Core polarizability of rubidium using spectroscopy of the ng to nh, ni Rydberg transitions

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We present a precise measurement of the rubidium ionic core polarizability. The results can be useful for interpreting experiments such as parity violation or black-body radiation shifts in atomic clocks since the ionic core electrons contribute significantly to the total electrical polarizability of rubidium. We report a dipole polarizability \( \alpha_d = 9.063 \pm 0.007 \, a_0^3 \) and quadrupole polarizability \( \alpha_q = 43 \pm 2 \, a_0^5 \) derived from microwave and radio-frequency spectroscopy measurements of Rydberg states with large angular momentum. By using a relatively low principal quantum number (17 \( \leq n \leq 19 \)) and high angular momentum (4 \( \leq \ell \leq 6 \)), systematic effects are reduced compared to previous experiments. We account for non-adiabatic corrections to the polarizability model, which resolves a previous discrepancy with theory but limits the accuracy of our results.

I. INTRODUCTION

The electric polarizability of an atom is of significant interest and importance. Accurate polarizability values are needed for many experiments, including atomic clocks, quantum computation, parity-nonconservation, thermometry, and studies of long-range molecules [1–5]. Polarizability measurements are also useful as benchmarks for theoretical calculations since the polarizability depends on the dipole matrix elements of the atomic wave functions, which are difficult to obtain using conventional spectroscopy. Calculation of matrix elements from first principles is very challenging for multi-electron atoms, so comparisons to experimental quantities, like polarizabilities, provide important checks. These motivations have prompted a series of improving polarizability measurements over the past several decades [6–13]. One promising new approach is tuneout spectroscopy [14], where the ac electric polarizability of an atom vanishes and the wavelength at which that occurs is measured. This technique can provide orders of magnitude improvement in the accuracy of the dipole matrix elements [10, 11, 13, 15].

Theoretical interpretation of the polarizability is simplest for alkali atoms, where most of the effect comes from the single valence electron. However, the contribution of the core electrons cannot be ignored. For instance, the core contributes about 3% to the total polarizability of a Rb atom [3], which is large compared to the 0.2% accuracy of a measurement such as in Ref. [9]. It can be useful to evaluate and subtract the core contribution from a measurement to obtain the valence polarizability alone since this provides the most direct connection to the matrix elements of the valence wave functions. This approach has been used with both dc and tuneout measurements [10], but it is limited by the accuracy to which the core polarizability is known. We present here a new experimental measurement of the core polarizability of Rb, with an accuracy approximately three times better than previously achieved. We expect this to be useful as tune-out spectroscopy and other polarizability measurement techniques continue to improve.

The core polarizability is obtained in our experiment through microwave spectroscopy of atomic Rydberg states. When the valence electron is far from the core, the atom behaves much like hydrogen; however, the field from the electron polarizes the core and lowers the atomic energy. By comparing the energy of the actual atom to hydrogen, the core polarizability can be determined [16, 17]. This method was previously used in Rb with Rydberg states having principle quantum number \( n \) in the range of 27 to 30 [12]. The accuracy of the spectroscopy measurements was principally limited by Stark shifts from stray dc electric fields. The dc polarizability of a Rydberg atom as a whole is very large, so even fields below 1 V/cm can be significant [12]. To address this problem, the work here uses lower principal quantum numbers: \( n = 17 \) to 19. Since the atomic polarizability scales as \( n^7 \), this reduces the electric field sensitivity by a factor of about 25 compared to previous work.

Because the valence electron produces a non-uniform field at the ion core, the energy of the Rydberg atom depends on both the dipole polarizability \( \alpha_d \) and the quadrupole polarizability \( \alpha_q \) of the core [18]. We use microwave spectroscopy to determine both of these parameters, and our results are consistent with previous measurements and theory [3, 12].

The Rydberg electron is moving, so its energy shift involves the dynamic, not just the static, polarizability of the core [19]. Since the Rydberg Bohr frequencies are much lower than the excitation frequencies of the core, this effect is small. We nonetheless find that it has a

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FIG. 1: Atomic states used in the measurement. Rubidium atoms in the $5s_{1/2}$ ground state are optically excited to $6p_{1/2}$, allowed to spontaneously decay to $4d_{3/2}$, and are then optically driven to the $nf_{5/2}$ Rydberg state for $n = 17 - 19$. The expanded diagram on the right shows microwave transitions from $nf$ to $ng$, $nh$, and $ni$ states using one, two, and three photon excitations, respectively. The $f - g$ interval is about 15 GHz, the $g - h$ interval is about 3 GHz, and the $h - i$ interval is about 1 GHz; the precise values depend on $n$.

significant impact on the quadrupole polarizability term. We develop an empirical approximation to account for this non-adiabatic effect, and using it we obtain good agreement with theoretical estimates for both the dipole and quadrupole core polarizabilities.

In the sections that follow, we describe the principle and setup of the experiments, the spectroscopic results, the analysis of the polarizabilities, and finally our conclusions.

II. EXPERIMENTAL APPROACH

In order to interpret the energy shifts of the Rydberg state in terms of the core polarizability, it is necessary for the valence electron to remain far from the core at all times. In addition to large $n$, this also requires the use of large angular momentum quantum number $\ell$. Core penetration in a Rydberg state causes its fine structure splitting to differ significantly from that of hydrogen. Such distortions are observed in Rb for $\ell \leq 3$, so we use only states with $\ell \geq 4$. The atoms are excited using the scheme shown in Fig. 1 where a laser pulse first excites atoms from the $5s_{1/2}$ ground state to the $6p_{1/2}$ excited state. About a third of the excited atoms spontaneously decay to the long-lived $4d_{3/2}$ state, from which they are excited by a second laser pulse to the $nf_{5/2}$ Rydberg state. From there, microwave and radio frequency pulses drive transitions to the $ng$, $nh$ and $ni$ states. We use the $g - h$ and $h - i$ intervals to determine the dipole ($\alpha_q$) and quadrupole ($\alpha_q$) polarizabilities of Rb$^+$.

The experiment is performed in an atomic beam apparatus, shown in Fig. 2. The Rydberg atoms are produced between two electric field plates separated by 1.5 cm. A potential difference of up to 6 kV can be applied between the plates. After the microwave pulse is applied, the electric field is ramped to a value sufficient to ionize the Rydberg states. By carefully controlling the timing and amplitude of the ramp, the atom ionization process can be made state selective such that atoms in $\ell \geq 4$ states are ionized while the $nf$ atoms remain neutral. Any ions produced are detected using a microchannel plate operating in analog mode with spatially integrated channels. The resulting signal current is accumulated using a gated integrator to produce the spectroscopy signal.

The laser excitation pulses are produced by a pair of home-built dye lasers. The first pulse is at a wavelength of 420 nm, and is produced using Stilbene 420 dye pumped by the third harmonic of a Quanta Ray Nd:YAG laser. The second pulse is tuned between 713 nm and 720 nm to populate the desired $nf$ state. This laser uses LD720 dye, pumped by the second harmonic of a Continuum Nd:YAG laser. Both laser pulses have 20 ns duration, and the second pulse is delayed by 250 ns with respect to the first. Both lasers are linearly polarized perpendicular to the field plates. While the $6p$ fine structure is resolved by laser tuning, the $nf$ fine structure is not.

The lifetimes of the $nf$ states are about 4 $\mu$s with an $n^3$ dependence, and the microwave spectroscopy pulses are applied 1 $\mu$s after the second laser pulse. In the case of the $nf$ to $ng$ transition, a single-photon transition is driven with a microwave frequency ranging from 11 to 17 GHz, depending on $n$. For the $nf$ to $nh$ transition, a two-photon transition is driven with microwaves at half the transition frequency, between 7 and 10 GHz. For the three-photon $nf$ to $ni$ transition, the two-photon microwave frequency is detuned from the $nh$ state, and apply an RF frequency near 1 GHz to couple $nh$ to $ni$. These three excitation schemes are illustrated in Fig. 1. The microwaves are produced by an Agilent

FIG. 2: Experimental apparatus (not to scale). A rubidium atomic beam is emitted from oven (a) and passes between electric field plates (b), which are separated by 1.5 cm. Two pulsed laser beams (c) excite the atoms into Rydberg states, and microwave horn (d) drives Rydberg state transitions. An electric field is applied to ionize the Rydberg atoms, and the ions are detected with microchannel plate (e).
In all cases, the duration of the spectroscopy pulse is 1 μs. For each measurement, the microwave frequency was swept across the resonance. Each frequency step in the sweep was repeated at least ten times, and the sweep in its entirety was repeated five times. The resulting signals were averaged to produce a line profile, such as the example data shown in Fig. 3. The profiles were least-squares fit to Lorentzian functions to determine the line centers. Uncertainty in the line center was taken from the uncertainty estimate of the fit. However, in cases where the line center uncertainty from the fit was below 10% of the fit linewidth, we instead assigned an uncertainty of 10% of the linewidth to reflect the fact that the actual lineshape is not well characterized.

Several sources of systematic uncertainty must be taken into account, including dc Stark shifts, ac Stark shifts, Zeeman shifts, and fine structure splitting.

Although dc Stark shifts are reduced by operating at relatively low $n$, they must still be accounted for. The conducting field plates suppress electric fields parallel to the plates, but any residual voltage difference produces a significant field normal to the plates. We are able to apply a bias voltage across the plates during the experiment, and Fig. 4(a) shows how the $nf \rightarrow ng$ transition frequency varies as a function of the bias voltage. We fit such data to a parabola and then set the bias voltage to the vertex of the fit. We perform this calibration daily, and observe day-to-day variations of about 0.25 V/cm, corresponding to Stark shifts of the $nf \rightarrow ng$ transition on the order of 0.1 MHz. The apparatus provides no direct way to measure or control the transverse electric field components, but other experiments with similar geometries show that the transverse fields are typically below 0.1 V/cm [12], corresponding to a shift here of less than 0.04 MHz.

There are no ac Stark shifts on the single-photon $nf$ to $ng$ transitions, but there are on the multiphoton transitions. These shifts are manifested as a linear variations of the transition frequency as a function of microwave or rf power. We compensate for it by taking data over a range of powers and extrapolating the results to zero power. Example data are shown in Fig. 4(b) and (c). The ac Stark shift is largest for the three-photon $nf \rightarrow ni$ transition, and the shift depends on the two-photon detuning from the $nh$ state. For these measurements, the microwave and rf powers were independently varied and extrapolated to zero. In addition, for each $n$ we used at least two different two-photon detuning values, with at least one on each side of the $h$ state resonance. The values obtained were consistent with the estimated uncertainties. In all cases, the extrapolation to zero power was performed using an error-weighted least squares fit to the data, and the uncertainty from this fit is reported as the uncertainty in the transition frequency measurement. The resulting values are reported in Table I. For the majority of transitions reported here, at least two measurements were completed on different days, and the results agreed within the stated uncertainty.

Zeeman shifts are nominally zero, since the linearly polarized laser beams produce a symmetric distribution of $m$ levels, and the microwave and rf fields are also linearly polarized. In this case, a magnetic field would only
broaden the transition to first order. We computed the second-order Zeeman shift and the second-order coupling between the Zeeman and dc Stark shift, and found both to be negligible for our environmental field of about 1 G. We experimentally verified these conclusions by applying a dc field of 1 G and observed no linear shift on the 17f to 17g transition. On this basis, we ignore the Zeeman effect as a source of uncertainty.

In hydrogen, the fine structure (FS) splittings of the ng, nh and ni states range from 3.0 MHz to 0.6 MHz. This is comparable to or less than our experimental linewidth, so the fine structure is not well resolved, but it is significant compared to our measurement accuracy. To avoid uncertainty due to unresolved FS we take advantage of the fact that the excitation scheme of Fig. 1 ensures that the Rydberg atoms are always in the lower j fine structure state, j = ℓ − 1/2. Accordingly, we have measured the intervals given in Table I.

We expect the ℓ ≥ 4 FS splittings in Rb to be similar to those of hydrogen, because the ℓ ≥ 4 states should not penetrate the core and the core polarization effect is independent of j. To verify this, we re-tuned the initial laser excitation pulse to the 6p3/2 state, which then allowed excitation of both the nf5/2 and nf7/2 states. The nf7/2 → ng7/2 transition is suppressed due to small Clebsch-Gordan coefficients, but we observed the nf7/2 → ng9/2 transition. Using the known f-state FS splitting [20], we obtained a value for the 17g FS splitting of 1.83 ± 0.06 MHz. This is in agreement with the hydrogenic value of 1.78 MHz and is consistent with the g-states being non-penetrating [21]. We therefore use the hydrogen FS values for the ℓ > 4 states. For the analysis described below, we use transition frequencies from which the FS shift has been removed by referencing the transition to the center of gravity of the FS manifold. These frequencies are listed in Table I.

III. ANALYSIS & DISCUSSION

In the adiabatic core polarization model the electric field from the quasistatic charge distribution of the Rydberg nl electron polarizes the ion core, which results in the polarization energy shift of the Rydberg nl state relative to the hydrogenic nl energy. The shift is given, in atomic units, by [17, 22]

\[ W = -\frac{1}{2} \alpha_d^{(a)} \left\langle \frac{1}{r^4} \right\rangle_{n\ell} - \frac{1}{2} \alpha_q^{(a)} \left\langle \frac{1}{r^6} \right\rangle_{n\ell}, \tag{1} \]

where \( \alpha_d^{(a)} \) and \( \alpha_q^{(a)} \) are the dipole and quadrupole core polarizabilities of Rb\(^{+}\), and r is the distance of the valence electron from the nucleus. The superscript denotes the use of the adiabatic approximation, which will be subsequently relaxed. If we assume the nl wavefunctions to be hydrogenic, there are closed form expressions for the required expectation values [17, 22, 23]. As a result, it is a straightforward matter to extract \( \alpha_d^{(a)} \) and \( \alpha_q^{(a)} \) from the high ℓ Rydberg energies.

Equation (1) gives the energy shift of a state relative to the corresponding state of hydrogen, but we do not have accurate values for the absolute energies of the nf states, so we cannot evaluate the energies of the high-ℓ states relative to hydrogen. Instead, we consider the energy difference between two states nl and nl′. Since the hydrogenic energies are independent of ℓ, the energy difference is

\[ \Delta W = -\frac{1}{2} \alpha_d^{(a)} \Delta_d^{(a)} - \frac{1}{2} \alpha_q^{(a)} \Delta_q^{(a)}, \tag{2} \]

where

\[ \Delta_d^{(a)} = \left\langle \frac{1}{r^4} \right\rangle_{n\ell} - \left\langle \frac{1}{r^4} \right\rangle_{n\ell'} \tag{3} \]

and

\[ \Delta_q^{(a)} = \left\langle \frac{1}{r^6} \right\rangle_{n\ell} - \left\langle \frac{1}{r^6} \right\rangle_{n\ell'} \tag{4} \]

The energy difference \( \Delta W \) corresponds to the FS-corrected transition frequencies reported in Table I.

To obtain the polarizabilities, we plot \( 2\Delta W/\Delta_d^{(a)} \) vs. \( \Delta_q^{(a)}/\Delta_d^{(a)} \), for (ℓ, ℓ′) pairs (4, 5) and (5, 6), with the results shown in Fig. 5. The subfigures detail the n dependence and show the least squares fit along with the data. The points are fit to a line, and the resulting intercept and slope correspond to \( \alpha_q^{(a)} = 9.059(3) \, a_0^6 \) and \( \alpha_q^{(a)} = 19.1(3) \, a_0^5 \). These are in reasonable agreement (3 standard deviations) with previous results \( \alpha_d^{(a)} = 9.12(2) \) and \( \alpha_q^{(a)} = 14(3) \) [12], but with reduced uncertainty.

However, we find that the adiabatic approximation is inadequate here and must be corrected to incorporate non-adiabatic effects [19, 24–27]. The non-adiabatic correction arises because Eq. (1) is an approximation to the second-order shift from the multipole expansion of the Coulomb interaction between the Rb\(^{+}\) ion core and the Rydberg electron. The same method of analyzing the experimental data can be used if we introduce correction factors \( k_{d,n\ell} \) and \( k_{q,n\ell} \) into Eq. (1), which then reads [22]

\[ W = -\frac{1}{2} k_{d,n\ell} \alpha_d \left\langle \frac{1}{r^4} \right\rangle_{n\ell} - \frac{1}{2} k_{q,n\ell} \alpha_q \left\langle \frac{1}{r^6} \right\rangle_{n\ell}. \tag{5} \]

In the adiabatic approximation, \( k_{d,n\ell} = k_{q,n\ell} = 1 \).

To show the origin of the non-adiabatic correction we consider the contribution of the dipole polarizability to the polarization shift of a Rb nl state [25, 28]. The atomic wavefunction is taken to be a direct product of the ion wavefunction and a hydrogenic wavefunction for the Rydberg electron. Consequently, the total energy is simply the sum of the ion and Rydberg energies. In a bound Rb nl state, the Rydberg electron is coupled to the ground 4p0 state of Rb\(^{+}\), which we denote as a, so the bound Rydberg state is denoted anlℓ. Similarly, a Rydberg nl′ℓ electron coupled to an excited state b of Rb\(^{+}\)
TABLE I: Measured transition frequencies and frequencies referenced to the center of gravity of the fine-structure doublet in MHz for \( n = 17 - 19, \ f \rightarrow g, \ f \rightarrow h, \) and \( f \rightarrow i. \)

| \( n \) | \( f_{5/2} \rightarrow g_{7/2} \) | \( f_{cg} \rightarrow g_{cg} \) | \( f_{5/2} \rightarrow h_{9/2} \) | \( f_{cg} \rightarrow h_{cg} \) | \( f_{5/2} \rightarrow i_{11/2} \) | \( f_{cg} \rightarrow i_{13/2} \) |
|---|---|---|---|---|---|---|
| 17 | 16528.66(3) | 16547.27(7) | 19929.5(3) | 19947.8(3) | 20992.5(6) | 21010.6(6) |
| 18 | 13945.16(9) | 13960.90(10) | 16815.6(1) | 16831.0(2) | 17713.2(6) | 17728.5(6) |
| 19 | 11872.25(6) | 11885.69(7) | 14317.0(1) | 14330.2(1) | 15082.9(8) | 15096.0(8) |

is denoted \( bn'\ell' \). We restrict our attention to ion states which are dipole coupled to the ground state. In the Rydberg atom, the \( an\ell \) state is coupled by the dipole term of the Coulomb expansion to the \( bn'(\ell - 1) \) and \( bn'(\ell + 1) \) states, as well as the \( be(\ell - 1) \) and \( be(\ell + 1) \) continua. The resulting dipole energy shift of the \( 4p^3n\ell \), the \( an\ell \) state is given explicitly by

\[
\Delta W_{d,n\ell} = \frac{1}{2} \sum_{b,n'} \left[ \frac{\ell(\ell + 1)}{(2\ell + 1)(W_{an\ell} - W_{bn'(\ell - 1)})} \right] r_1^2 \left\| \langle n'\ell | r_2^2 | n'\ell \rangle \right\|^2 \left\langle n'\ell | r_2^2 | n'\ell \rangle \right\|^2,
\]

where the sums are understood to include the continua above the Rydberg and ion limits. Here \( r_1 \) represents a core electron and \( r_2 \) the Rydberg electron. The \( r_2^2 \)

matrix elements are computed using Numerov’s method, and their accuracy is verified using the sum rule [25]

\[
\langle n\ell | r_2^2 | n\ell \rangle = \sum_{n'} \langle n\ell | r_2^2 | n'\ell \rangle^2.
\]

The energy denominators of Eq. (6) can be rewritten as

\[
W_{an\ell} - W_{bn'\ell'} = W_a - W_b + W_{an\ell} - W_{bn'\ell'}.
\]

The adiabatic expression of Eq. (1) is the result of taking \( W_{an\ell} - W_{an'\ell'} = 0 \), since it is much smaller than \( W_b - W_a \). However, the squared \( \langle n\ell | r_2^2 | n'\ell' \rangle \) matrix elements actually do cover a substantial energy range, as shown by the \( 18g \) example of Fig. 6. Here the matrix elements cover an energy range that is about 15% of \( W_b - W_a \).

Rather than neglecting \( W_{an} - W_{an'\ell'} \) entirely, we consider Taylor expanding Eq. (6) with \( |W_{an} - W_{an'\ell'}|/|W_a -
$W_k'$ as a small parameter. In first order, it is possible to show that the sum over the ion transitions can be replaced by an effective transition to a single ion state at energy $W_{I_d}$ above the ground state, with $W_{I_d}$ given by

\[
\frac{1}{W_{I_d}} = \frac{\sum_b \langle a|r_1|b\rangle^2}{\sum_b (W_a - W_b)^2},
\]

which is an appropriately weighted average of $1/(W_a - W_b)$. Similarly, we can obtain an effective matrix element

\[
\langle a|r_1|I\rangle^2 = \left(\frac{\sum_b \langle a|r_1|b\rangle^2}{\sum_b (W_a - W_b)^2}\right)^2.
\]

Replacing the sum over the excited states of the ion with the effective state $I$ allows the ion dipole matrix element to be removed from the sum, leaving

\[
\Delta W_{d,n\ell} = \frac{1}{3} \langle a|r_1|I\rangle^2 \sum_{n'} \left\{ \frac{\ell(n\ell r_2^{-2}|n' (\ell - 1)2}{(2\ell + 1)(W_{an\ell} - W_{In' (\ell - 1)})} + \frac{(\ell + 1)(n\ell r_2^{-2}|n' (\ell + 1)2}{(2\ell + 1)(W_{an\ell} - W_{In' (\ell + 1)})} \right\}.
\]

In practice, it is not necessary to evaluate $\langle a|r_1|I\rangle^2$ since in this approximation, the ion polarizability is itself simply $\langle a|r_1|I\rangle^2/6W_{I_d}$.

We do need to determine $W_{I_d}$, which requires a knowledge of the distribution of oscillator strength $f_{n\ell}$ from the ion ground state. Unfortunately, this is not well known. However, the photoionization cross section, proportional to $df_{n\ell}/dW$, is known and similar to to the photoionization cross section of the isoelectronic neutral Kr [29, 30]. For Kr the oscillator strengths are known for both the bound states and the continuum [31], and using then we computed $W_{I_d}$ for Kr. We find a value 6% higher in energy than the first ionization limit of Kr at 112 900 cm$^{-1}$. We estimate the value for Rb$^+$ to also be 6% higher than the ionization limit at 220 100 cm$^{-1}$, resulting in $W_{I_d} = 232,300$ cm$^{-1}$.

Using $\langle a|r_1|I\rangle^2/3 = 2\alpha_d W_{I_d}$, we can obtain an expression for $k_d$ as

\[
k_{d,n\ell} = \frac{W_{I_d}}{\langle n\ell|r_2^{-4}|n'\ell'\rangle} \sum_{n'} \left[ \frac{\ell(n\ell r_2^{-2}|n' (\ell - 1)2}{(2\ell + 1)(W_{an\ell} - W_{In' (\ell - 1)})} + \frac{(\ell + 1)(n\ell r_2^{-2}|n' (\ell + 1)2}{(2\ell + 1)(W_{an\ell} - W_{In' (\ell + 1)})} \right].
\]

The values of $k_d$ computed in this way are given in Table II.

**TABLE II: Non-adiabatic correction factors, calculated as in Eq. (12). The lower-\(n\) values are relevant to the data taken here, and the higher-\(n\) values are for the data of Ref. [12].**

| \(n\) | \(\ell = 4\) | \(5\) | \(6\) | \(k_d\) | \(k_q\) |
|---|---|---|---|---|---|
| 17-19 | 0.978(2) | 0.990(1) | 0.994(1) | 0.921(15) | 0.967(7) | 0.984(3) |
| 27-30 | 0.977(2) | 0.990(1) |  | 0.921(15) | 0.967(7) |

To obtain an estimate of the uncertainty in $k_d$, we note that $W_{I_d}$ is roughly bounded by the lowest ionic excited state energy and the second ionization energy. For instance, a calculation of $W_{I_d}$ in atomic hydrogen gives a value just above the $1s - 2p$ transition energy, which reflects the fact that this transition contains over half of the total oscillator strength. In contrast, neutral Kr has six times as much oscillator strength in the first 20 eV above the ionization limit as in the bound states [31], which explains why $W_{I_d}$ is comparable to the ionization energy in that case. The first excited state of Rb$^+$ lies at 134 000 cm$^{-1}$, about 40% below the ionization limit. This sets the scale for the uncertainty range, but we believe the isoelectronic analogy to Kr to be reasonably sound, so we estimate an uncertainty of ±10% for $W_{I_d}$. This translates directly to a 10% uncertainty in $(1 - k_{d,n\ell})$ and provides the uncertainties shown in Table III.

The quadrupole correction factor $k_{q,n\ell}$ is calculated in much the same way as $k_{d,n\ell}$. In this case the $\langle n\ell|r_2^{-2}|n'\ell'\rangle$ matrix elements are required, and they are similarly evaluated numerically for hydrogenic wave functions. To assign an effective energy $W_{I_q}$ accounting for the ionic quadrupole transitions, we use an expression analogous to Eq. (9). Lacking better information, we calculate $W_{I_q}$ for hydrogen and obtain 122 465 cm$^{-1}$, which is 12% lower than the ionization limit. Taking the same to be true for Rb$^+$ we obtain $W_{I_q} = 254 000$ cm$^{-1}$. Using this value of $W_{I_q}$ in the quadrupole analog of Eq. (12), we calculate $k_{q,n\ell}$. Since there is no analog to the Kr oscillator strength distribution for comparison, we assign a ±20% uncertainty to $W_{I_q}$ and thus to $1 - k_{q,n\ell}$. The results are also shown in Table III.

Since we measure energy differences $\Delta W$, we again use Eq. (2), but the definitions of $\Delta_d$ and $\Delta_q$ now include $k_{d,n\ell}$ and $k_{q,n\ell'}$ and are given by

\[
\Delta_d = \frac{1}{2} k_{d,n\ell} \langle \frac{1}{r^4} \rangle_{n\ell} - \frac{1}{2} k_{d,n\ell'} \langle \frac{1}{r^4} \rangle_{n\ell'}
\]

and

\[
\Delta_q = \frac{1}{2} k_{q,n\ell} \langle \frac{1}{r^6} \rangle_{n\ell} - \frac{1}{2} k_{q,n\ell'} \langle \frac{1}{r^6} \rangle_{n\ell'}.
\]

As before, we plot $\Delta W/\Delta_d$ vs. $\Delta_q/\Delta_d$, for $(\ell, \ell')$ pairs (4, 5) and (5, 6), with the result shown in Fig. 7. We also include higher-\(n\) results for $(\ell, \ell') = (4, 5)$ taken from Ref. [12]. The points are fit to a line, and the resulting
TABLE III: Quantum defects for \( n = 17 \) to 19, \( g, h, i \) states, and the Ritz expansion coefficients of Eq. (16).

| \( \ell \) | \( \delta \) |
|------|------|
| \( n = 17 \) | \( g \) | 0.003908(2) |
| \( h \) | 0.0013697(5) |
| \( i \) | 0.0005762(2) |
| 18 | \( g \) | 0.003918(2) |
| \( h \) | 0.0013750(5) |
| \( i \) | 0.0005794(2) |
| 19 | \( g \) | 0.003927(2) |
| \( h \) | 0.0013794(5) |
| \( i \) | 0.0005821(2) |
| \( \delta_0 \) | \( g \) | -0.0299(6) |
| \( h \) | -0.0156(8) |
| \( i \) | -0.0086(4) |

FIG. 7: Determination of core polarizabilities including non-adiabatic corrections. The plot is analogous to that of Fig. 5, but now using Eqs. (13) and (14) for the \( \Delta \) variables. The data reported here are plotted as filled circles. We also include previous data at higher \( n \) from Ref. [12] as open circles. The higher-\( n \) data consist of energy shifts relative to hydrogen, rather than energy differences, so for those points we instead plot \( 2W/\langle k_{d,n\ell}(r^{-4})_{n\ell} \rangle \) vs. \( \langle k_{q,n\ell}(r^{-6})_{n\ell} \rangle \). All of the points are fit to a line, whose slope and intercept give \( \alpha_d \) and \( \alpha_q \). The dark gray band is a graphical representation of line fit errors. The light gray band shows the range of values obtained when \( k_d \) and \( k_q \) are varied by their uncertainties from Table III.

Table: Quantum defects for \( n = 17 \) to 19, \( g, h, i \) states, and the Ritz expansion coefficients of Eq. (16).

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| \( h \) | 0.0013794(5) |
| \( i \) | 0.0005821(2) |
| \( \delta_0 \) | \( g \) | -0.0299(6) |
| \( h \) | -0.0156(8) |
| \( i \) | -0.0086(4) |

Adiabatic \( \alpha_q \) of value 14(3) reported in [12].

Although we measure transition frequencies, we can use the extracted polarizabilities to calculate the abolute energy of the Rydberg states, and thus obtain the quantum defects. For this we use Eq. (1) and the adiabatic polarizability values \( \alpha_d^{(a)} \) and \( \alpha_q^{(a)} \), since that avoids the uncertainty in the non-adiabatic correction factors. The quantum defects are then found by setting

\[
W_{nl} = \frac{1}{2n^2} - \frac{1}{2(n-\delta_{nl})^2}.
\]

The results are listed in Table III. The variation of the quantum defect with \( n \) can be parameterized using the Ritz expansion [32]

\[
\delta(n) = \delta_0 + \frac{\delta_2}{(n-\delta_0)^2}.
\]

By combining our data with those of Ref. [12], we obtain the \( \delta_0 \) and \( \delta_2 \) values shown.

### IV. CONCLUSIONS

We have demonstrated microwave spectroscopy of the high-\( \ell \) states of Rb with precision improved by a factor of ten compared to previous results, and extending the measurements to \( \ell = 6 \). Using these data, we determined the dipole and quadrupole polarizabilities of the Rb\(^+\) ionic core, including corrections for non-adiabatic effects. These corrections significantly impact and resolve discrepancies between previous work and theory, particularly for the quadrupole term.

We can consider methods to obtain yet higher accuracy. A straightforward improvement would be to use
a more sophisticated atomic structure calculation to account for the non-adiabatic effects, which would allow more precise polarizability values to be extracted from our existing data. Without such a calculation, improvements to the experiment itself would not be useful.

If the non-adiabatic correction factors can be determined more accurately, then the measurements could be improved in several ways. One possibility is to extend the measurements to higher $\ell$ states. This would provide more points in Fig. 7 and allow a better test of the underlying core polarization model. However, this is challenging because the signal-to-noise ratio on the $nf \rightarrow nj$ transition would be low in our existing apparatus, and the decreasing value of $\Delta W$ makes the relative frequency uncertainty more significant. A different approach would be to perform absolute spectroscopy of the $nf$ state so that the energy shifts relative to hydrogen of the $nq$, $nh$ and $ni$ states could be used independently. We cannot carry out such spectroscopy with our current apparatus: although precise spectroscopy of the $nd$ states is available [33], at low $n$ values the $nd - nf$ frequency intervals are too large to access with our microwave technology.

The precision of the microwave measurements themselves could be improved by using a longer microwave pulse duration to obtain narrower transitions. This would require magnetic shielding to reduce line broadening from the Zeeman effect, and would benefit from a more complex field plate structure that allowed adjustment of all three components of the background bias field to better eliminate dc Stark shifts.

We also hope that the improved core polarizability values determined here will be useful for precision measurements such as atomic clocks and tune-out spectroscopy. In regards to our own interest in tune-out spectroscopy, the core polarizability was a source of uncertainty in the determination of the ratio of the $5p_{3/2}$ to $5p_{1/2}$ dipole matrix elements. Our original analysis in [10] used $\alpha_d = 9.08(10)$ au. Using the improved value found here, we reduce the relative uncertainty in the ratio from 18 ppm to 14 ppm, where the core contribution is no longer a significant factor in the uncertainty. The value of the ratio, 1.992 17, remains unchanged. Ultimately, we hope to further use tune-out spectroscopy to constrain all the valence dipole matrix elements of Rb and support a future parity non-conservation measurement [10].

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