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Rydberg Constant and Emission Spectra of Gases

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Abstract

The quantized nature of atomic energy levels is investigated through the analysis of the hydrogen emission spectrum. Using Bohr's atomic model and the Rydberg equation, the wavelengths of emitted photons are related to electron transitions between discrete energy states. The theoretical framework of this report outlines the Bohr model, its assumptions, and its limitations, emphasizing its historical role as the foundation of quantum mechanics.

Contents

1 Introduction

The study of atomic emission spectra provides fundamental evidence for the quantization of energy in atoms. When electrons in an atom absorb energy, they transition to higher discrete energy levels. As they return to lower levels, photons are emitted with energies corresponding to the difference between these quantized states. Each element emits light at characteristic wavelengths, forming a unique line spectrum that reflects the underlying electronic structure of the atom.

In the early 20th century, Niels Bohr developed a model of the hydrogen atom to explain these discrete spectral lines [1]. Building on Planck's quantum hypothesis and Rutherford's nuclear model, Bohr postulated that the electron orbits the nucleus in specific allowed circular paths where its angular momentum is quantized according to

$$L = n\hbar, \quad n = 1, 2, 3, \ldots \tag{1}$$

where $\hbar = \frac{h}{2\pi}$ is the reduced Planck constant.

Using this quantization condition, Bohr derived the total energy of an electron in the nth orbit as

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2} = -R_{EH}\frac{1}{n^2}, \tag{2}$$

where $R_{EH} = 13.6\,\text{eV}$ is the Rydberg energy constant. When an electron transitions between two levels n_i and n_f $(n_i > n_f)$, the atom emits a photon with energy

$$E = hf = R_{EH}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right), \tag{3}$$

leading to the Rydberg formula for the wavelength of emitted light:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right), \tag{4}$$

where $R_H = 1.097 \times 10^7\,\text{m}^{-1}$ is the Rydberg constant for hydrogen [2]. The visible portion of the hydrogen spectrum, known as the Balmer series, corresponds to transitions ending at $n_f = 2$ and lies within the visible region of the electromagnetic spectrum.

While Bohr's model successfully explained the hydrogen spectrum and introduced the concept of quantized energy levels, it has several limitations. It fails to accurately describe atoms with more than one electron, as it does not include electron–electron interactions or account for quantum mechanical principles such as the uncertainty principle and wave–particle duality [3]. Additionally, Bohr's model treats the electron as a particle in a fixed orbit rather than as a probability distribution described by a wavefunction. These limitations were later resolved through the development of quantum mechanics, particularly the Schrödinger equation, which provides a more complete and accurate description of atomic structure.

Understanding the Bohr model, despite its simplifications, remains crucial because it marks the historical transition from classical to quantum physics and provides the foundation for modern atomic theory.

2 Materials and Methods

2.1 Apparatus Description

The experimental setup used to study the emission spectra of gases is shown in Figure 1. It consists of a prism spectrometer with a calibrated constant λ_0, a series of discharge tubes containing gases such as hydrogen and helium, a sodium vapor lamp, and two power supplies. The discharge tubes are evacuated glass containers with metal electrodes connected to a high-voltage source. Applying a potential difference between the electrodes accelerates electrons toward the anode, resulting in collisions that excite and ionize the gas atoms.

The spectrometer was capable of resolving wavelengths to approximately 0.1 nm. Its scale contained 50 divisions, with 20 divisions corresponding to the visible portion of the spectrum and a vernier resolution of 0.01 divisions. The spectrometer was aligned by focusing the eyepiece crosshairs on a spectral line image and adjusting the slit width to optimize both brightness and clarity. The resulting emission lines from each gas were then used to perform wavelength calibration and spectral analysis.

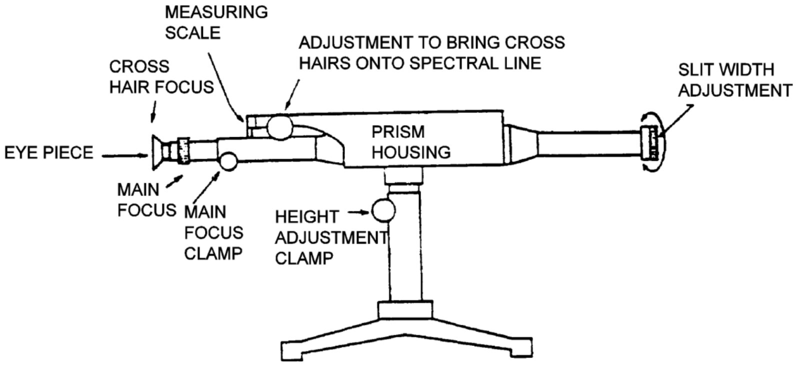

Figure 1: Rydberg constant experimental setup.

2.2 Experimental Procedure

Spectrometer Calibration

The calibration was performed using helium and hydrogen discharge tubes. The known spectral lines of these gases were used to establish the relationship between the spectrometer reading y and the wavelength λ of the emitted light.

Measurement of Emission Spectra

After calibration, the discharge tube was replaced with one containing an unknown gas. The visible spectral lines were observed through the spectrometer, and corresponding scale readings were recorded. Using the calibration equation, the observed readings were converted into wavelengths. These measured wavelengths were then compared with data provided in lab manual to identify the unknown gas.

Determination of the Rydberg Constant

The hydrogen discharge tube was used to determine the Rydberg constant. The wavelengths of the hydrogen Balmer series lines were measured, and the following relation was applied:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right), \tag{5}$$

where $n_f = 2$ and $n_i > 2$.

Measurement of Sodium Doublet Separation

The sodium vapor lamp was used to evaluate the spectrometer's resolution. Once the lamp stabilized and emitted a bright yellow light, the two closely spaced yellow spectral lines were observed and measured.

3 Data and Analysis

3.1 Calibration with the Hartmann Relation Method

The purpose of this part of the experiment is to calibrate the prism spectrometer. Helium and hydrogen discharge tubes were used for calibration. The calibration constant specific to the spectrometer used in this experiment was recorded as:

$$\lambda_0 = 282.8 \pm 0.4 \text{ nm}.$$

The calibration relationship is given by:

$$\lambda = \lambda_0 + \frac{m}{y+b}, \tag{6}$$

where λ_0 is the instrument constant, and m and b are determined from the linear fit of the experimental data. A linear relationship between y and $(\lambda - \lambda_0)^{-1}$ is used to determine these constants through regression analysis.

Table 1: Measured y-values for helium and hydrogen emission lines used in spectrometer calibration.

	Helium strong lines						**Hydrogen strong lines**			
λ (nm)	447.1	471.3	492.2	501.6	587.6	667.8	410.2	434.0	486.1	656.3
Color	Blue	Blue	Blue	Cyan	Yellow	Red	Violet	Violet	Blue	Red
y	14.13	12.57	11.54	11.13	8.51	7.11	17.61	15.09	11.77	7.25
$\lambda - \lambda_0$ (nm)	164.3	188.5	209.4	218.8	304.8	385.0	127.4	151.2	203.3	373.5

The vernier scale of the spectrometer has a resolution of 0.01 divisions. Therefore, the uncertainty in each measured scale reading is estimated as:

$$u_y = \pm 0.005 \text{ divisions}.$$

The obtained data were plotted to determine the slope (m) and intercept (b) of the Hartmann relation, which were then used to convert subsequent spectrometer readings into accurate wavelength values for identifying unknown gases.

The calibration data were analyzed using the least-squares method with uncertainty $u_y = 0.005$ divisions. The corresponding Python script is in (Appendix A). The output of python is summarized below:

- $m = 1997.350 \pm 8.387$ div · nm
- $b = 1.9489 \pm 0.0430$ div
- $\chi^2 = 589.415$
- $\chi^2_{\text{red}} = 73.677$
- $R^2 = 0.99986$

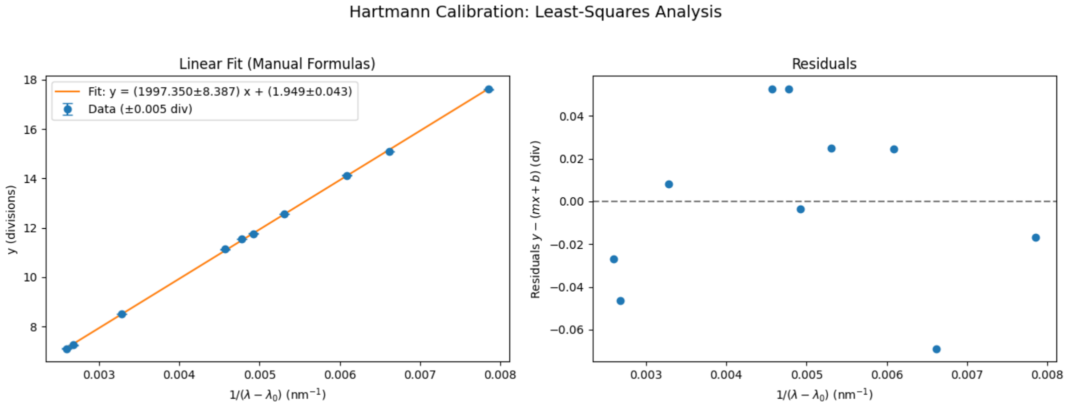

Figure 2: Hartmann calibration linear fit and residuals plot

The very high coefficient of determination ($R^2 = 0.99986$) confirms an excellent linear relationship between y and $1/(\lambda - \lambda_0)$, indicating that the Hartmann relation accurately models the calibration data. However, the reduced chi-squared value of $\chi^2_{\text{red}} = 73.68$ is significantly greater than unity, suggesting that the assumed uncertainty of $u_y = 0.005$ divisions is unrealistically small. This implies that random and systematic uncertainties in the spectrometer readings are larger than initially estimated, possibly due to reading resolution limits or optical alignment inaccuracies. The residual plot on the right of Figure 2 shows points scattered about zero without an obvious pattern, confirming the linearity of the data.

3.2 Identification of the Unknown Gas

The emission light from the unknown gas appeared **red**, as shown in Figure 3. According to the lab manual, only **neon** produces a distinctly red discharge colour, suggesting that the unknown gas is likely neon.

The most clearly visible and accurately measurable spectral lines of the unknown gas were recorded and converted to wavelengths using the calibration function from Part 1:

$$y = 1997.35\left(\frac{1}{\lambda - 282.8}\right) + 1.9489.$$

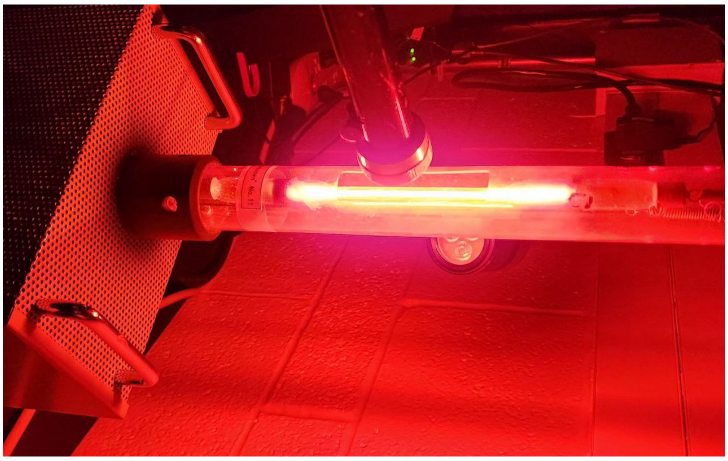

Figure 3: Emission glow of the unknown discharge tube.

Table 2: Measured y-values, calculated wavelengths, and observed colours for the unknown gas (see Appendix B for Uncertainty Propagation)

No.	$y_i \pm u_y$ (divisions)	$\lambda_i \pm u_\lambda$ (nm)	Observed Colour
1	9.72 ± 0.005	537.8 ± 0.3	Green
2	8.57 ± 0.005	584.4 ± 0.4	Yellow
3	8.13 ± 0.005	605.6 ± 0.4	Orange
4	7.37 ± 0.005	651.5 ± 0.5	Red
5	7.16 ± 0.005	665.9 ± 0.5	Red

The measured y-values, calculated wavelengths, and observed colours are summarized in Table 2. The wavelengths correspond well with the neon emission lines listed in the lab manual appendix.

The measured spectral lines show a smooth transition from green to deep red, consistent with the characteristic orange–red band of the neon emission spectrum. Figure 4 show the recorded spectra of the unknown gas compared to the reference spectrum from the lab manual appendix. The position and relative intensity pattern of the lines agree closely, confirming that the unknown discharge tube contains **neon gas**.

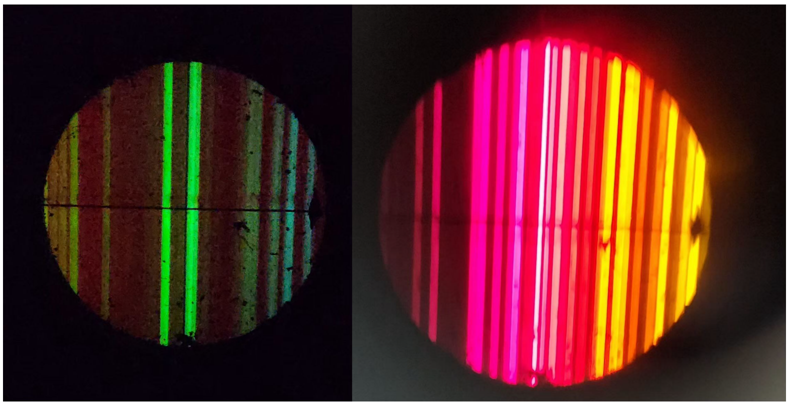

Figure 4: Observed emission spectrum of the unknown gas showing resemblance with Neon.

3.3 The Rydberg Constant

Applying equation (4) to the 4 given Hydrogen strong lines with appropriate energy levels from Balmer series gives $R_H = 1.097(2) \times 10^7$ m^{-1} (see Appendix C for error propagation).

The specific energy of a photon is given by:

$$E_f = hf = \frac{hc}{\lambda}, \tag{7}$$

where h is Planck's constant, c is the speed of light, and λ is the wavelength. Combining equation (7) with (3) and (4), the relationship between R_{EH} and R_H is:

$$R_{EH} = R_H \, h \, c, \tag{8}$$

Taking $h = 6.626070040(81) \times 10^{-34}$ J·s and the speed of light as $c = 2.99792458 \times 10^8$ m·s^{-1}, the Rydberg constant in energy units for hydrogen is calculated to be $R_{EH} = 2.180(4) \times 10^{-18}$ J $= 13.60(3)$ eV(see Appendix D for error propagation).

This agrees with the given value of $R_{EH} = 2.179872 \times 10^{-18}$ J $= 13.605693$ eV, within error. The small difference is entirely due to rounding, limited mostly by the accuracy of the calculated wave length values. This confirms the consistency between the empirical Balmer–Rydberg formula and Bohr's quantum atomic model.

The calculated R_{EH} value of hydrogen is exactly the same as the ionization energy of atomic hydrogen. This is because ionization energy is the energy required to remove the electron completely from a hydrogen atom in its ground state (n = 1). Which is equal to R_{EH} according to equation (2). Thus, the physical significance of R_{EH} is that it is the ionization energy of atomic hydrogen.

3.4 Calculating the Separation of Spectral Lines in the Yellow Doublet of Sodium

Table 3: Measured y-values (with uncertainties), calculated wavelengths, and tabulated wavelengths for the sodium doublet using the calibration parameters from Part 1.

	Sodium doublet lines	
	D$_1$	**D$_2$**
y (div)	4.56 ± 0.005	4.54 ± 0.005
λ_{calc} (nm)	589.6 ± 1.20	589.8 ± 1.21
λ_{tab} (nm)	588.9950	589.5924

Two distinct yellow lines can be seen on the spectrometer, their readings are taken and converted into wavelengths using the model and calibration parameters from Part 1, as shown in table 3. The doublet has a separation of 0.2 nm, indicating that the spectrometer has good resolution, and is able to distinguish waves 0.2 nm apart. The wave lengths calculated matche well with the tabulated wavelengths of the sodium doublet, within error, as shown in table 3. The resolution $R = \frac{\lambda_{\text{avg}}}{\Delta\lambda} = \frac{589.7}{0.2} = 2.9(2) \times 10^3$, which is large, indicating good resolution. These show that the spectrometer is well calibrated, and the measurement uncertainty and error values are appropriate.

4 Discussion and Conclusion

The spectrometer was calibrated using the Hartmann relation method, producing a reliable wavelength–scale relationship. The calibration was verified with the sodium doublet, where a wavelength separation of approximately 0.2 nm confirmed the spectrometer's resolution and accuracy. Using this calibrated model, the emission spectrum of an unknown gas was analyzed and identified as neon based on its characteristic line pattern. The energy Rydberg constant was determined to be $R_{EH} = 2.180(4) \times 10^{-18}\,\mathrm{J} = 13.60(3)\,\mathrm{eV}$, in excellent agreement with the accepted value $R_{EH} = 2.179872 \times 10^{-18}\,\mathrm{J} = 13.605693\,\mathrm{eV}$. This constant represents the ionization energy of the hydrogen atom, confirming the consistency between experimental spectroscopy and theoretical predictions.

The results are internally consistent and in good agreement with theoretical models and accepted values, indicating no significant systematic discrepancies. However, two main sources of uncertainty contributed most to the overall experimental error. First, the spectrometer alignment was disturbed when the setup had to be adjusted during a lamp replacement issue, resulting in a slight change in the calibration geometry. Second, the manual reading of the sodium doublet introduced uncertainty, as accurately aligning the crosshair with the two very narrow and closely spaced lines was difficult due to the instrument's optical limitations.

5 References

The lab is associated with the following report: https://www.physics.utoronto.ca/~phy293lab/experiments/rydberg.pdf

1. Bohr, N. (1913). On the Constitution of Atoms and Molecules, Part I. *Philosophical Magazine*, 26(151), 1–25.

2. Rydberg, J. R. (1890). On the Structure of the Line-Spectra of the Chemical Elements.

3. Griffiths, D. J. (2018). *Introduction to Quantum Mechanics* (3rd ed.). Cambridge University Press.

Appendix A: Linear Fit Python Code

See the code below for linear fit and residual plot along with the other parameter calculations.

```python
import numpy as np
import matplotlib.pyplot as plt

lambda0 = 282.8
lam = np.array([447.1, 471.3, 492.2, 501.6, 587.6, 667.8,
                410.2, 434.0, 486.1, 656.3])
y = np.array([14.13, 12.57, 11.54, 11.13, 8.51, 7.11,
              17.61, 15.09, 11.77, 7.25])

uy = np.full_like(y, 0.005, dtype=float)
x = 1.0 / (lam - lambda0)
N = len(x)
sum_x  = np.sum(x)
sum_y  = np.sum(y)
sum_x2 = np.sum(x**2)
sum_xy = np.sum(x*y)
Delta  = N*sum_x2 - (sum_x)**2

m = (N*sum_xy - sum_x*sum_y) / Delta
b = (sum_y*sum_x2 - sum_x*sum_xy) / Delta
residuals = y - (m*x + b)
s2 = np.sum(residuals**2) / (N - 2)
sm = np.sqrt(N * s2 / Delta)
sb = np.sqrt(s2 * sum_x2 / Delta)

chi2 = np.sum((residuals / uy)**2)
dof = N - 2
chi2_red = chi2 / dof
R2 = 1 - np.sum((y - (m*x + b))**2) / np.sum((y - np.mean(y))**2)
print(f"m = {m:.6f} ± {sm:.6f}  [div·nm]")
print(f"b = {b:.4f} ± {sb:.4f}  [div]")
print(f"Variance s² = {s2:.6f}")
print(f"² = {chi2:.3f}, reduced ² = {chi2_red:.3f}")
print(f"R² = {R2:.6f}")

fig, (ax1, ax2) = plt.subplots(1, 2, figsize=(13,5))

ax1.errorbar(x, y, yerr=uy, fmt='o', capsize=4, label='Data (±0.005 div)')
x_fit = np.linspace(x.min(), x.max(), 300)
ax1.plot(x_fit, m*x_fit + b, '-', label=f'Fit: y = ({m:.3f}±{sm:.3f}) x +
↪  ({b:.3f}±{sb:.3f})')
ax1.set_xlabel(r'$1 / (\lambda - \lambda_0)$ (nm$^{-1}$)')
ax1.set_ylabel('y (divisions)')
ax1.set_title('Linear Fit (Manual Formulas)')
ax1.legend()
ax2.axhline(0, color='gray', linestyle='--')
ax2.plot(x, residuals, 'o')
ax2.set_xlabel(r'$1 / (\lambda - \lambda_0)$ (nm$^{-1}$)')
ax2.set_ylabel(r'Residuals $y - (mx+b)$ (div)')
ax2.set_title('Residuals')

plt.suptitle('Hartmann Calibration: Least-Squares Analysis', fontsize=14)
plt.tight_layout(rect=[0, 0, 1, 0.95])
plt.show()
```

Appendix B: Uncertainty Propagation in Wavelength Calculation

The wavelength for each line is obtained from:

$$\lambda = \lambda_0 + \frac{m}{y-b},$$

where λ_0, m, and b are calibration constants and y is the measured spectrometer reading.

The total uncertainty in λ is found by standard propagation of independent errors:

$$u_\lambda^2 = \left(\frac{\partial\lambda}{\partial y}\,u_y\right)^2 + \left(\frac{\partial\lambda}{\partial b}\,u_b\right)^2 + \left(\frac{\partial\lambda}{\partial m}\,u_m\right)^2 + \left(\frac{\partial\lambda}{\partial\lambda_0}\,u_{\lambda_0}\right)^2.$$

partial derivatives:

$$\frac{\partial\lambda}{\partial y} = -\frac{m}{(y-b)^2}, \qquad \frac{\partial\lambda}{\partial b} = \frac{m}{(y-b)^2}, \qquad \frac{\partial\lambda}{\partial m} = \frac{1}{y-b}, \qquad \frac{\partial\lambda}{\partial\lambda_0} = 1.$$

Substituting into formula:

$$u_\lambda = \sqrt{\left[\frac{m}{(y-b)^2}\right]^2\left(u_y^2+u_b^2\right) + \left(\frac{u_m}{y-b}\right)^2 + u_{\lambda_0}^2}.$$

Plugging in the values we get uncertainites outlined in the table of waves.

Appendix C: Uncertainty Propagation for the Rydberg Constant

Starting from the Balmer/Rydberg relation, equation (4),

$$\frac{1}{\lambda} \;=\; R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right),$$

define

$$x \;=\; \frac{1}{n_f^2} - \frac{1}{n_i^2}.$$

Rearranging for the Rydberg constant gives

$$R_H \;=\; \frac{1/\lambda}{x} \;=\; \frac{1}{x\,\lambda}.$$

Partial derivative:

$$\frac{\partial R_H}{\partial\lambda} \;=\; -\frac{1}{x}\frac{1}{\lambda^2} \;=\; -\frac{R_H}{\lambda}.$$

Uncertainty propagation: Since n_i and n_f are exact integers (no uncertainty in x), the uncertainty in R_H comes only from the uncertainty in λ:

$$u_{R_H} \;=\; \left|\frac{\partial R_H}{\partial\lambda}\right| u_\lambda \;=\; \frac{R_H}{\lambda}\,u_\lambda.$$

Appendix D: Uncertainty Propagation for the Energy Rydberg Constant

The energy Rydberg constant is

$$R_{EH} = R_H \, h \, c.$$

Partial derivatives:

$$\frac{\partial R_{EH}}{\partial R_H} = h \, c, \qquad \frac{\partial R_{EH}}{\partial h} = R_H \, c, \qquad \frac{\partial R_{EH}}{\partial c} = R_H \, h.$$

Uncertainty propagation: The value for speed of light is exact, resulting in:

$$u_{R_{EH}}^2 = (h \, c \, u_{R_H})^2 + (R_H \, c \, u_h)^2.$$