Precision measurements of quantum defects in the $n\text{P}_3/2$ Rydberg states of $^{85}\text{Rb}$

B Sanguinetti, H O Majeed, M L Jones and B T H Varcoe

School of Physics and Astronomy, University of Leeds, Leeds, LS2 9JT, UK

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Abstract

Rydberg states are used in our one atom Maser experiment because they offer a large dipole moment and couple strongly to low numbers of microwave photons in a high-$Q$ cavity. Here, we report the absolute frequencies of the $\text{P}_3/2$ states for principal quantum numbers $n = 36$–63. These measurements were made with a three step laser excitation scheme. A wavemeter was calibrated against a frequency comb to provide accurate absolute frequency measurements over the entire range, reducing the measurement uncertainty to 1 MHz. We compare the spectroscopic results with known frequency measurements as a test of measurement accuracy. (Some figures in this article are in colour only in the electronic version)

1. Introduction

Accurate knowledge of the excitation energies of Rydberg states is an important ingredient in increasing the accuracy of atomic structure calculations [1]. Experimentally, Rydberg atoms are also attractive because they offer a large dipole moment and a large number of closely spaced energy levels. Therefore, there has been an increasing effort in the field of quantum information processing recently, where Rydberg states have been proposed for increasing the interaction strength between atoms [2–5], in cavity QED schemes for quantum computing [6] and quantum optics research [7, 8].

For this experiment, the Rydberg states in $^{85}\text{Rb}$ between $n = 36$ and $n = 63$ were excited using a three step laser excitation process as shown in figure 1. The steps are a 780.24 nm transition $5\text{S}_1/2, F = 3$ to $5\text{P}_3/2, F = 4$, a 775.9 nm laser resonant with the $5\text{P}_3/2, F = 4$ to $5\text{D}_5/2, F = 5$ transition and finally a 1256 nm laser to excite $n\text{P}$ Rydberg states. This method of excitation was preferred over a single UV step both because of the convenience and reliability of diode lasers and readily available optical fibres. The accuracy of the results was verified with a Menlo system frequency comb and we calculate values of the modified Rydberg–Ritz formula with significant improvements on previous results, which produces absolute values for the energies, in contrast to other work (for example, [9, 10]) which give relative values. A schematic of the laser system is shown in figure 2.

During the experiment the first two laser steps are stabilized to atomic reference transitions and the frequency of the transitions is measured with a frequency comb. The first step is locked to the $5\text{S}_1/2, F = 3$ to $5\text{P}_3/2, F = 4$ transition of $^{85}\text{Rb}$ using a polarization spectrum [11], which offers a dispersion curve without the need to modulate the laser frequency. Using the comb we determined that the locked laser linewidth is 300 kHz with a 1 s Allan deviation $\lesssim 10$ kHz.

The second step laser is locked to the $5\text{P}_3/2, F = 4$ to $5\text{D}_5/2, F = 5$ transition. The locking signal is, however, derived from an enhanced transmission of the first step laser light rather than directly from the second step laser. Enhanced transparency of the first step is used because it has a much higher signal-to-noise ratio at low intensities than any other signal and it therefore produces a better locking curve. The feedback signal is derived by applying a small modulation to the second step and the locking curve is extracted using a lock-in amplifier. This is free from Doppler broadening because only zero Doppler class atoms are excited by the first step laser, which is tightly locked to the Doppler free polarization spectrum.

The third step laser is a broadly tunable ‘Stry’ design [12] diode laser. This laser has a stability of better than 1 MHz over a second, can be tuned accurately by a few gigahertz using a low-voltage piezo actuator and by nearly 100 nm with a stepper motor. This laser is scanned over the $5\text{D}_5/2, F = 5$
to \( nP_{1/2} \) transition of interest by applying a voltage from a 16 bit optically isolated DAC to the piezo actuator.

The beamline consists of a room temperature vacuum chamber \((P \simeq 5 \times 10^{-8} \text{ mbar})\) in which we placed a rubidium dispenser [13], a fibre coupled excitation region and a detector consisting of a set of field ionization plates with a small electric field ramp from 20 to 30 V cm\(^{-1}\) and the resulting electrons are detected with a channel electron multiplier. The arrangement of these components inside the vacuum chamber is shown schematically in figure 3. The lasers are launched into single mode optical fibre and passed into the vacuum using a fibre feedthrough. One single mode fibre (Nufern 780HP) carries the first and second step lasers and a second fibre (Corning SMF28) is used for the third step laser (principally because the third step requires a larger core diameter fibre). The fibres are terminated in collimating lenses that produce a 2 mm diameter beam. The output of the two fibres is arranged so that they are counter-propagating but meet the atomic beam in a perpendicular direction. A useful property of the counter-propagating lasers is the ability to check correct alignment as some light from the 780/776 nm fibre is coupled into the 1260 nm fibre when they are correctly aligned.

The self-referenced femtosecond frequency comb [14] was used to translate precision RF frequencies from an SRS FS725 rubidium atomic clock to optical frequencies with an accuracy of \(6 \times 10^{-16} \) [15] allowing direct frequency measurement with the accuracy of the RF reference to be made. The atomic clock provides an absolute frequency accuracy of better than \(5 \times 10^{-10} \) based on the manufacturers specification of the aging rates of the oscillator. For a \(10^{15} \) Hz transition this corresponds to a potential absolute error of 500 kHz. The laser frequencies are measured using beat detection units that beat a closely lying comb line with the laser to be measured. The fixed frequency lasers can be simultaneously and continuously measured with this set up. To detect the frequency of the scanning third step laser we use a calibrated wavemeter. The wavemeter draws a comparison between two high finesse Fabry–Perot cavities and achieves an absolute accuracy of 60 MHz. Using the frequency comb we have determined that the relative accuracy of the wavemeter, immediately following calibration, is \(10^{-7} \) at 780 nm (the comparison wavelength). During the experiment, the wavemeter was continuously calibrated against the first step laser ensuring that the absolute frequency accuracy of the wavemeter was asserted with the frequency comb. Under this condition the wavemeter was disciplined to give an absolute accuracy of 1 MHz. The frequency comb was also used to calibrate the accuracy of the target measurement conditions by observing the agreement between the comb and the wavemeter.
in the 1260 nm range. At 1260 nm the accuracy had degraded a little and the precision of 1260 measurements was 4 MHz. Finally spectral lines corresponding to the rubidium Rydberg transitions were acquired by scanning the third step laser over a transition, and simultaneously recording the count rate and the third step laser wavelength using a computer controlled data acquisition system. The experimental aim was to achieve an overall accuracy of 10 MHz, as this is the approximate linewidth of the transition and it is the maximum error level tolerated by the frequency comb electronics.

The excitation region is a monolithic piece of aluminium machined to include both collimating holes for the atomic beam and fibre collimators, so that the alignment was as accurate as possible. The atomic beam is created with a 2 cm long rubidium dispenser oven [13]. The entire collimated cone is therefore filled by the beam and the finite angle of this cone will result in a finite Doppler broadening. This broadening is however much smaller than the linewidth of the first step rubidium transition.

The stability of the first laser is important for this experiment because it is used to calibrate the wavemeter and as velocity selection for the second step lock. The Allan variance of this was measured to be below 10 kHz for all the times relevant to the experiment. The second step lock uses an equivalent setup. The frequencies for these lasers were measured with the comb. In this paper, we chose to use the combined two photon transition frequency from [16] which is known to 8 kHz.

The stability of the wavemeter was measured against the first step laser while the laser was locked to the 5S–5P atomic transition (780 nm). The absolute accuracy of the wavemeter remains below 2 MHz for a few hours (see figure 4) which is much longer than an individual scan but shorter than the entire experimental run, the wavemeter was therefore re-calibrated every hour. This calibration translates to 4 MHz accuracy on the 1260 nm laser (the last recorded digit in the figures). Systematic errors in the transfer of this calibration are therefore the largest error. The wavelength of the laser is read by the computer directly and therefore all plots and fitting routines use the absolute wavemeter reading as read at the time of the experiment. Finally, we determine the accuracy of the calibration by comparing the frequency of the combined transition from the 5S1/2 → 5D5/2 states of 770 570 285(1) MHz which is consistent with the precision two photon measurement of Nez [16] who found 770 570 284 734(8) kHz. This demonstrates that the calibration procedure for the wavemeter was sufficient for the target accuracy.

The detector field ionizes the atoms and detects the subsequent electrons in a channel electron multiplier. The slew rate of the field in the detector is designed to be non-state selective, thus enabling the detector to collect electrons from any neighbouring Rydberg states may have been populated by black body radiation. The dark count rate of the detector was ≤0.3 Hz making the signal-to-noise ratio S/N = 300.

These systematic errors are not correlated resulting in a total systematic error of 5.7 MHz. An overview of the errors is shown in table 1. Subsequently we present the results of a scan from n = 36 to n = 63 in table 2.

The measured frequencies, together with a calculated value of the quantum defect obtained from

\[ E_n = E_i - \frac{R_{\text{Rb}}}{[n - \delta(n)]^2} \]  

are presented in table 2. The values of \( E_n \) were obtained by adding the measured third step frequency to the 5S1/2 → 5D5/2 transition frequency 770 570 285(1) MHz. We scanned over each line 10 times which revealed that the results presented below are repeatable to 1 MHz. An example line at \( n = 46 \) is shown in figure 5. The fitting procedure is explained in detail below and includes Rydberg transitions from [17].
Table 2. Measured frequencies for the $nP_{3/2}$ states and respective quantum defects. $E_n$ is measured from the centre of mass of the lower and upper states and contains a small correction to the wavevector calibration. The third step data are reported exactly as measured.

| $n$ | Third step $E_n$ (MHz) | $\delta$ | $\delta$ Error ($\times 10^{-3}$) |
|-----|------------------------|----------|----------------------------------|
| 36  | 326 496 706            | 1007 068 254 | 2.641 87 | 2.3                      |
| 37  | 326 666 310            | 1007 237 858 | 2.641 79 | 2.5                      |
| 38  | 326 821 728            | 1007 393 277 | 2.641 70 | 2.7                      |
| 39  | 326 964 479            | 1007 536 027 | 2.641 75 | 2.9                      |
| 40  | 327 095 926            | 1007 667 475 | 2.641 77 | 3.2                      |
| 41  | 327 217 235            | 1007 788 783 | 2.641 73 | 3.4                      |
| 42  | 327 329 406            | 1007 900 954 | 2.641 76 | 3.7                      |
| 43  | 327 433 360            | 1008 004 909 | 2.641 62 | 4.0                      |
| 44  | 327 529 853            | 1008 101 402 | 2.641 60 | 4.3                      |
| 45  | 327 619 595            | 1008 191 144 | 2.641 56 | 4.6                      |
| 46  | 327 703 191            | 1008 274 740 | 2.641 63 | 5.0                      |
| 47  | 327 781 211            | 1008 352 760 | 2.641 51 | 5.3                      |
| 48  | 327 854 117            | 1008 425 666 | 2.641 54 | 5.7                      |
| 49  | 327 922 362            | 1008 493 911 | 2.641 48 | 6.1                      |
| 50  | 328 046 352            | 1008 557 870 | 2.641 55 | 6.5                      |
| 51  | 328 102 791            | 1008 617 901 | 2.641 67 | 6.9                      |
| 52  | 328 155 879            | 1008 672 439 | 2.641 73 | 7.3                      |
| 53  | 328 205 906            | 1008 727 427 | 2.641 61 | 7.8                      |
| 54  | 328 253 103            | 1008 777 455 | 2.641 59 | 8.2                      |
| 55  | 328 297 662            | 1008 869 210 | 2.641 39 | 9.2                      |
| 56  | 328 339 780            | 1008 911 329 | 2.641 48 | 9.8                      |
| 57  | 328 379 637            | 1008 951 185 | 2.641 58 | 10.3                     |
| 58  | 328 417 400            | 1008 988 949 | 2.641 41 | 10.9                     |
| 59  | 328 453 197            | 1009 024 746 | 2.641 51 | 11.5                     |
| 60  | 328 487 172            | 1009 058 721 | 2.641 51 | 12.1                     |
| 61  | 328 519 445            | 1009 090 994 | 2.641 51 | 12.7                     |
| 62  | 328 550 123            | 1009 121 672 | 2.641 65 | 13.4                     |

Figure 6. Quantum defects from the three different fitting methods. Data points for $n = 5$ and $n = 6$ were included in the calculations but are not shown, as their quantum defects are off the scale: 2.707 178 and 2.670 358, respectively.

for the transitions outside of the range of this experiment. Some re-analysis was required for the older data to take into account the changes in the recommended Rydberg constant $R_{Rb} = 10 973 660.672 249$ (73) (using [18, 19]) since the publication of the previous paper. From these results we obtain the fit results in table 3.

2. Analysis

The modified Rydberg–Ritz formula is obtained by expanding the effective quantum number $n^*$ as follows:

$$n^* = n - \delta(n)$$  

$$= n - \delta_0 - \frac{\delta_2}{(n - \delta(n))^2} - \frac{\delta_4}{(n - \delta(n))^4} - \cdots$$  

This creates an ‘extended Rydberg–Ritz formula’ that can be rearranged to give the quantum defect $\delta(n)$:

$$\delta(n) = n - n^* = \delta_0 + \delta_2 t_n + \delta_4 t_n^2 + \cdots$$  

where

$$t_n = \left[\frac{1}{n - \delta(n)}\right]^2 = \frac{E_i - E_{n,j}}{R_{Rb}}.$$  

It is possible to make approximations to simplify the fitting procedure, for example as in [17], at the expense of the physical meaning of the parameters. The following three different fitting procedures were implemented in the analysis of our data.

**Method 1.** The first method uses a simple fit routine. The quantum defect can be obtained as a function of $n$ if we approximate $\delta(n)$ by $\delta_0$ [20]:

$$\delta(n) = \delta_0 + \frac{a}{(n - \delta_0)^2} + \frac{b}{(n - \delta_0)^4} + \cdots$$  

in which case the equation can be fitted directly, results are shown in table 3 (method 1). The fitting constants obtained in this way lose their physical meaning [1] owing to differences in the fitting procedures. This means that the fitting parameters obtained in this manner cannot be directly compared across experiments.

However, these fitting parameters can be substituted into

$$E_n = E_i - R_{Rb} \left(n - \delta_0 - \frac{a}{(n - \delta_0)^2} - \frac{b}{(n - \delta_0)^4} - \cdots\right)^{-2}$$  

(7)

for the energy

$$E_{n,j} = \frac{E_n - E_{n,2j - 1}}{2}.$$  

(7)

**Method 2.** To align this analysis with that of Lorenzen and Niemax [17] the second method is an iterative fit involving first equation (6) to obtain an accurate value of the ionization energy $E_i$ and then substituting this value as a fixed parameter in a subsequent fit of equation (7). This method yields the results shown in table 3 (method 2) and figure 6.

Previous experiments [9, 10, 17] were not sufficient to resolve a discrepancy between these two fitting methods, but the increased accuracy of the current experiment exposed a one standard deviation offset, making the precise definition of the fit more important. Drake and Swainson [1] discuss, in detail, the advantage of each method together with the physics that can be learned from more accurate measurements of the quantum defect, thus there is some merit in considering a method of extracting the fit parameters from the data directly.
error in the data as suggested in [26]. Here we use the MINPACK set of algorithms [24] (a modified accurate and numerically stable fitting routine is critical.

number of data points within each Lorentzian, the usage of (method 3). It is important to note that due to the small iterative procedure and the result of this fit is shown in table3.

Algorithms built around MINPACK were also used for fitting equation (7) exclusively. Method 3 uses (high signal-to-noise ratio and low dark count rate, as shown in figure5) which eliminates any ambiguity in the fitting. (method 3). It is important to note that due to the small number of data points within each Lorentzian, the usage of an accurate and numerically stable fitting routine is critical. We have presented a precision measurement of the \( n = 36 \) to \( n = 63 \) \( \hbar/2 \) Rydberg levels of \( ^{85}\text{Rb} \). We have analysed these results and found that we have made a significant improvement on the knowledge of the modified Rydberg–Ritz formula for \( ^{85}\text{Rb} \) P-states. The results represent an order of magnitude improvement in the predictive capability for the \( n\hbar/2 \) rubidium Rydberg state and we obtain an improved ionization energy of \( E_i = 1010024700(7) \) MHz compared with \( E_i = 1010024684(90) \) MHz from [17] and \( E_i = 101002500 \) GHz from [27]. The next stage of this research will be to adapt the experimental setup to allow us to access lower values of \( n \).

**3. Conclusion**

We have presented a precision measurement of the \( n = 36 \) to \( n = 63 \) \( \hbar/2 \) Rydberg levels of \( ^{85}\text{Rb} \). We have analysed these results and found that we have made a significant improvement on the knowledge of the modified Rydberg–Ritz formula for \( ^{85}\text{Rb} \) P-states. The results represent an order of magnitude improvement in the predictive capability for the \( n\hbar/2 \) rubidium Rydberg state and we obtain an improved ionization energy of \( E_i = 1010024700(7) \) MHz compared with \( E_i = 1010024684(90) \) MHz from [17] and \( E_i = 101002500 \) GHz from [27]. The next stage of this research will be to adapt the experimental setup to allow us to access lower values of \( n \).

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