PHYSICS 202 LAB 11: ATOMIC SPECTRA
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THEORETICAL DISCUSSION

All photons have a definite energy E_γ which can be written in terms of the photon frequency ν or wavelength λ as

$$E_\gamma = h\nu = \frac{hc}{\lambda}$$

where $c = 2.997\,924\,58 \times 10^8 \approx 3.0 \times 10^8$ m/s is the speed of light and h is a constant called *Planck's constant*. The numerical value of Planck's constant is

$$h = 6.626\,068\,96 \times 10^{-34}\ \mathrm{J \cdot s}$$

in SI units, or

$$h = 4.135\,667\,33 \times 10^{-15}\ \mathrm{eV \cdot s}$$

in atomic units. In either case, h has the dimensions of an energy times a time and it is, along with the speed of light c and the fine structure constant α[1], one of the most fundamental and important physical constants known to modern physics. It's not obvious, but h also has the same dimensions as angular momentum[2]. It was Niels Bohr's hypothesis that the angular momentum of an electron in orbit around a nucleus is quantized in units of h that led him to propose the so-called *Bohr model* of the hydrogen atom. This model explained the discrete light spectrum emitted by an electrically excited hydrogen plasma perfectly, and, although it was later shown to be an incomplete description of atomic spectra in general, it provided the first theoretical description of an otherwise unfathomable phenomenon in terms of the newly developed quantum theory. Our lab today entails observing and making measurements of the hydrogen spectrum in order to verify the essential elements of Bohr's atomic model.

Quantizing the electron orbit: Although a complete description of the Bohr model is far beyond the scope of this course, the fundamentals of the theory are surprisingly easy to grasp. If you assume that the electron follows a circular orbit around the nucleus[3], the angular momentum L of the electron is equal to

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[1] The fine structure constant is a measure of the fundamental strength of the electrostatic force. It is given by $\alpha = \frac{e^2}{2\varepsilon_0 hc}$, and its numerical value is $\alpha = 7.2973525376 \times 10^{-3} \approx \frac{1}{137}$. It is a dimensionless number.

[2] Angular momentum is linear momentum times a length, which works out to have the dimensions of $[L] = \frac{(\text{mass}) \times (\text{length})^2}{(\text{time})}$. This is the same as $(\text{Energy}) \times (\text{time})$.

[3] This assumption is not, strictly speaking, correct. However, the quantities we are interested in—the angular momentum, average velocity and electrostatic potential energy—can all be correctly calculated for

$$L = mvr \qquad \textbf{Eqn. 1}$$

where m is the electron mass, v is the tangential velocity of the electron in its orbit and r is the orbital radius. The magnitude of the (centripetal) electric force acting on the electron due to the proton is equal to

$$F = \frac{e^2}{4\pi\varepsilon_0 r^2} \qquad \textbf{Eqn. 2}$$

where $e = 1.602\,176\,487 \times 10^{-19}\ \mathrm{C}$ is the magnitude of the charge of both the electron and the proton.

For an object in uniform circular motion, the central force that maintains this circular motion is related to the orbital velocity and the orbital radius according to

$$F = \frac{mv^2}{r} \qquad \textbf{Eqn. 3}$$

Combining equations 2 and 3, and noting that it is the electron that is orbiting the proton[4], gives

$$\frac{e^2}{4\pi\varepsilon_0 r^2} = \frac{m_e v^2}{r}$$

which you can solve for v^2 to get

$$v^2 = \frac{e^2}{4\pi m_e \varepsilon_0 r} \qquad \textbf{Eqn. 4}$$

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the hydrogen atom as if this assumption were true. This is because, even though quantum mechanics tells us that the actual trajectory of any given electron in its orbit cannot be predicted in advance, or even observed without modifying it, the average orbit of an electron does follow the classic circular trajectory and we can calculate certain quantities as if the hydrogen atom were a classical system, subject to certain quantum mechanical constraints. A system for which quantum mechanical constraints can be applied *ex post facto* to the classical dynamical variables of that system is called *semi-classical*. The hydrogen atom is amenable to a semi-classical analysis, but atoms in general are not, and the derivation presented here does not work for atomic energy levels in the general case.

[4] This is why we use the electron mass in the following equation. Strictly speaking, we ought to use the so-called *reduced mass* μ, which for the proton-electron system is equal to $\mu = \frac{m_p m_e}{\left(m_p + m_e\right)}$, but since the proton mass is so much greater than the electron mass, it turns out that $\mu \approx m_e$.

Bohr's hypothesis that the angular momentum of the electron's orbital motion is quantized means that only certain values of L are allowed. In particular, the angular momentum can only have the values

$$L_n = m_e v r = \frac{nh}{2\pi} \qquad n = 1, 2, 3, \ldots \qquad \textbf{Eqn. 5}$$

You can write the quantization condition in terms of v as

$$v = \frac{nh}{2\pi m_e r}$$

and substituting this expression into equation 4, we can obtain the quantization condition for the orbital radius r.

$$\begin{gathered} v^2 = \frac{e^2}{4\pi m_e \varepsilon_0 r} = \frac{n^2 h^2}{4\pi^2 m_e^2 r^2} \\ \Downarrow \\ r_n = \frac{n^2 h^2 \varepsilon_0}{\pi m_e e^2} \end{gathered} \qquad \textbf{Eqn. 6}$$

where the label n on the radius tells you which quantum orbit the electron is in. The lowest energy orbital is the first, with $n = 1$; higher energy (more loosely bound) orbital radii can be calculated by inserting $n = 2, 3, \ldots$

Quantizing the electron energy levels: The kinetic energy K of the electron in its orbit is simply

$$K = \frac{1}{2} m_e v^2 = \frac{e^2}{8\pi \varepsilon_0 r} \qquad \textbf{Eqn. 7}$$

where we have used the result from equation 4. The potential energy U can be found from Coulomb's law[5]. It is

$$U = -\frac{e^2}{4\pi \varepsilon_0 r} = -2K \qquad \textbf{Eqn. 8}$$

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[5] Recall that $k = \frac{1}{4\pi\varepsilon_0}$.

The total energy E is just the sum of the kinetic and potential energies. Combining equations 7 and 8, we have

$$E = K + U = \frac{e^2}{8\pi\varepsilon_0 r} - \frac{e^2}{4\pi\varepsilon_0 r} = -\frac{e^2}{8\pi\varepsilon_0 r} \qquad \textbf{Eqn. 9}$$

By substituting the expression for the quantized radii (equation 6) in the above expression, we get the energy levels of the hydrogen atom:

$$E_n = -\frac{e^2}{8\pi\varepsilon_0 r_n} = -\left(\frac{e^2}{8\pi\varepsilon_0}\right)\left(\frac{\pi m_e e^2}{n^2 h^2 \varepsilon_0}\right) = -\frac{m_e e^4}{8n^2 h^2 \varepsilon_0^2} \qquad n = 1, 2, 3, \ldots \qquad \textbf{Eqn. 10}$$

The hydrogen line spectrum: When an electron changes from one energy level to another, the energy of the atom must change as well. It requires energy to promote an electron from one energy level to a higher one. This energy can be supplied by a photon whose energy E_γ is given in terms of its frequency ν or wavelength λ as

$$E_\gamma = h\nu = \frac{hc}{\lambda} \qquad \textbf{Eqn. 11}$$

Since the energy levels are quantized, only certain photon wavelengths can be absorbed. If energy is put into the atomic gas, the electrons will be promoted to higher energy levels and will then fall back down into the lowest energy state (ground state) in a cascade of transitions. Each time the energy level of the electron changes, a photon will be emitted and the energy (wavelength) of the photon will be characteristic of the energy difference between the initial and final energy levels of the atom in the transition. The energy of the emitted photon is just the difference between the energy levels of the initial (n_i) and final (n_f) states.

$$E_\gamma = \frac{hc}{\lambda} = E_{n_i \to n_f} = E_{n_i} - E_{n_f} = -\frac{m_e e^4}{8h^2\varepsilon_0^2}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = \frac{m_e e^4}{8h^2\varepsilon_0^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \qquad \textbf{Eqn. 12}$$

The spectral lines for a given final state n_f are generally close together. In the hydrogen atom they are given special names. The states for which $n_f = 1$ are called the *Lyman series*. These transitions are in the ultraviolet. The states for which $n_f = 2$ are called the *Balmer series* and many of these spectral lines are in the visible. We will be measuring the wavelengths of the Balmer series lines in today's lab.

PROCEDURE AND ANALYSIS

The ``colors" associated with some of the Balmer series lines are shown in figure 1.

n_i	"color"	spectroscopic label
3	red	H_α
4	blue	H_β
5	violet	H_γ

Fig. 1: The Balmer series of the hydrogen spectrum

1. Measure the wavelengths for the $n_i = 3, 4,$ and 5 lines in the Balmer series of hydrogen using the diffraction grating and the spectrometer. Recall that the relation between the wavelength and the observation angle θ for the 1st order images (m = 1) is given by the grating equation:

$$\lambda = d \sin\theta .$$

The measurement will be very similar to last week's lab except in this case you will use the angle table on the spectrometer rather than trigonometry to determine the observation angles for the various spectral lines. Bear in mind that the observation angle is always measured with respect to the normal to the diffraction grating. A diagram of the spectrometer table is shown in figure 2.

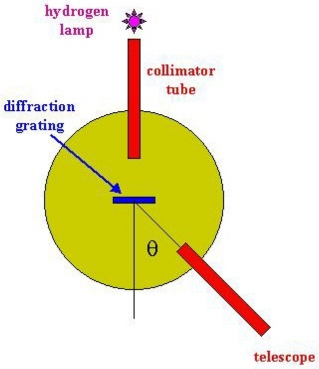

Fig. 2: The spectrometer table

2. Calculate the photon energies for each of your measured lines using equation 11 and the value of Planck's constant[6] in units of eV·s, and report these energies in electron volts (eV).

3. Calculate the corresponding transition energies for the Balmer series lines from equation 12. Numerically, the factor $R = \dfrac{m_e e^4}{8h^2\varepsilon_0^2}$ is easiest to evaluate by noting that

$$R = \frac{m_e e^4}{8h^2\varepsilon_0^2} = \frac{\alpha^2 m_e c^2}{2},$$

where α is the fine structure constant. Using the mass-equivalent energy of the electron, we find that

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[6] See the table of fundamental constants at the end of this write-up.

$$R = \frac{\alpha^2 m_e c^2}{2} = \frac{\left(7.2973525376\ \times 10^{-3}\right)^2 \left(5.10998910\ \times 10^5\right)}{2} = 13.606\ \text{eV}.$$

and the transition energies to the $n_f = 2$ state are therefore given (in eV) by

$$E_{n_i \to 2} = R\left(\frac{1}{2^2} - \frac{1}{n_i^2}\right) = R\left(\frac{1}{4} - \frac{1}{n_i^2}\right).$$

Report your transition energies in electron volts (eV).

4. Numerically compare your photon energies to your transition energies by calculating their fractional discrepancy. Recall that the fractional discrepancy between two values is given by

$$\delta = 2\frac{|A - B|}{|A + B|}.$$

USEFUL CONSTANTS AND PARAMETERS

Constant or Parameter	Value
diffraction grating spacing	$d = \frac{10^{-3}}{600}\ \text{m} = 1.667 \times 10^{-6}\ \text{m}$
fine structure constant	$\alpha = 7.297 \times 10^{-3}$ (dimensionless)
energy equivalent of the electron mass	$m_e = 5.11 \times 10^5\ \text{eV}/c^2$
Rydberg constant	$R = \frac{\alpha^2 m_e c^2}{2} = 13.606\ \text{eV}$
Planck’s constant (in electron-Volts)	$h = 4.14 \times 10^{-15}\ \text{eV} \cdot \text{s}$
speed of light	$c = 2.998 \times 10^8\ \text{m/s}$