

At01 Atomic Spectroscopy & Electron Spin Resonance

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1 Introduction

Two key atomic concepts were investigated during this experiment: the atomic spectrum of hydrogen and the spin resonance of electrons. These two experiments are closely linked and are of key importance when studying atomic characteristics. By studying the electron spin we can find that some energy levels of atoms obtained from spectroscopic techniques are further split into smaller energy levels called *multiplets* [3]. From this other phenomena can be more accurately investigated, such as investigating the chemical composition of stars.

Electrons occupy energy levels in atoms that orbit around the nucleus. When electrons gain energy, for example from a collision with an external electron or absorption of a quantum ‘packet’ of energy called a *photon*, they move up to the next energy level and are then said to be *excited*. After a period of time, they de-excite back to their original energy level emitting a photon equivalent to the energy difference of the two levels

$$h\nu = E_f - E_i \quad (1)$$

where $h = 6.63 \times 10^{-34}$ Js, is the Planck constant, ν is the photon frequency, E_f is the excited energy level, E_i is the original equilibrium energy level. These photon energies can act as ‘finger prints’ for atoms and hence the particular type of atomic species can be identified by analysing the emitted or absorption spectrum of an atom. Where the absorption spectrum will have particular wavelengths of light missing from a continuous spectrum due to the absorption of photons by the atom from the excitation process. In this experiment we will be analysing the *emitted* spectrum of hydrogen [1].

In addition, all electrons have a spin angular momentum associated with them [2]. The electron spin component is given by

$$S_z = m_s \hbar \quad (2)$$

where S_z is the electron spin angular momentum by considering the z-component, $m_s = \pm \frac{1}{2}$ refers to the spin quantum number either ‘spin up’ (positive) or ‘spin down’ (negative) respectively and $\hbar = \frac{h}{2\pi}$. This concept can be likened to an analogy of a spinning sphere [3] where the spin angular momentum is the momentum associated with the body about z-axis. The magnitude of the spin angular momentum is

$$S = \hbar \sqrt{s(s+1)} \quad (3)$$

where $s = |m_s| = \frac{1}{2}$ and is the spin quantum number. Because electrons have a charge associated with them, they will be affected as they pass through a magnetic field. This experiment investigates this effect further and obtains some fundamental information from this process.

2 Theory

The energy levels of a simplified diagram for the hydrogen atom is shown in Figure 1.

These energy levels can be determined by using the Bohr model or by solution to the Schrödinger equation [1] and is given by

$$E_n = -\frac{Ry}{n^2} \quad (4)$$

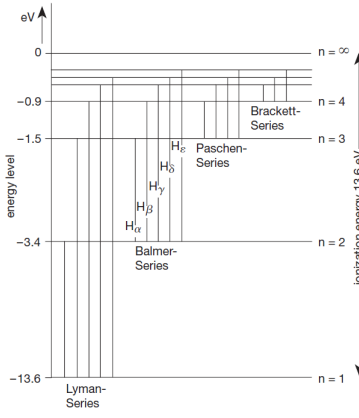


Figure 1: A simplified diagram showing the energy levels of the hydrogen atom. Where n is the principle quantum number. $n = 1$ is the ground state and $n = \infty$ corresponds to the ionisation energy required to liberate the bound electron [1].

where Ry is the Rydberg constant and has a value of 13.6 eV and n is the energy level number in the atom. The experiment considered transitions to the $n = 2$ energy level, i.e. the Balmer Series, for the photon energies as the first few photons in the Balmer Series lie in the visible region of light. This because the first few energy transitions for this series is in the visible region and can easily be observed. The transitions occur by exposing the the spectral tube to an electric field and this ionises the gas releasing electrons [1]. These free electrons then collide with other electrons bound by hydrogen atoms, as mentioned in Section 1. This excites the bound electrons in the atoms to an excited state. Then, these electrons would de-excite via the emission of a photon, producing a constant output beam. Therefore by considering the relation (1), equation (4) becomes

$$E_n = -Ry \left(\frac{1}{n^2} - \frac{1}{2^2} \right) = Ry \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \quad (5)$$

For a more detailed derivation of the energies levels for the hydrogen atom using the Bohr model please refer to [4].

Electrons are negatively charged particles, therefore they have an associated magnetic moment

$$\mu = -g \frac{e}{2m} \mathbf{S} \quad (6)$$

μ is the magnetic moment, g is the spectroscopic splitting factor, e and m are the charge and mass of the electron respectively [2]. As mentioned in Section 1 the spinning motion of the electron is effected as it passes through a magnetic field \mathbf{B} because the magnetic dipoles of the electron and field interact with each other. This means that the electron will precess about the magnetic field, \mathbf{B} , in one of two orientations as shown in Figure 2 [2].

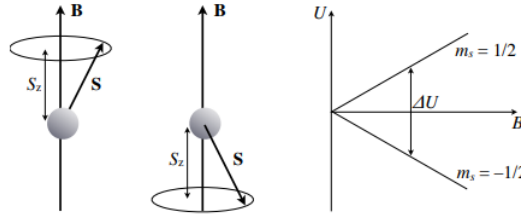


Figure 2: Left: orientation of electron 'spin up' and 'spin down' are given in a magnetic field \mathbf{B} . Right: dependence of the two energy states on \mathbf{B} is shown [2].

The magnetic energy is given by [2]

$$U = -\mu \cdot \mathbf{B} = -\mu_z B \quad (7)$$

Where μ_z is the z-component, $\mu_z = -g \frac{e}{2m} S_z$, of the magnetic moment. By substituting (2) into (7), we now have

$$U = g \frac{e}{2m} (m_s \hbar) B = g \mu_B B \quad (8)$$

where $\mu_B = \frac{e\hbar}{2m}$ is the Bohr magneton. Therefore, from Figure 2 and (8) we can see that the difference in energy be determined by [2]

$$\Delta U = g \mu_B B \left(\frac{1}{2} - \left(-\frac{1}{2} \right) \right) = g \mu_B B. \quad (9)$$

For further information regarding this derivation arriving it equation (9), please refer to [3]. By considering the electron energy changes involved with the atomic spectroscopy mentioned earlier, we can therefore deduce that the electron can either go up or down an energy state by photon absorption or emission receptively. Hence the energy of the photon required for such a transition is given by

$$h\nu = g \mu_B B \quad (10)$$

where ν is again the frequency of the absorbed or emitted photon.

3 Method

3.1 Atomic Spectroscopy

The exerimental set-up is shown in Figure 3.

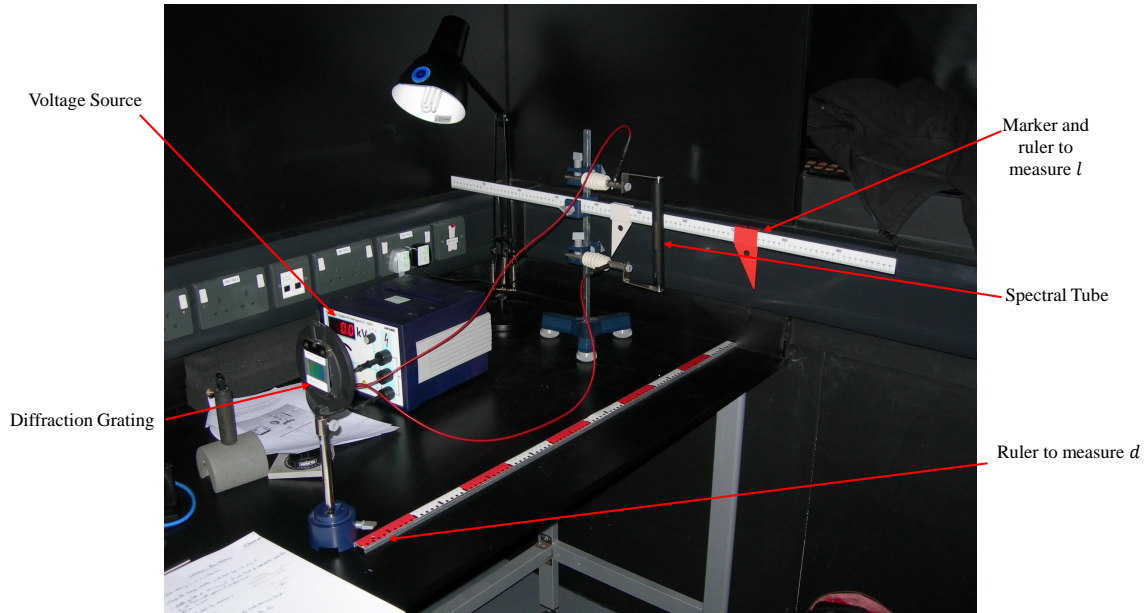


Figure 3: Experimental set-up for the atomic spectroscopy experiment.

First the Hydrogen spectral tube, marker and ruler used to determine l were carefully set-up. The tube was positioned in the centre of the ruler and the measurement taken along with the uncertainty. Then, the diffraction grating was positioned to make the distance from the spectral tube, d , as big as possible. This was carefully measured, along with the associated uncertainty. The low pressure hydrogen gas in the tube was then exposed to an electric field by carefully adjusting the voltage source as shown in Figure 3 so that the spectral tube produced as constant output beam ready for observation. These emission lines were then observed through a diffraction grating as shown in Figure 4 and the marker shown in Figure 3 was adjusted so that the spectral line position could be measured.

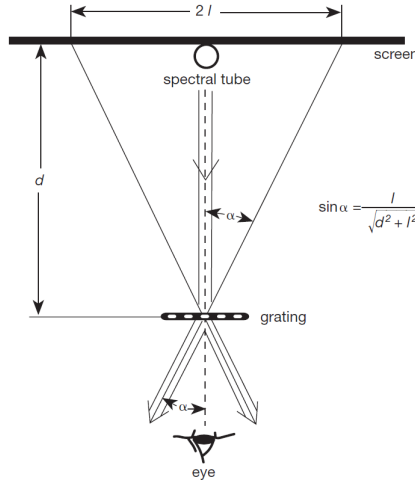


Figure 4: A plan view of the experimental set-up [1].

The difference between the central position of the tube and measured position was then determined along with the associated uncertainties in order to get a value for l . The diffraction grating was then moved in 50mm decrements towards the tube until the lines spectral lines were unclear to view. After this had been undertaken, the diffraction grating was moved back to its original value of d and the above process was then undertaken a total three times to improve accuracy and reduce errors.

The next step was then to use the marker, as shown in Figure 3, to measure the length l of mercury emission lines along the ruler using the mercury lamp in place of the spectral tube in Figure 4 to determine the grating spacing constant d_g . This process was similar to measuring the hydrogen emission lines as outlined above. These measurements were performed for the three furthest distances of d as these were the most accurate. This was repeated a total of three times to reduce uncertainty and improve accuracy. An average of these obtained values of d_g was taken along with its uncertainty carefully determined. Then, by using the known wavelengths of mercury given in [1] and the diffraction grating equation

$$m\lambda = d_g \sin \alpha \quad (11)$$

we can determine d_g the grating constant and since we were observing the first bright fringe order, $m = 1$ in this case. By using the obtained values of l and d an appropriate graph was plotted of l vs $\sqrt{d^2 + l^2}$. The gradient of this graph, $\frac{\lambda}{d_g}$ and the gradient error was used in conjunction with the determined value of d_g and its associated error to determine the wavelength, λ of the sample and error respectively for each of the bright fringes observed.

Once the wavelengths were determined, the energies can be obtained from the relation

$$E = \frac{hc}{\lambda} \quad (12)$$

where, c is the speed of light and λ is the wavelength of the emission lines. Then a graph can be plot using (5) to determine a value for the Rydberg constant Ry .

3.2 Electron Spin Resonance

The sample tested was an organic compound called DPPH (1, 1-diphenyl-2-picrylhydrazil) molecule [2]. The experimental geometry is shown in Figure 5.

A series of preliminary experiments were conducted before the main experiment. First, the magnetic field produced by the Helmholtz pair of coils were be measured over a range of DC currents using a Gauss meter. A relation describing the magnetic field for this set-up in Figure 5 is given by

$$B = \mu_0 \left(\frac{4}{5} \right)^{3/2} \frac{nI}{r} \quad (13)$$

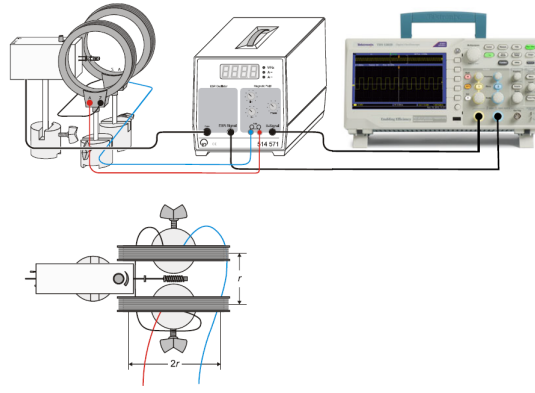


Figure 5: The experimental geometry for investigating electron spin resonance of DPPH [2].

where μ_0 is the permeability of free space, n is the number of turns per coil ($n = 320$ in this case), I is the current through each coil and r is the distance between the two coils in this case it is the coil radius (6.75cm) [2]. Once a range of magnetic field measurements had been obtained in conjunction with the corresponding currents, these currents were used in (13) to obtain the magnetic field. When comparing the values of the magnetic field measured using the Gauss meter to the ones obtained by relation (13), they were of the same order of magnitude. Therefore, this verified that (13) is a valid way of determining the magnetic field from a range of currents and the next steps in the experimental method could proceed.

The final preliminary check was to see that removing energy from a circuit will put load on the circuit and reduce the output voltage [2].

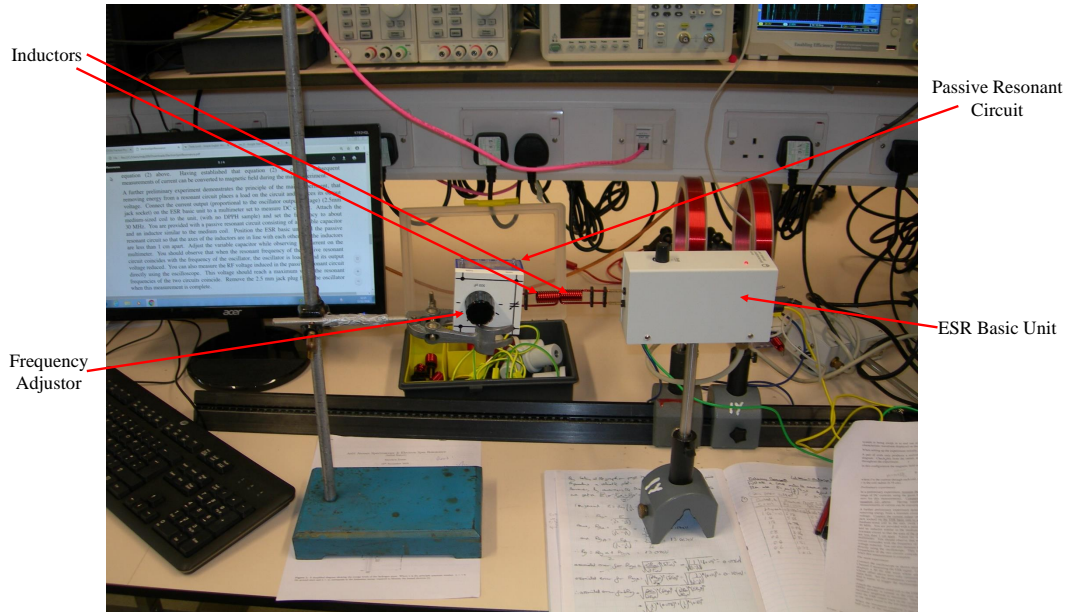


Figure 6: Preliminary Experimental set-up demonstrating a reduction in output voltage due to a load put on a circuit.

The current output from the ESR unit, see Figure 6 was be connected to a multimeter to measure the DC current. Then a passive circuit with a medium inductor coil was positioned close to a medium inductor coil attached to the basic ESR unit, see Figure 6. By adjusting the frequency of the passive circuit, the current reading on the multimeter dropped. This therefore demonstrated that by removing energy from a resonant circuit placed a load on the circuit and the output voltage was reduced. After this principle was checked, the main experiment commenced.

Upon successful completion of the preliminary checks, the DPPH sample was placed in one of the three coils provided and the experiment was set-up in the configuration as shown in Figure 7.

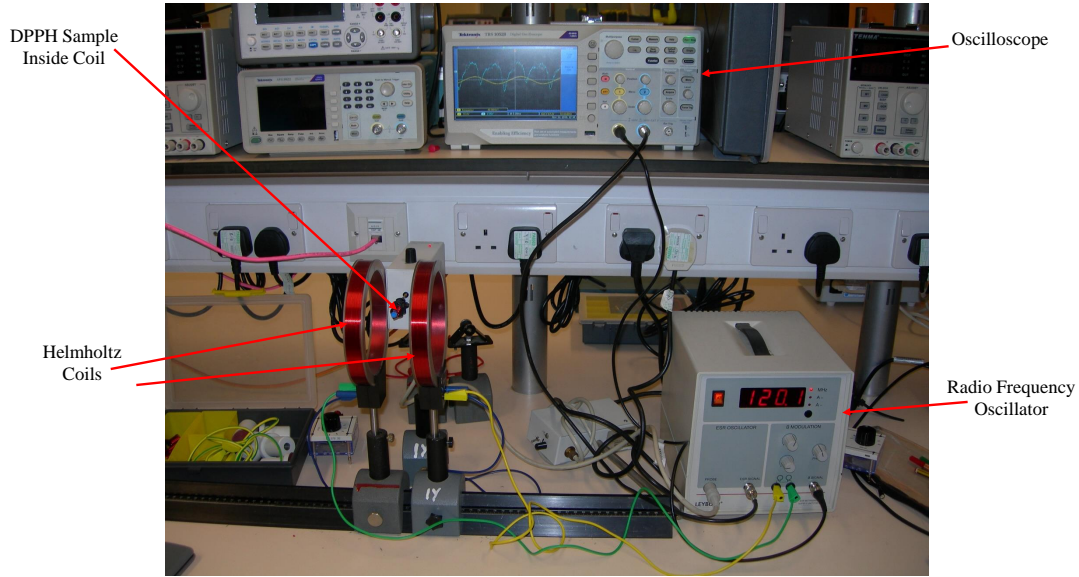


Figure 7: The experimental set-up for investigating the electron spin resonance of DPPH.

Once all the relevant connections had been made to the oscilloscope and the ESR unit, the frequency was altered on the radio frequency oscillator over a range of frequencies from 15 to 130 MHz [2] at different resonances as shown in Figure 8. The range of frequencies were covered by using a selection of sizes for the coils to insert the DPPH sample: small, medium and large.

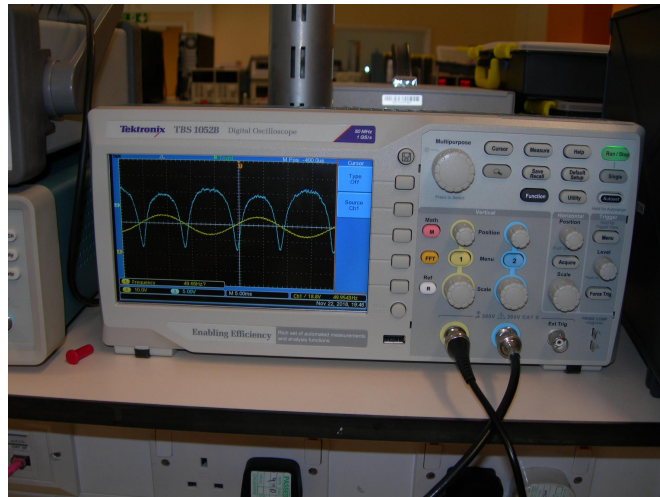


Figure 8: A picture showing the resonant frequency condition as shown on the oscilloscope trace.

Along with these resonant frequencies, the current and corresponding error in the current, obtained from the modulating current, were measured at different resonances from the radio frequency oscillator unit. These resonances were due to a radio frequency photon coming in and exiting an electron from one spin state to another. This takes energy out of the system and is observed as dips on the oscilloscope trace at resonance as shown in Figure 8. Once several resonance

measurements for the current had been obtained, using the small, medium and large coils they were all repeated a total of three times and an average current, with corresponding error was taken. This was done to improve accuracy and reliability. Then (13) was used to obtain the corresponding magnetic fields. These magnetic field measurements along with the corresponding frequency measurements were used in (10) to obtain a value for g by plotting an appropriate straight-line graph.

3.3 Safety

During both experiments there were many sensitive electrical components used; such as a radio frequency oscillator, an oscilloscope and power supplies. Therefore, no food or drink were consumed whilst working in the laboratory and any exposed metal should not be touched when any power supply is switched on [1]. In addition to this, the glass discharge tubes for the Atomic Spectroscopy experiment are fragile. So, when they required moving or changing the demonstrator or laboratory technician were present to handle these pieces of equipment.

4 Results

Figure 9 and Figure 10 show a plot of l against $\sqrt{d^2 + l^2}$ for the two observed hydrogen emission lines.

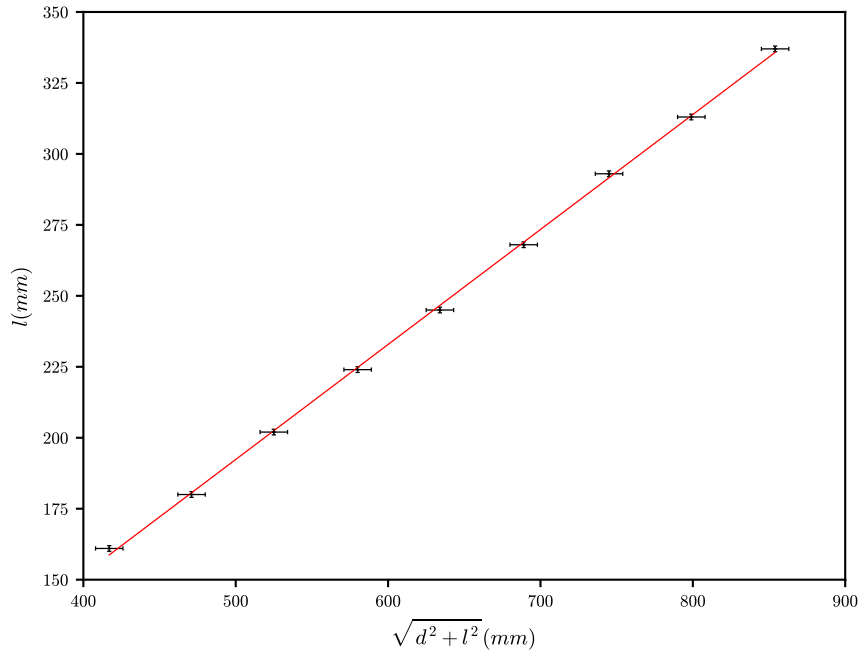


Figure 9: A graph of length l against $\sqrt{d^2 + l^2}$ for the H_α transition.

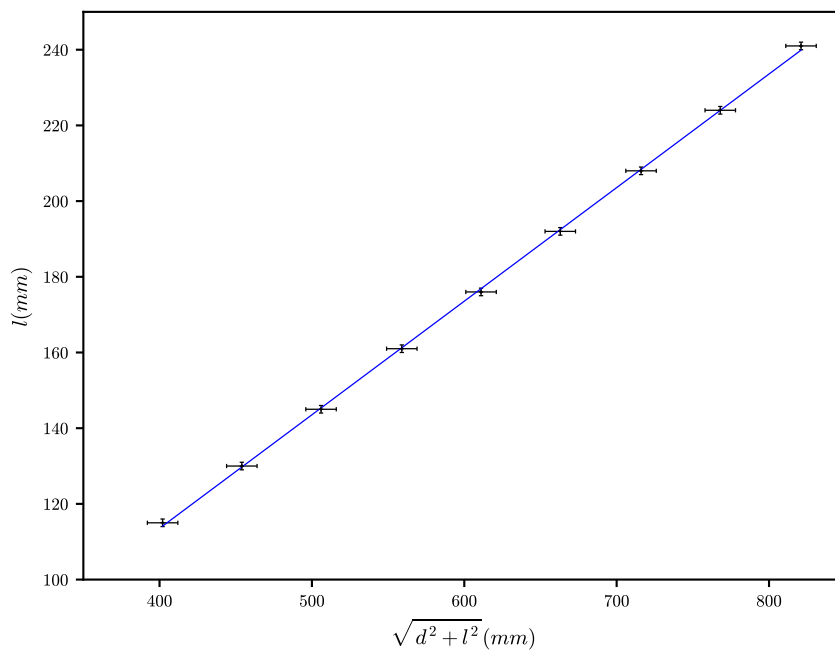


Figure 10: A graph of length l against $\sqrt{d^2 + l^2}$ for the H_β transition.

References

- [1] Atomic Spectroscopy worksheet.
- [2] Electron Spin Resonance worksheet.
- [3] Young and Freedman, *University Physics*, 13th Edition, Chapter 41, pages 1519 - 1527.
- [4] Young and Freedman, *University Physics*, 13th Edition, Chapter 39, pages 1427 - 1437.