Measurement of Rb \(g\)-series quantum defect using two-photon \(ng \rightarrow (n+2)g\) microwave spectroscopy

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Weutilizetwophotonhigh-precisionmicrowavespectroscopyof\(ng \rightarrow (n+2)g\) transitions to precisely measure the high-angular-momentum \(g\)-series quantum defect of \(^{85}\)Rb. The samples of cold Rydberg atoms in the \(ng\) state are prepared via a three-photon optical excitation combined with controlled electric-field mixing and probed with 40-\(\mu\)s-long microwave interaction pulses. We compare our results with a recent measurement and find our measurement to be consistent and one order of magnitude more precise. The experimental procedure includes a careful cancellation of stray electric fields in all three dimensions. Future extensions towards precision measurements of atomic polarizabilities are discussed.

I. INTRODUCTION

Measurements of atomic transition frequencies are the cornerstone of precision spectroscopy, used in applications ranging from atomic clocks [1] to measuring gravitational redshifts [2] and the radius of the proton [3]. Often, cold atoms are used in these measurements. Alkalai atoms, which have a single valence electron similar to hydrogen, are easier to laser-cool than hydrogen due to a lower recoil energy and near-infrared cooling-transition wavelengths. However, in an alkali atom such as rubidium (Rb), the interaction between the ionic core of the atom and the valence electron depresses the energy levels of the valence electron below the expected hydrogenic levels (the “quantum defect”). In precision spectroscopy, it is imperative to determine this quantum defect for each commonly-used alkali species. Moreover, precision measurements of quantum defects can serve as a check for advanced theoretical calculations and contribute to a better understanding of the electronic structure in atoms.

Here, we measure the high-angular-momentum \(ng\)-series quantum defect of Rb (\(n\) is the principal quantum number). For electrons in high-angular-momentum states, the quantum defect is dominated by the polarizability of the ionic core, which may be extracted from high-angular-momentum defect measurements. In the most recent experimental measurement of the \(ng\)-series quantum defect, microwave spectroscopy of \(nd \rightarrow (n+1)g\) transitions [4] was performed, whereas we use sub-THz spectroscopy to measure \(ng \rightarrow (n+2)g\) transitions in a field-free environment. Our two-photon transition depends only on one set of quantum defects and takes advantage of equal Landé-\(g\) factors in the lower and upper states. We measure the \(ng\)-series \(\delta_0\) and \(\delta_2\) quantum defects (where \(\delta_0\) and \(\delta_2\) are the Ritz expansion coefficients [5]) of \(^{85}\)Rb with a precision improved by one order of magnitude each, better characterizing this hydrogen-like species for future precision measurements. Our results may pave the way towards an improved Rb\(^+\) polarizability measurement, which is necessary for the precision measurement of the Rydberg constant using circular Rydberg states [6, 7] and can help to solve the proton radius puzzle, for which an inaccurate Rydberg constant has been named as a possible answer [3, 8].

II. METHODS

The experimental setup is shown in Fig. 1(a), the energy level diagram is shown in Fig. 1(b), and the timing sequence of the experiment is shown in Fig. 1(d). Atoms are laser-cooled and trapped in a magneto-optical trap (MOT). During each experimental cycle, we prepare atoms in an initial Rydberg \(ng\) state via an on-resonant three-stage optical excitation under simultaneous application of a perturbative DC electric field. The weak DC field admixes a small \(nf\) character into the \(ng\) state, allowing the single-photon \(5d \rightarrow ng\) optical transition (see Fig. 1(b)). As it can be seen from the experimental Stark map shown in Fig. 1(c), we observe significant population in the initial Rydberg \(ng\) state, well-isolated from the neighboring \(nh\) state and the hydrogenic manifold. After state preparation, the perturbative DC electric field is adiabatically lowered (see Fig. 1(d)) to the pre-determined zero-field value, thereby producing a sample of pure \(ng\)-state atoms. Next, a rectangular microwave pulse is applied for \(\tau=40\ \mu\)s, driving the \(ng \rightarrow (n+2)g\) transition. We scan the microwave frequency across resonance and detect the population in the target state \((n+2)g\) via state-selective field ionization (SSFI) [9].

In our microwave system, microwaves are first generated in a synthesizer (Agilent N5183A). Next, they
are frequency-quadrupled in an active frequency multiplier (Norden Millimeter N14-4680). The frequency-quadrupled output power can be varied over a limited range by adjusting the input power supplied by the synthesizer. While the input-to-output power relation may be nonlinear, it nevertheless allows us to continuously vary the intensity at the location of the atoms over a range that allows us to observe the progression of the spectral lines from being indiscernible from the noise floor to being severely broadened, or until we have spanned the available multiplier input-power range. The sub-THz intensity control is important in quantifying the AC-Stark shifts of the transitions when evaluating systematic uncertainties.

We measure the sub-THz frequency intervals covering the $ng \rightarrow (n + 2)g$ transition for four choices of $n$. For each interval, we take six data series. Five of the series are to evaluate systematics, as outlined in the following sections, and the final, longer data series is averaged to produce a measurement result with low statistical uncertainty.

We have specifically chosen to probe $\Delta l = 0$ ($\Delta j = 0$) transitions. This allows us to select transitions with equal

| Shift(Hz) | $38g \rightarrow 40g$ | $39g \rightarrow 41g$ | $40g \rightarrow 42g$ | $41g \rightarrow 43g$ |
|----------|----------------------|----------------------|----------------------|----------------------|
| DC Stark (z) | $100 \pm 14000$ | $10 \pm 4710$ | $80 \pm 4370$ | $20 \pm 4120$ |
| DC Stark (x) | $10 \pm 2560$ | $0 \pm 2550$ | $3 \pm 765$ | $459 \pm 924$ |
| DC Stark (y) | $0 \pm 1550$ | $10 \pm 1140$ | $0 \pm 1430$ | $0 \pm 1780$ |
| AC Stark | $0 \pm 978$ | $0 \pm 965$ | $0 \pm 161$ | $0 \pm 452$ |
| “Clock” | $0 \pm 11$ | $0 \pm 10$ | $4780 \pm 191$ | $0 \pm 9$ |

Landé-\(g\) factors in the lower and upper states, eliminating broadening due to the MOT or other external magnetic fields. Thus, the selected transitions have no Zeeman shifts.

A summary of frequency corrections of our measurements is shown in Table I. One can see that the residual DC-Stark shifts represent the largest source of uncertainty. In the following sections, the procedure of the uncertainty evaluation is discussed in more detail.

### A. Statistical uncertainty evaluation and microwave-frequency calibration

By averaging many data sets in the absence of systematic drift, we observe a Fourier-limited sinc\(^2\)-shaped spectral peak centered on resonance at $\nu_0$ (Fig. 2). For our microwave interaction time $\tau$, the expected Fourier-sideband zeros at $m \times 25$ kHz ($m$ is a nonzero inte-

![FIG. 2: (Color online) Two-photon microwave spectrum of the $40g \rightarrow 42g$ transition. Black squares, fraction of atoms detected in $42g$, detuned from $\nu_0$ (black line). The statistical uncertainty on $\nu_0$ is less than the width of the black line. Uncertainty on the final corrected interval frequency (gray region), listed in Table II, reflects systematic uncertainty. Error bars on data points are SEMs. Red curve is a Lorentzian fit.](image_url)

We have specifically chosen to probe $\Delta l = 0$ ($\Delta j = 0$) transitions. This allows us to select transitions with equal

| Transition interval detuning (kHz) | Fraction in 42G |
|-----------------------------------|-----------------|
| $-150$ | $0.3$ |
| $-100$ | $0.2$ |
| $-50$ | $0.1$ |
| $0$ | $0.0$ |
| $50$ | $0.0$ |
| $100$ | $0.0$ |
| $150$ | $0.0$ |

In this Figure, the systematic corrections exhibited in Table I have not yet been applied to $\nu_0$.
A measurement, we achieve a statistical uncertainty of the line centers on the 100-Hz level. Since the frequencies $\nu_{n_1,n_2}$ of the transition intervals (as defined in Eqn. (2)) exceed 0.1 THz, this amounts to a relative frequency uncertainty of $10^{-9}$.

In order to achieve this precision, it was critical to lock the internal crystal oscillator of our microwave synthesizer to a factory-calibrated, external atomic clock (SRS 725) with a relative uncertainty of $\pm 5 \times 10^{-11}$. The absolute instrument uncertainty for the measured $n_g \rightarrow (n+2)g$ frequency interval is $\approx 10$ Hz. This instrument uncertainty is well below systematic uncertainties.

For the $40g \rightarrow 42g$ frequency-interval measurement, we used a different atomic clock (DATUM LPRO) because the SRS 725 was not available. The LPRO clock had an unknown calibration and a maximum relative uncertainty of $10^{-9}$ due to aging. We have determined the LPRO clock shift by beating the LPRO clock with the calibrated SRS 725 used in the data sets for $n = 38, 39$, and 41. We determined that the LPRO runs faster by a relative amount of $2.53 \times 10^{-8}$, showing that a correction accounting for the LPRO’s clock shift was important. The frequency correction applied to the $40g \rightarrow 42g$ measurement that results from the LPRO clock shift is explicitly listed in Table I.

B. Systematic uncertainty evaluation

In this experiment, systematic uncertainties include shifts in the resonance frequency due to electromagnetic external fields or Rydberg-atom interactions.

We have timed the excitation sequence such that optical light is not present during the measurement interval, eliminating optical AC Stark shifts (see Fig. 1(d)).

In order to minimize the shifts due to static electric fields, which are controlled in all three direction, we follow the standard procedure [4]. These field zeros are determined by varying a field direction $E_i$ ($i = x, y, z$) while holding the other directions fixed until a minimum shift of the transition frequency $\nu$ is observed. This is determined by measuring $\nu$ as a function of the DC tuning voltage that corresponds to field direction $i$ and fitting the result to a parabola. The uncertainty in the parabolic fit determines the uncertainty in the residual DC Stark shift contributed by the field direction $i$. The procedure is iteratively performed for all directions. The corrections and uncertainties derived from this procedure are listed in Table I (the listed uncertainties include the noise of the tuning voltage sources). The uncertainty corresponding to the DC Stark shift in the $z$-direction is the dominant systematic. We attribute this to the fact that the $z$-direction field is applied via a high-voltage amplifier that is needed for SSFI.

The microwave intensities at the atom location are unknown due to nonlinearities in the frequency multiplier and other unknowns in the system. For that reason, we have determined the AC Stark shift (and corresponding uncertainty) for each measured transition by analyzing the relationship between the power-broadened peak width and the center frequency location as the microwave intensity is continuously varied (Fig. 3(a)). As the full-width-half-maxima $\omega_L$ of the Lorentzian spectral profiles broaden as a function of microwave power, microwave-induced AC Stark shifts $\Delta \nu_{\perp}$ of the two-photon transition frequency between lower state $|n_g\rangle = |1\rangle$ and upper state $|(n+2)g\rangle = |3\rangle$ become evident. We observe this relation experimentally (Fig. 3(c)). Explicitly [10],
Here, $\beta$ is a proportionality constant that includes the intermediate AC Stark shifts of the transition, the two-photon state-coupling, the natural decay rate of state $|3\rangle$, and the decay rate $\gamma_{13}/2$ of the $|1\rangle - |3\rangle$ coherence $\rho_{13}$.

We expect the spectral linewidth $\omega_L$ to approach the Fourier-limited linewidth $\gamma_F = 0.89/\tau = 22.3$ kHz at low powers, indicating little or no AC Stark shift. Therefore, for each transition we assign $\gamma_{13}$ to be the weighted average of the peak widths that fall within $\pm50\%$ of $\gamma_F$ (the gray region in Fig. 3(b)). Results are $\gamma_{38g-40g} = 29.3 \pm 2.1$ kHz, $\gamma_{39g-41g} = 29.2 \pm 2.0$ kHz, $\gamma_{40g-42g} = 27.4 \pm 1.1$ kHz, and $\gamma_{41g-43g} = 25.1 \pm 1.3$ kHz. These are largely consistent with each other and are just slightly higher than $\gamma_F$, indicating that additional sources of dephasing in the system have almost no effect.

For each transition, we use these values of $\gamma_{13}$ to plot $\Delta_{41}^2$ versus $\omega_L^2 - \gamma_{13}^2$ (Fig. 3(c)) as we increase the microwave intensity at the location of the atoms. The linear relationship is consistent with the prediction of Eqn. (1). Moreover, the cluster of data points near the origin indicates that there is no measurable AC-Stark shift $\Delta_{41}$ for the peaks of width $\omega_L \approx \gamma_{13}$. The peak width of the spectrum obtained in each final data set is equal to or slightly less than $\gamma_{13}$ to within the Lorentzian-fit uncertainty. Therefore, we take the AC Stark shift to be zero for all transition frequencies reported in Table II. For each transition, the uncertainties of the zero-shifts (Table I) are given by the uncertainty in the weighted average of the center frequencies of all data points that contribute to the calculation of $\gamma_{13}$ (for $n = 38$, the points within the gray region in Fig. 3(b)).

Finally, we have identified a maximum number of Rydberg atoms that may be excited per detection cycle without inducing collisional shifts affecting the result, thereby optimizing the signal/noise ratio while minimizing that source of uncertainty. In Fig. 4, we show the mea-

$$
\Delta_{41}^2 = \beta (\omega_L^2 - \gamma_{13}^2).
$$

(1)

FIG. 4: (Color online) Rydberg-Rydberg shift analysis for the $40g \rightarrow 42g$ transition. This analysis is representative of the procedure used for all measured transitions. Data points (black squares) represent measured peak locations versus average Rydberg counts per detection cycle, detuned from the final measured value in Table II. Vertical error bars are the standard errors of fit (Lorentzian model). Horizontal error bars are the standard deviations of the counts. Insets display measured resonance peak (black squares) and Lorentzian fit (red curve), detuned from final measured value in Table II. The dashed red curve indicates that a Lorentzian is not an ideal fit function for the asymmetric peak.

FIG. 5: (Color online) Quantum defect determination. (a) Determination of $\delta_0$. Black circles are data. Error bars are errors propagated from the final frequency-interval results (see Table II). Red line is a weighted linear fit to data. (b) Determination of $\delta_0$ and $\delta_2$. Residual errors in nonlinear least-squares fit to data using model in Eqn. (2) are initialized using $\delta_0$ and $\delta_2$. Error bars are errors propagated from the final frequency-interval results (see Table II). See text for details.
sured peak position versus average total detected Rydberg counts per cycle for the 40\text{g} \rightarrow 42\text{g} transition. Although an increase in detected Rydberg counts can improve the signal/noise ratio, Rydberg-Rydberg interactions cause a red shift of the detected transition frequency, as well as asymmetric broadening (compare insets of Fig. 4). The asymmetric lineshape observed at high Rydberg counts (in the inset of Fig. 4) is attributed to an attractive long-range electrostatic van der Waals interaction between Rydberg atoms. Although a Lorentzian is not an ideal choice as a fit function for these asymmetric shapes, it still provides an approximate value for the peak shift and broadening as a function of detected Rydberg counts. Importantly, for each transition, we observe that below about ten detected Rydberg counts, the peak position and width converge to the interaction-free values. Therefore, we limit our final data sets to this Rydberg-count region.

III. RESULTS

We list the systematic corrections for each measured transition frequency in Table I. The uncertainties have been reported to three significant digits, so as to not lose information in the calculations of the corrected transition frequencies (which are rounded to two significant digits in Table II) [11].

To obtain values for the \(n\)-\(g\)-series \(\delta_0\) and \(\delta_2\) quantum defects, we follow the procedure of [12]. First, we obtain an average quantum defect \(\delta^* (n,n+2)\) for the pair of appropriate levels using

\[
\nu_{n_1,n_2} = R_{Rb} c \left( \frac{1}{(n_1 - \delta(n_1))^2} - \frac{1}{(n_2 - \delta(n_2))^2} \right),
\]

where \(R_{Rb}\) is the Rydberg constant using the rubidium reduced mass. Here, we substitute \(\delta(n_1) = \delta(n_2) = \delta^* (n,n+2)\). In Table II, we list the final reported transition frequencies \(\nu_{n,n+2}\), including corrections from Table I, along with the corresponding values of \(\delta^* (n,n+2)\).

Next, in Fig. 5(a) we plot \(\delta^* (n,n+2)\) versus \(n_{A}^{-2}\), where \(n_{A}^* = n + 1 - \delta_0^G\). Here, \(\delta_0^G\) is the previous value of \(\delta_0\) determined by [4]. Extrapolating to \(n_{A}^* = 0\), we obtain an initial estimate \(\delta_0^G = 0.00399976\).

For each frequency interval, we use Eqn. (2) and substitute \(\delta(n) = \delta_0^G + \delta_2/(n - \delta_0^G)^2\) to solve for \(\delta_2\). Averaging the four results yields a preliminary value \(\delta_0^G = -0.0209603\).

Using \(\delta_0^G\) and \(\delta_2^G\) as initial values for the two free parameters \(\delta_0\) and \(\delta_2\), we perform a nonlinear least-squares fit of Eqn. (2) to the transition-frequency values listed in Table II, where \(n\) is the independent variable. The residual error is plotted in Fig. 5(b). We use a Levenberg-Marquardt algorithm with assigning weights of the data points to \(1/\sigma_i^2\) (\(\sigma_i\) being a frequency uncertainty of the \(i\)-th data point).

\[
\begin{array}{c|c|c}
 n & \text{Transition frequency (GHz)} & \delta^* (n,n+2) \\
\hline
38 & 222.199268(14) & 0.00397661(84) \\
39 & 205.932535(58) & 0.00397784(38) \\
40 & 191.2159300(47) & 0.00397919(33) \\
41 & 177.8690737(46) & 0.00397980(36) \\
\end{array}
\]

Our final results for the \(ng\)-series quantum defects are \(\delta_0 = 0.0039997(26)\) and \(\delta_2 = -0.0209(26)\). The uncertainties are the standard error of the fit. These results are consistent with recent previous \(ng\)-series measurements [4], but at least one order of magnitude more precise.

Finally, we have explored how to use our precise \(ng\)-series energy-interval measurements to extract a new estimate of the \(Rb^+\) polarizability, using the polarizability model found in [4]. Unlike [4], however, our measurements are constrained to energy intervals between the same \(l\). Consequently, to extract \(\alpha_d\) and \(\alpha_q\), we must instead adapt the method of [4] to measurements of shifts of transition energies relative to their quantum-defect-free values, \(\delta W\), by writing (in atomic units)

\[
2 \delta W \frac{1}{\langle 1/r^4 \rangle_D} = \alpha_d + \alpha_q \frac{(1/r^6)_D}{\langle 1/r^4 \rangle_D}
\]

Here \(\langle 1/r^4 \rangle_D = \langle 1/r^4 \rangle_{n,l} - \langle 1/r^4 \rangle_{n+2,l}\). Using Eqn. (3) to plot our data, we find that our data is consistent with the polarizability results in [4]. However, as can be seen by examining the \(\langle 1/r^4 \rangle_{n,l}\) functions in [13], the variation in \(\langle 1/r^4 \rangle_{n,l}\) has a much stronger \(l\)-dependence than \(n\)-dependence at the quantum numbers used in this experiment. As a result, the strong \(n\)-dependence of \(\delta^* (n,n+2)\) evident in Table II is not sufficient to allow for a precise determination of \(\alpha_d\) and \(\alpha_q\). Therefore, to reach a definitive improvement on the measurements of \(\alpha_d\) and \(\alpha_q\), in the future a measurement of the \(nh\)-series quantum defect will be required on our setup as well. The \(\Delta l = 0\) sub-THz method presented in this paper is well-suited to use for such a measurement, and thus to determine improved \(Rb^+\) polarizability values in future experiments. The systematics listed in Table I suggests that the substantial experimental improvement is additionally possible through a re-design of the SSFI apparatus.

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Note added. - Recently, we became aware of related work that reported precision measurements of the Rb-core dipole and quadrupole polarizabilities and sub-
sequently extracted quantum defects for $g-$, $h-$ and $i-$series using $n = 17, 18, 19$ Rydberg levels [14].

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