Investigating the Quantum Defect values for Lithium

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ABSTRACT

This report investigates the quantum defect for numerous states in the lithium atom. This was achieved using a spectrograph, which was calibrated using the known mercury spectrum. Photographic film was then exposed to carbon-lithium light, and the lithium emission lines were measured with a traveling microscope. The quantum defects for the 2s and 2p state were measured to be \( A_{S2} = 0.409 \pm 0.004 \) and \( A_{P2} = 0.035 \pm 0.008 \) respectively. This demonstrated that the quantum defect is strongly dependent on the orbital angular momentum \( l \). Measurement of the 4s state was also obtained \( A_{S4} = 0.417 \pm 0.086 \), showing that the dependence on \( n \) is much less significant.

I. INTRODUCTION

Alkali metals, such as lithium, can create a similar emission spectrum to hydrogen. However, this resemblance is not perfect with the energy levels in lithium differing slightly from those same states in hydrogen. These departures from hydrogen are quantified by the quantum defect for each state. This report will focus on measuring the quantum defect for various states of lithium, and investigates how these defects depend on the quantum numbers \( n \) and \( l \). The lithium spectrum was obtained using a spectrograph, and exposing film to carbon-lithium light. An example spectrum was used to isolate the lithium emission lines into Principal and Diffuse series. This then allowed for a measurement of the quantum defects of the 2s and 2p states. This report also presents the quantum defects for the Sharp series.

II. THEORY

An emission spectrum is created when electrons in the atom transition to lower energy states, emitting energy in the form of a photon. However, the electron can only transition between a certain number of discrete energy levels, unique to that atom, which creates a distinctive emission spectrum for each element. The energy of each level depends on the principle quantum number \( n \), and the difference in energy levels (\( \Delta E \)) for hydrogen are described in equation 1.

\[
\Delta E = \frac{hc}{\lambda} = Rhc\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right),
\]

where \( h \) is Planck’s constant; \( c \) is the speed of light; \( \lambda \) is the wavelength of light emitted (with units \( m \)); \( n_i \) is the initial state of the electron; \( n_f \) is the final state of the electron and \( R \) is Rydberg’s constant with units of \( m^{-1} \).

The symmetrical nature of the Coulomb potential means that the wavefunction for the electron can be separated into a angular and radial parts, known as spherical harmonics. This means that the states no longer depend solely on \( n \) but another quantum number \( l \) that represents the orbital angular momentum for each state. This is represented by the letters s, p, d for \( l \) equal to 0, 1, 2 respectively. For hydrogen there is \( n \) fold degeneracy of \( l \) for each value of \( n \) as this potential is symmetric.

Lithium is an example of an alkali metal, which means that the inner electrons are tightly bound to the nucleus, with an outer valence electron orbiting at a greater distance. In the case of lithium, the two inner electrons shield the nucleus (of charge +3e) so that the valence electron effectively sees a nucleus of +1e charge. The filled states create a spherical distribution of charge, meaning that the same Coulomb potential is present in lithium and hydrogen. This therefore means that the lithium atom can behave much like hydrogen, creating a similar emission spectrum.

Unlike hydrogen, the orbital angular momentum number \( l \) can have an effect on the energy levels within the lithium atom. Low \( l \) states have a highly elliptical orbit, allowing the valence electron to become more penetrating. This means that the valence electron has a higher probability of being within the filled inner states. The effect of this is to distort the shielding of the nucleus, so that the valence electron no longer sees a Coulomb potential (discussed in the lab book page 105 [1]). This perturbs the energy level of that state, meaning it is more tightly bound than the corresponding state in hydrogen. This perturbation is quantified by
the quantum defect, $A_{ln}$, in equation 2 (the modified version of equation 1).

$$\frac{1}{\lambda} = R\left(\frac{1}{(n_f - A_{ln_f})^2} - \frac{1}{(n_i - A_{ln_i})^2}\right),$$  \hspace{1cm} (2)

where $A_{ln_f}$ and $A_{ln_i}$ are the quantum defects of the $n_f$ and $n_i$ states for a given $l$ [2].

The effect of these quantum defects is to lift the degeneracy of each energy level, as each value of $n$ now has several different values of $l$ each with a differing energy. This creates the Grotrian diagram for lithium as shown in Fig I. The exact set of transitions is determined by the selection rules for various quantum numbers, most notable here is that $\Delta l = \pm 1$ which defines the three series analysed in this report.

![Fig I. Shows the Grotrian diagram for lithium compared to hydrogen (right). The three series are shown in green (Principal), blue (Diffuse) and red (Sharp).](image)

The quantum defect is therefore dependent on the quantum number $l$, such that for values $l \geq 3$ the quantum defect is negligible and lithium behaves like hydrogen. This dependence on $l$ is demonstrated by the radial probability densities shown in Fig II. The $2s$ state ($l = 0$) has a greater probability of being within the $1s$ orbital than the $2p$ ($l = 1$) state, demonstrating that the $2s$ state is more penetrating. There should also be a weak dependence on $n$, as in the limit of large $n$ the valence electron is far away from the inner shell, so the shielding effect should be strong [3].

![Fig II. Shows the electron probability with respect to distance from the nucleus (r). Demonstrates there is a greater penetration within 1 Bohr radius for the 2s than 2p state. Adapted from [4].](image)

### III. METHOD

A spectrograph was used to record the spectra onto photographic film, using the setup shown in Fig III. Source light is first shone through a thin slit, this reduced the effects of flickering in the source light by creating an approximate point source. A lens, placed a focal length away, was used to collimate the light before it was refracted by a quartz prism, which split the light into its constituent wavelengths. The light was then focused onto the film which was placed at an angle so that each wavelength was equally focused regardless of refractive index.

![Fig III. Shows the experimental set for the spectrograph. The light source was changed between lithium-carbon, carbon and mercury light. The blue lines represent shorter wavelengths.](image)

The lithium spectrum was created by doping carbon electrodes with lithium chloride. This burned the lithium creating a pink light that illuminated the spectrograph for 20s. However, this method also meant that the emission lines for carbon appeared on the film. So, a spectrum of solely carbon must also be taken to identify which emission lines are carbon and which are lithium.

In order to calculate the wavelength of each line, the film must also be exposed to a calibration spectrum. In
this case the mercury spectrum was used, as it has a distinct pattern with known wavelengths. The mercury spectrum was obtained by shining a low pressure mercury lamp through the spectrograph. A larger exposure time of 30s was used due to the dim nature of the light. The height of these emission lines was reduced so that they could be recorded over other spectra and still be distinguishable.

Fig IV. Shows the calibration curve used to convert between position on the film and wavelength. The corresponding uncertainties are discussed in the lab book page 93 [1].

Once the three spectra were exposed to the film, it was developed and then a traveling microscope was used to measure the position of each emission line along the film. Each mercury emission line was matched to its corresponding wavelength and plotted to give Fig IV. A polynomial of order 4 was fitted to the data points and gave the calibration curve that was used to convert between position along the film and wavelength.

IV. RESULTS AND ANALYSIS

The Principal series is defined as the transitions from p states to the 2s state (shown in Fig I), where it is assumed that the quantum defect for state np \((AP_n)\) is negligible compared to the quantum defect for the 2s state \((A_{S2})\). This holds due to the dependence on \(l\) outlined in section II. Therefore, equation 2 can be modified with this condition (shown in the lab book page 96 [1]), giving the equation for a straight line when \(1/\lambda\) is plotted against \(1/n_{2p}^{2}\) as seen in Fig V with an intercept of \(CS_{2}\).

\[
A_{S2} = 2 - \sqrt{\frac{R}{CS_{2}}} \tag{3}
\]

Equation 3 was then used to determine the quantum defect for the 2s state as \(A_{S2} = 0.409 \pm 0.004\). This value corroborates with the accepted value of 0.411 for the 2s state in lithium [5].

Fig V. Shows the results for the Principal series when plotting \(1/\lambda\) is plotted against \(1/n_{2p}^{2}\), with an intercept of \(CS_{2} = 4.33 \pm 0.02 \times 10^{6}m^{-1}\).

The same analysis can be done for the Diffuse series, which are the transitions from d states to the 2p state. The assumption for this series is that \(AD_n\) is much smaller than \(AP_2\), allowing equation 2 to be transformed into a straight line once more with \(1/\lambda\) plotted against \(1/n_{2d}^{2}\). This is shown in Fig VI, which means that \(AP_2 = 0.035 \pm 0.008\) using the same relation as equation 3 with the intercept for the Diffuse series \((CP_2)\).

This result shows that the assumption for the Principal series holds. This result also agrees with an accepted answer of 0.040 for the 2p state in lithium [5]. The associated errors for the Principal and Diffuse series are discussed in the lab book pages 95-98 [1].

The reduction in the quantum defect from 2s to 2p is as expected from section II, with a higher value of \(l\) meaning less distortion to the potential and therefore a lower quantum defect.

Fig VI. Shows the results for the Diffuse series when plotting \(1/\lambda\) is plotted against \(1/n_{2d}^{2}\), with an intercept of \(CP_2 = 2.84 \pm 0.02 \times 10^{6}m^{-1}\).
The Sharp series are the transitions from the s states \((n \geq 3)\) to the 2p state. However, in this series the electrons transition to states with a higher value of \(l\). This means that the same analysis cannot be carried out as \(A_{Sn}\) will be larger than \(A_{P2}\). There are now three variables in equation 2, so a graph cannot be plotted. Instead, equation 2 was re-written making \(A_{Sn}\) the subject and is shown in equation 4, with the error discussed in the lab book page 102 [1].

\[
A_{SN} = n_s - \left( \frac{R}{2 - \frac{A_P}{A_{P2}}} \right)^{\frac{1}{2}} \tag{4}
\]

Unlike the previous series, the sharp series allows us to calculate the quantum defect for multiple states as \(A_{P2}\) is known to be \(0.035 \pm 0.008\) from previous analysis. The measured values for the 4s, 5s and 6s states are shown in Fig VII. Whilst the accepted answers fall within the measured value range, the error is deemed too high to conclude any correlation between \(n\) and \(A_{Sn}\). The dependence on \(n\) was noted in section II, however, as shown in the accepted values this correlation is too weak to be noticed with such errors. Although the measured values of the 2s and 4s states do indicate that the dependence on \(n\) is negligible compared to that of \(l\).

<table>
<thead>
<tr>
<th>Quantum Defect</th>
<th>Measurement</th>
<th>Error</th>
<th>Accepted Value</th>
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<tr>
<td>(A_{P2})</td>
<td>0.035</td>
<td>0.008</td>
<td>0.040</td>
</tr>
<tr>
<td>(A_{S2})</td>
<td>0.409</td>
<td>0.004</td>
<td>0.411</td>
</tr>
<tr>
<td>(A_{S4})</td>
<td>0.417</td>
<td>0.086</td>
<td>0.402</td>
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<td>(A_{S5})</td>
<td>0.312</td>
<td>0.171</td>
<td>0.401</td>
</tr>
<tr>
<td>(A_{S6})</td>
<td>0.290</td>
<td>0.289</td>
<td>0.400</td>
</tr>
</tbody>
</table>

**Fig VII. Shows the results for all the quantum defects measured and errors, with their associated accepted answers from [5].**

**V. CONCLUSION**

The purpose of this report was to investigate the quantum defects for various states within the lithium atom. This was achieved by using a spectrograph, and exposing carbon-lithium light onto photographic film. A mercury spectrum was also taken to allow for a conversion between position and wavelength when the lithium emission lines were isolated. Analysis of the Principal series allowed for the measurement of the quantum defect on the 2s state, with a value \(A_{S2} = 0.409 \pm 0.004\) which agrees with the accepted value of 0.411. The same analysis of the Diffuse series allowed for a measurement of \(A_{P2} = 0.035 \pm 0.008\), which again corroborates with the accepted value of 0.04. These results show that the quantum defect is strongly dependent on the quantum number \(l\). The quantum defect of the 4s state was calculated to be \(A_{S4} = 0.417 \pm 0.086\) showing that the dependence on \(n\) is negligible compared to that of \(l\). An improvement could see a wider range of wavelengths recorded, as this would give a larger number of emission lines for each series and allow for better analysis. Further study could see the same experimental set up measure the quantum defect for another element, for example sodium which has higher quantum defects.

**REFERENCES**