type material respectively. An LED consists of a junction between a region of p-type and a region of n-type semiconductor; see Figure 2. When an LED is operated, a voltage is applied to the junction such that some of the electrons in the conduction band of the n-type material flow into the p-type region of the device where there is a high concentration of holes, whilst some of the holes in the p-type region flow into the n-type material where there is a high concentration of electrons in the conduction band. Under these circumstances the electrons in the p-type material and the holes in the n-type material rapidly recombine with carriers of the opposite sign, and in an LED substantial amounts of light are emitted.
Figure 2. A schematic diagram of a p-n junction in an LED. The p-type material contains an excess of holes and the n-type an excess of electrons in the conduction band. When an external potential is applied the carriers move, recombining near the junction and so emit light.

It is a feature of p-n junctions that if excess electron hole pairs are present and no external voltage is applied, then the electrons at the edge of the junction will try to move into the p-type material and the holes at the edge of the junction will try to move into the n-type material. If the two sides of the junction are connected together in an external circuit, then at steady state the current flowing through the junction and hence external circuit is proportional to the density of excess carriers at the junction which is in turn proportional to the rate at which they are being excited. Thus, in the present practical, the current flowing through the 10 MΩ resistor, and hence the potential across it, is proportional to the rate at which electron hole pairs are created at, or close to, the junction. When the carriers are created by light the current is called the photocurrent.
In the case of practical LEDs the packaging can absorb ultra-violet light \((\lambda < 390 \text{ nm})\) before it reaches the p-n junction. In addition, semiconductor devices comprise very thin layers of material which can produce interference effects at certain wavelengths. In this way, a “ripple” can sometimes be observed superimposed on the emission and absorption spectra of such devices.