The fine-structure constant ($\alpha$) is a fundamental parameter of quantum electrodynamics (QED), whereas the ionization energy of hydrogen ($E_{\text{hyd}}(I)$) can be predicted within QED with a precision of about 0.9 parts per trillion. Using the recently developed relativistic Ritz approach to analyze a subset of measured hydrogen transitions, I determine that $\alpha^{-1} = 137.035\,999\,163(29)$, in good agreement with the value obtained by other methods and without relying on a separately determined Rydberg constant. Likewise, I find that $E_{\text{hyd}}(I) = 13.598\,434\,599\,712(24)$ eV, in agreement with QED at 1.8 parts per trillion. Through a separate analysis I find support for the hypothesis that correlated errors exist within a substantial fraction of extant hydrogen spectral data. This study therefore demonstrates the potential of the relativistic Ritz approach to aid in testing QED with the spectra of hydrogenic atoms.

INTRODUCTION

The Standard Model of particle physics describes the fundamental interactions between particles on the smallest length scales. Despite its many successes, there are already apparent cracks in the model. For example, it does not account for the observation of neutrino oscillations (e.g., [1]) nor does it provide an explanation for the excess of matter over antimatter in the Universe [2]. At much larger scales, where gravity is concerned, there are other mysteries; for example, the mass in the Universe in the form of Standard Model particles appears to have been incapable of gravitationally coalescing since the big bang to form the astrophysical structure observed today [3]. Testing the Standard Model at high precision thus remains a primary motivator to perform new physics experiments. High-energy particle colliders have, historically, provided a wealth of information about fundamental particle physics, but as the energies of these colliders has increased, so has their cost and time-to-completion, making the construction of new colliders harder to justify.

In recent decades it has become apparent that high-precision experiments involving atoms and molecules are a complementary means to test the Standard Model and to probe for new physics [4]. Such experiments include very precise measurements of the transitions between atomic states and are accompanied by either the emission or absorption of photons whose energy (or frequency) can be very precisely measured. The most precise experiments are performed with hydrogenic systems, like hydrogen or its isotopic cousin, deuterium; similarly, more exotic atoms can be created, like positronium, composed of an electron bound to a positron. Additionally, atomic measurements allow for the determination of some of the fundamental constants of nature. In particular, the fine-structure constant ($\alpha$) quantifies the strength of interaction between electrically charged particles and plays a pivotal role in physics and chemistry. Independent methods of measuring such constants are crucial both for building confidence in those values and also for testing physical theory.
Bound-state quantum electrodynamics (BSQED) is the primary theoretical tool for predicting transition energies and for extracting fundamental constants from atomic spectra. Improving the precision of the theory is challenging [5], while spectroscopy may subject to unanticipated sources of error [6]. Recently, a semi-empirical theory that asymptotically approaches BSQED at long distances has been developed, dubbed the relativistic Ritz approach [7]. Conceptually, the approach is intuitive, an illustration of which is shown in Figure 1. Relativistic quantum field theory can describe many atomic-scale effects that can broadly be categorized into two classes: (1) kinetic relativistic effects, due to particle speeds being at a significant fraction of the speed of light and (2) short-ranged interactions, such as those that arise due to finite particle size, spin coupling, vacuum polarization, and particle self-energy.

Within the Standard Model, the largest length scale associated with these effects is the (reduced) Compton wavelength of the electron, \( r_{\text{QED}} = \frac{\hbar}{mc} \), whereas the orbital scale of the hydrogen atom in its n’th excited state is \( r_{\text{atom}} = r_{\text{QED}} n^2 \approx 137 r_{\text{QED}} n^2 \). By analyzing the quantum dynamics at long distance, i.e. \( r_{\text{atom}} \gg r_{\text{QED}} \), it is possible to treat the both the electron and proton as relativistic point-like objects and “work inward”, accounting for the omitted short-ranged interactions empirically through the use of free parameters contained in the quantum defect, \( \delta \). For hydrogen, long distance means \( n \gg \sqrt{\alpha} \), which is true even for the ground state. Here I apply the relativistic Ritz model to extant hydrogen spectroscopic data, demonstrating a novel method of determining the fine-structure constant and for testing QED.

MODEL SUMMARY

The energy levels of a hydrogenic atom composed of two particles of mass \( m_1 \) and \( m_2 \) in the relativistic Ritz approach were shown to asymptote at large principal quantum number to [7]

\[
E = \sqrt{m_1^2 + m_2^2 + \frac{2m_1m_2}{\sqrt{1 + \left( \frac{2a}{n_s} \right)^2}}} - (m_1 + m_2),
\]

where the effective quantum number,

\[
n_* = n - \delta.
\]

The quantum defect, \( \delta \), causes the wavefunctions to deviate from their canonical “pure Coulomb” forms and accounts for omitted short-ranged interactions [8–11]. The standard defect ansatz is to posit that it admits a series expansion in energy, but the following modified ansatz was shown to be equivalent and is significantly easier to use for data fitting

\[
\delta_{ij} = \delta_{(0)ij} + \frac{\delta_{(2)ij}}{(n - \delta_{(0)ij})^2} + \frac{\delta_{(4)ij}}{(n - \delta_{(0)ij})^4} + \frac{2\delta_{(2)ij}(n - \delta_{(0)ij})}{(n - \delta_{(0)ij})^3} + \frac{\delta_{(6)ij}}{(n - \delta_{(0)ij})^6} + \frac{6\delta_{(2)ij}\delta_{(4)ij}}{(n - \delta_{(0)ij})^7} + \ldots,
\]

where \( \ell \) and \( j \) are the orbital and total angular quantum numbers, respectively. Additional terms may be found in Ref [7].

I. ANALYSIS OF HYDROGEN SPECTRAL DATA: \( S_{1/2} \to S_{1/2} \) & \( D_{5/2} \)

The data I ultimately considered for the final analysis are measured transition frequencies of hydrogen coming primarily from the NIST Atomic Spectral Database (ASD) [12], which uses the 2010 hydrogen compilation [13], updated with a recent measurement of the \( 2S_{1/2} \to 8D_{5/2} \) transition [14], and supplemented by the measurement of the \( 1S_{1/2} \to 3S_{1/2} \) transition [15]. I omit the ASD \( 2S_{1/2} \to 6S_{1/2}/D_{5/2} \) transitions from analysis, as they had not been directly observed at the time the 2010 compilation was published. Relevant details may be found in Appendix A.

The defined CODATA [16] values \( h = 6.62607015 \times 10^{-34} \) J·s, \( c = 299792458 \) m/s, and \( e = 1.602176634 \times 10^{-19} \) C are used. The input masses of the electron and proton depend on the atomic mass unit, \( u \). At present the best determination of \( u \) comes from the rubidium recoil experiment of Ref [17], hence all four of the mass-related measurements summarized in Table 1 are needed. I consider excitation transitions of the form \( n_\ell f_{i,j} \to n_f \ell f_{j,i} \).  

\[\text{As explained in Ref. [13], those data reported in Ref. [12] had only been determined from a combination of other measurements and from the (nonrelativistic) Ritz value of the } 1S_{1/2} - 3S_{1/2} \text{ frequency. I thank Alexander Kramida for clarifying this point.} \]
the frequencies ($\Delta \nu$) that correspond to these transitions are fit with the equation

$$\hbar \Delta \nu = E_{n_i \ell_j j} - \begin{cases} E_0 & (n_i = 1) \\ E_{n_i \ell_j j} & (n_i \neq 1) \end{cases} \tag{4}$$

where $E_{n_i \ell_j}$ is the term energy defined in equation 1, $E_0$ is the ground state energy, the magnitude of which is the ground state ionization energy, $E_I$.

| TABLE I. Mass-related parameters |
|---------------------------------|
| Quantity | Value | Reference |
|---------|-------|-----------|
| $h/m^{35}\text{Rb}$ | $4.59135925890(65) \times 10^{-9}$ m$^2$/s | 17 |
| $m^{37}\text{Rb}$ | $86.9091805316(60)$ u | 18 |
| $m_\rho$ | $1.007276466583(15)(29)$ u | 19 |
| $m_r$ | $5.48579909065(16) \times 10^{-4}$ u | 20 |

The modified defect series, equation 3, must be truncated at some order for data analysis. At lowest order ($O_{\ell j} = 0$) only the defect parameter $\delta_{(0)\ell j}$ is included, at next-to-lowest order ($O_{\ell j} = 1$) both $\delta_{(0)\ell j}$ and $\delta_{(2)\ell j}$ are included, and so on. I have not been able to identify a well-defined place to truncate the series, and there may not be one, hence there are multiple (nested) models to consider, implying a model selection uncertainty. There are two distinct reasons for this. Firstly, parsimony is generally a guiding principle in model selection which attempts to optimize for the inherent tradeoff between bias and parameter variance; too few model parameters can result in significant bias and an overestimate of precision, while too many parameters can result in higher variance 21.

The second reason for model selection uncertainty is because of the asymptotic foundation of the Relativistic Ritz model. It is well-known that asymptotic series expansions, of which I conservatively assume equation 1, to be, have an optimal truncation beyond which the approximation becomes less accurate; in fact, the series may diverge. However, useful information may be contained within all terms of such a series 22, suggesting that analysis of models with more than the optimal number of parameters may be fruitful.

Given the uncertainty inherent to model selection, as well as the psychological dangers associated with data dredging, e.g., the discovery of spurious results, I have performed several exploratory analyses involving subsets of hydrogen transitions which are described in Appendix A. As a result, presented below is a summary of fits and model-averaging with 19 transitions between $S_{1/2} \rightarrow S_{1/2}/D_{5/2}$ states (see Table II), having removed the $1S_{1/2} \rightarrow 3D_{5/2}$ transition as I found it to be substantially inconsistent ($\approx 3\sigma$) with the other transitions 7.

| Number | Transition | Residual (kHz) | Standardized Res. |
|--------|------------|----------------|-------------------|
| 1      | $1S_{1/2} \rightarrow 2S_{1/2}$ | 130. | 0.40 |
| 2      | $1S_{1/2} \rightarrow 11D_{5/2}$ | -51. | -0.24 |
| 3      | $1S_{1/2} \rightarrow 1S_{1/2}$ | 390. | 1.2 |
| 4      | $1S_{1/2} \rightarrow 10S_{1/2}$ | 360. | 1.1 |
| 5      | $1S_{1/2} \rightarrow 9D_{5/2}$ | -31. | -0.15 |
| 6      | $1S_{1/2} \rightarrow 9S_{1/2}$ | 280. | 0.88 |
| 7      | $1S_{1/2} \rightarrow 7D_{5/2}$ | 20. | 0.097 |
| 8      | $1S_{1/2} \rightarrow 7S_{1/2}$ | -200. | -0.63 |
| 9      | $1S_{1/2} \rightarrow 5D_{5/2}$ | - | - |
| 10     | $1S_{1/2} \rightarrow 5S_{1/2}$ | 490. | 1.2 |
| 11     | $1S_{1/2} \rightarrow 3S_{1/2}$ | $1.1 \times 10^{-3}$ | 1.9 |
| 12     | $1S_{1/2} \rightarrow 2S_{1/2}$ | $-2.9 \times 10^{-6}$ | -2.1 |
| 13     | $2S_{1/2} \rightarrow 12D_{5/2}$ | -0.18 | -0.80 |
| 14     | $2S_{1/2} \rightarrow 10D_{5/2}$ | -7.4 | -0.63 |
| 15     | $2S_{1/2} \rightarrow 8D_{5/2}$ | -0.15 | -1.8 |
| 16     | $2S_{1/2} \rightarrow 8S_{1/2}$ | 4.7 | 1.9 |
| 17     | $2S_{1/2} \rightarrow 4D_{5/2}$ | 5.0 | 1.6 |
| 18     | $2S_{1/2} \rightarrow 4S_{1/2}$ | -1.4 | -1.8 |
| 19     | $3S_{1/2} \rightarrow 3D_{5/2}$ | -4.8 | -1.9 |
| 20     | $4S_{1/2} \rightarrow 4D_{5/2}$ | 180. | 1.6 |

Remarkably, the removal of this single datum brings the statistical uncertainty (due to data fitting) in both $\sigma$ and the ionization energy down by about 50%. The results are summarized in Tables III and IV.

| TABLE III. Second-order Akaike criteria (AICc) for hydrogen $S_{1/2}/D_{5/2}$ transitions. Lower values of AICc tend to indicate better (more parsimonious) models. Bolded values identify the models used for averaging. |
|----------------|--------|--------|--------|
| $O_S$ | $O_D$ | 0 | 1 | 2 |
|---------|---------|--------|--------|--------|
| 0       | -329.1  | -332.4 | -327.0 |
| 1       | -421.3  | -422.5 | -438.3 |
| 2       | -442.9  | $-459.4$ | $-457.9$ |
| 3       | -436.2  | $-458.0$ | $-449.1$ |

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3 Care must be taken when performing such analyses. I advise all future workers using this approach to be transparent about their methodologies when publishing their results.
TABLE IV. Akaike weights and some parameter fits for the $S_{1/2}/D_{5/2}$ transitions in Table II fit with models RR21, RR22, RR31, and RR32, described in detail in Appendix A.

|         | RR21        | RR22        | RR31        | RR32        |
|---------|-------------|-------------|-------------|-------------|
| $w_i$   | 0.5010      | 0.2391      | 0.2570      | 0.0029      |
| $(\alpha^{-1} - 137.035999) \times 10^9$ | 159(18)     | 194(22)     | 150(16)     | -653(941)   |
| $-(E_0 + 13.598434599\text{ eV}) \times 10^{12}$ | 714(21)     | 695(20)     | 718(19)     | 1148(504)   |

FIG. 2. Standardized residuals for the RR21, RR22, RR31, RR32 model fits. Transition numbers are identified in Table II.

Second-order Akaike criteria (AICc) are given in Table III and the model comparison and data analysis follows as in the exploratory analysis in Appendix A.2. The four models (in the form $RR_O S O_D$) RR21, RR22, RR31, and RR32 were used in model-averaging the parameter fits; their fit values are summarized in Table IV and a plot of the standardized residuals is shown in Fig. 2. From this analysis

$$\alpha^{-1} = 137.035\,999\,163(27)_{\text{data}}(11)_{\text{mass}}$$

$$= 137.035\,999\,163(29),$$

where I distinguish the uncertainty due to transition data fitting and model-averaging (data) from the uncertainty due to the mass-related inputs (mass) of Table I. This is in near agreement with a recent determination inferred using the Rydberg constant [17],

$$\alpha^{-1} = 137.035\,999\,150(33)_{\text{exp}}(2)_{\text{theory}},$$

and is in complete agreement with the determination based of the electron g-factor [23] [24],

$$\alpha^{-1} = 137.035\,999\,150(33)_{\text{exp}}(2)_{\text{theory}}.$$  \hspace{1cm} (7)

The hydrogen ground state ionization energy is simultaneously determined to be

$$E_I^{(\text{hyd})} = 13.598\,434\,599\,712(24)\text{ eV},$$ \hspace{1cm} (8)

which agrees with the Standard Model prediction [12],

$$E_I^{(\text{hyd, SM})} = 13.598\,434\,599\,702(12)\text{ eV},$$ \hspace{1cm} (9)

at the level of 1.8 parts per trillion.
II. EVIDENCE FOR CORRELATED ERRORS IN THE ASD 2010 COMPILATION

I made attempts to fit more of the transitions from the NIST ASD 2010 hydrogen compilation [12], including all transitions between the 5 angular momentum channels $S_{1/2}, P_{1/2}, P_{3/2}, D_{3/2},$ and $D_{5/2}$, updated with the recent $2S_{1/2} \rightarrow 2P_{1/2}$ measurement [25] and $2S \rightarrow 4P$ measurements by Beyer et al. [26]. However, the fit was so poor as to provide little reliable information. Instead, I deemed it more illuminating to analyze the data described above, but without including any $2S \rightarrow 4P$ transitions, the details of which are found in Appendix [11].

From the fits on the data mentioned above I have made model-averaged predictions of the two $2S \rightarrow 4P$ transitions, shown in Table V and compared both with the ASD 2010 compilation [12] values and the results from Beyer et al. [26]. If the measurements of Beyer et al. are indeed accurate, the striking consistency of the relativistic Ritz model predictions with the older ASD 2010 values supports the hypothesis that a substantial number of inter-correlated errors exist within that data set, at least insofar as $S \rightarrow P$ transitions are concerned; this may be due to the quantum interference phenomenon discussed in Refs [26], [27], and [6]. Given these apparent errors, I made no further attempt to analyze transitions beyond those described in the previous section.

### TABLE V. Comparing predictions of the relativistic Ritz model-averaged value of the $2S \rightarrow 4P$ transitions to the ASD 2010 hydrogen compilation value [12] and 2017 Beyer et al. value [26].

| Transition          | Rel. Ritz Fit (kHz) | ASD 2010 (kHz) | Beyer et al. (kHz) |
|---------------------|---------------------|----------------|-------------------|
| $2S_{1/2} \rightarrow 4P_{1/2}$ | 616 520 017 542(24) | 616 520 017 568(15) | 616 520 152 555.1(3.0) |
| $2S_{1/2} \rightarrow 4P_{3/2}$ | 616 521 388 669(27) | 616 521 388 672(10) | 616 521 519 990.8(3.0) |

III. DISCUSSION AND OUTLOOK

Historically, in order to determine the fine-structure constant ($\alpha$) from spectroscopic data, bound-state QED has been employed to extract the Rydberg constant from which the determination is made. The nuclear radius also must be accounted for with that approach, but here such detailed modeling is not needed. Instead, substantial statistical power can be leveraged when using the relativistic Ritz approach to analyze a modest number of atomic transitions. This may turn out to be of particular relevance because the method can be used to determine $\alpha$ even if short-ranged beyond-the-standard-model phenomena are discovered to affect hydrogenic atoms.

New and more precise measurements of atomic transitions, especially within hydrogen, deuterium, and positronium, may provide more accurate determinations of the fine-structure constant and ground state energies of simple atoms, thus allowing for a new way to test the Standard Model with precision atomic physics. Further analysis is warranted to determine what precision may be possible with future experimental data, but this is beyond the scope of the present article. Lastly, as demonstrated here, this method may in some cases allow for the detection of spurious data and/or reveal systematic measurement errors.

ACKNOWLEDGMENTS

I am grateful to Alexander Kramida for correspondence and for conversations with Gabe Duden, Maggie Rasmussen, Gloria Clausen, and Frédéric Merkt. The spectral data used in this analysis is taken from the NIST ASD 2010 hydrogen compilation unless otherwise noted. This research was funded, in part, by a Charles A. Dana Research Fellowship at Norwich University.

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4 I thank Alexander Kramida for pointing out this possibility.
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Appendix A: Exploratory Analyses of Data

1. $S_{1/2}$ transitions and statistics with AICc

Here I consider only the transitions between the $S_{1/2}$ states, of which there are 10 direct measurements, listed in Table XII in the following section. All measurements are taken from the ASD 2010 hydrogen compilation except for the inclusion of the recent measurement of the $1S_{1/2} \rightarrow 3S_{1/2}$ transition. I also exclude the $2S_{1/2} \rightarrow 6S_{1/2}$ transition, as described in the main text of this article.

The relativistic Ritz models at various points of truncation of equation 3 in the main text are labeled RR in the following section. Multi-model inference is employed in Mathematica, weighting each transition interval by the inverse-square of its measurement uncertainty. A selection of 5 models were fit to this data, and the second-order Akaike information criterion
(AICc) values, discussed below, are reported in Table VI. Ref [21] contains an excellent discussion of the use of AICc for comparing the goodness of fit of various models to data. This criterion is defined by

$$\text{AICc}_i = -2 \log \mathcal{L}(\hat{\theta}) + 2K \left( \frac{n}{n-K-1} \right),$$  \hspace{1cm} (A1)

where $\mathcal{L}(\hat{\theta})$ is the maximum likelihood for the set of best-fit model parameters, $\hat{\theta}$ (conditional on the chosen model), $n$ is the sample size, and $K$ is the number of model parameters. AICc, as opposed to the original AIC, is used according to the rule of thumb that the former should be used whenever $n/K < 40$ [21].

The “best” model has the minimum value of AICc. The AICc differences are defined by

$$\Delta_i \equiv \text{AICc}_i - \text{AICc}_{\text{min}},$$  \hspace{1cm} (A2)

and the evidence of model $i$ relative to model $j$ is given by

$$\exp \left( -\frac{1}{2} (\Delta_i - \Delta_j) \right),$$  \hspace{1cm} (A3)

indicating that RR1 is by far the best model. The parameters fit using this model are reported in Table VII.

Consider that a recent determination of the fine-structure constant, inferred from the Rydberg constant and a rubidium recoil measurement [17], yielded

$$\alpha^{-1} = 137.035999372(12).$$  \hspace{1cm} (A4)

Although the relative difference between [A4] and the value of $\alpha^{-1}$ reported in Table VII is remarkably small, given the statistical error, there appears to be a substantial bias affecting the determination of $\alpha^{-1}$ in this exploratory analysis if the result from [17] is accurate. Nevertheless, in the following section the analysis is repeated including transitions involving $D$ states.

2. $S_{1/2}$ and $D_{5/2}$ transitions, model-averaging, and error analysis

Here I consider the transitions between the $S_{1/2}$ and $D_{5/2}$ states, of which there are 20 direct measurements, summarized below in Table VIII. The relativistic Ritz model at various points of truncation of equation (3) in the main text are labeled RRO$_S O_D$. A selection of 12 models were fit to this data, and the AICc values are reported in Table VIII. I do not consider models in addition to those indicated; although there could conceivably be models that have even lower AICc values, from experience I have learned that they would almost certainly be overfit and lead to spurious results.

### Table VII. Fit parameters for RR1 applied to the $S_{1/2}$ states.

| $\delta_{000}^{0}$ | $2.53459(3) \times 10^{-7}$ |
|-------------------|------------------------|
| $\delta_{120}^{0} | 4.48(5) \times 10^{-8}$ |
| $E_0$ [eV] | $-13.598434999454(30)$ |
| $\alpha^{-1}$ | $137.035999372(12)$ |

The AICc differences ($\Delta_i$) suggest that models RR20 and RR21 are comparably good, indicating that both should be included in any reasonable and honest analysis. The parameter fits from the RR20 and RR21 model analyses are reported in Tables IX and X, respectively. Two types of uncertainty are already apparent, namely the conditional sampling error estimate (values in parentheses), and a model selection uncertainty (the variation in parameter values between Tables IX and X).

As a check of the conditional sampling error estimate, a bootstrap analysis has been performed, resampling and replacing each of the 20 transition measurements with a random value drawn from a normal distribution whose mean is the measured value and standard deviation is equal to the measurement uncertainty. One thousand ($B = 1000$) such resamplings were performed and analyzed with the RR20 model, the results of which give standard deviations $\sigma_{E_0} = 52 \times 10^{-12}$ eV and $\sigma_{\alpha^{-1}} = 29 \times 10^{-9}$, in good agreement with the conditional sampling error estimates shown in Tables IX and X.

Note that there are significant correlations amongst the model parameters; see Table XI for the RR20 correlation matrix.

To combine the results from different models I follow closely the procedure suggested in Ref. [21]. For purposes of model averaging, the Akaike weights for model
TABLE IX. Fit parameters for RR20 applied to $S_\frac{1}{2}/D_\frac{3}{2}$ transitions.

| $\delta_{00\frac{1}{2}}$ | $2.53414(8) \times 10^{-9}$ |
| $\delta_{20\frac{1}{2}}$ | $6.7(5) \times 10^{-8}$ |
| $\delta_{40\frac{1}{2}}$ | $-4.4(1.1) \times 10^{-8}$ |
| $\delta_{02\frac{1}{2}}$ | $8.8710(5) \times 10^{-6}$ |
| $E_0 [eV]$ | $-13.598434599636(42)$ |
| $\alpha^{-1}$ | $137.035999242(23)$ |

TABLE X. Fit parameters for RR21, as in Table IX.

| $\delta_{00\frac{1}{2}}$ | $2.5338(2) \times 10^{-9}$ |
| $\delta_{20\frac{1}{2}}$ | $8.3(9) \times 10^{-8}$ |
| $\delta_{40\frac{1}{2}}$ | $-8.0(1.9) \times 10^{-8}$ |
| $\delta_{02\frac{1}{2}}$ | $8.867(2) \times 10^{-6}$ |
| $\delta_{22\frac{1}{2}}$ | $1.8(8) \times 10^{-8}$ |
| $E_0 [eV]$ | $-13.598434599714(52)$ |
| $\alpha^{-1}$ | $137.035999160(44)$ |

Table entries are introduced:

$$w_i = e^{-\Delta_i} \sum_{j=1}^{R} e^{-\Delta_j}, \quad (A5)$$

where $R$ is the number of models under consideration. The value of generic model parameter $\theta_a$ will have a best estimate, conditional on model $i$, denoted here by $\hat{\theta}_{a,i}$. The model-averaged estimate for $\theta_a$ is

$$\langle \hat{\theta}_a \rangle = \sum_{j=1}^{R} w_i \hat{\theta}_{a,i}. \quad (A6)$$

I seek an estimate of the error in (A6) that is not conditional on a particular model, hence referred to as an unconditional error estimate. The procedure described in [21] includes both the conditional variance estimate, $\hat{\text{var}}(\hat{\theta}_{a,i})$, and a “variance component” due to the conditional parameter values fluctuating around their model average, $(\hat{\theta}_{a,i} - \langle \hat{\theta}_a \rangle)^2$. The estimate of the unconditional standard error (se) is given by

$$se(\hat{\theta}_a) = \sum_{i=1}^{R} w_i \sqrt{\hat{\text{var}}(\hat{\theta}_{a,i}) + (\hat{\theta}_{a,i} - \langle \hat{\theta}_a \rangle)^2}. \quad (A7)$$

Despite the above well-established procedures for model averaging and error estimation, there is still freedom in the decision of which models to include in the analysis. At the very least, it would seem, models RR20 and RR21 should be included in the average, but what others? Models RR20 and RR21 differ in their number of $D$-state defect parameters; it therefore seems prudent to also explore a variation in the number of $S$-state parameters. For this reason, I also include models RR30 and RR31 as they appear to have the second-best AICc values. This creates a contiguous and compact exploration of the $(O_S, O_D)$ parameter space.

The results of the 4 models are summarized in Table XI and a plot of standardized residuals is given in Figure 3 with transition numbers identified in Table XII. The weighted averages with unconditional error estimates are, according to equations (A6) and (A7),

$$\alpha^{-1} = 137.035999203(53)_{\text{data}} \quad (A8)$$

and

$$E_0 = -13.598434599673(61)_{\text{data}} \text{eV}. \quad (A9)$$

The subscript “data” indicates that this statistical uncertainty is due to transition data fitting and model averaging.

In addition to these statistical considerations, the mass-related inputs given in Table I have uncertainty that must be accounted for. To this end, I performed a bootstrap analysis, resampling and replacing each of the 4 mass-related measurements with a random value drawn from a normal distribution whose mean and standard deviation are given by its measured value and uncertainty, respectively. One thousand ($B = 1000$) such resamplings were performed and analyzed with all four RR models, the results of which give very similar standard deviations $\sigma_{E_0} \leq 10^{-16} \text{eV}$ (negligible) and $\sigma_{\alpha^{-1}} = 11 \times 10^{-9}$.
Finally, I can report from this exploratory analysis
\[
\alpha^{-1} = 137.035\,999\,203(53)_{\text{data}}(11)_{\text{mass}} = 137.035\,999\,203(54)
\]  
(A10)

and
\[
E_0 = -13.598\,434\,599\,702(12)\text{ eV}.
\]  
(A11)

The very good agreement between (A10) and the recent value found by Morel et al. [17] suggests that this analysis is reliable and therefore the determination in equation (A11) can be trusted and compared with the prediction from BSQED [12],
\[
E_0^{\text{QED}} = -13.598\,434\,599\,702(12)\text{ eV},
\]  
(A12)

implying agreement between the Standard Model and experiment at the level of $4.5 \times 10^{-12}$.

Given the remarkable success of this exploratory analysis, the following procedure is proposed to guide future analyses of other data sets. Consider the set of possible models as occupying points in a $k$-dimensional model space with coordinates $\{O_1, \ldots, O_k\}$. Use the AICc-best
model as an anchor point and explore a small, contiguous k-dimensional region that includes the AICc-second-best models. If there are multiple AICc local minima, the model that is most parsimonious (fewest parameters) should be chosen as the anchor.

It is noteworthy that the 1S\(_{1/2}\) → 5D\(_{5/2}\) transition has a large negative standardized residual approximately equal to –3 in all 4 models, indicating that it is significantly inconsistent with the other 19 transitions. For this reason I omit it from the final analysis summarized in the main text.

Appendix B: On the correlated errors in the ASD 2010 compilation

Here I describe analysis with the ASD 2010 hydrogen compilation [12] that includes all transitions between the 5 angular momentum states \(S_{1/2}, P_{1/2}, P_{3/2}, D_{3/2},\) and \(D_{5/2},\) updated with the recent 2\(S_{1/2}\) → 2\(P_{1/2}\) measurement [25], but omitting the two 2\(S\) → 4\(P\) transitions. The AICc values for each model fit are listed in Tables XV through XVIII. Despite the fact that model RR203 gives the lowest AICc value, the local minimum in the space of \((O_S, O_P, O_D)\) that corresponds to the most parsimonious model is for (2,1,0), or model RR210, whose fit parameters are displayed in Table XIV This model is the anchor. To explore a compact and contiguous region within this parameter space, I used the eight best relativistic Ritz models that contain the anchor – RR210, RR220, RR310, RR320, RR211, RR221, RR311, and RR321 – to make model-averaged predictions of the 2\(S\) → 4\(P\) transitions, summarized below in Section B.1 and shown in Table V of the main text. The striking consistency of the relativistic Ritz model prediction with the older ASD 2010 compilation suggests that a substantial number of inter-correlated errors exist within that data set [6], at least insofar as \(S\) → \(P\) transitions are concerned.

1. 2\(S\) → 4\(P\) transition predictions and error estimate

Here I consider model predictions by using equation (4) of the main text. Consider a particular transition to be predicted by

\[
\Delta \nu = f(\Theta),
\]

where \(f\) represents the right hand side of equation (4) and \(\Theta\) is the vector of best-fit parameters from a particular fit. The uncertainty in \(\Delta \nu\), \(\sigma_{\Delta \nu}\) is given by

\[
\sigma_{\Delta \nu}^2 = g'^T C g
\]

where the components of the vector \(g\) are

\[
g_a = \frac{\partial f}{\partial \Theta_a}
\]

and the covariance matrix has components

\[
C_{ab} = \text{cov}(\Theta_a, \Theta_b),
\]

both of which can be easily obtained with mathematical software, such as Mathematica.

As an illustration, I summarize the main points in the analysis of the RR210 model for the transition 2\(S_{1/2}\) → 4\(P_{1/2}\). With those best-fit parameters,

\[
\Delta \nu(2S_{1/2} \rightarrow 4P_{1/2})_{\text{RR210}} = 616520017547\text{ kHz}.
\]

I take the components of \(g\) to be listed in the same order as that of Table XIV. Taking the derivatives of \(f(\Theta)_{\text{RR210}}\) with respect to those parameters and evaluating with the best-fit values,

\[
g = \begin{pmatrix}
8.22 \times 10^{11} \\
2.06 \times 10^{11} \\
5.14 \times 10^{10} \\
-1.03 \times 10^{11} \\
-6.42 \times 10^{9} \\
0 \\
0 \\
0 \\
0 \\
0 \text{ eV}^{-1}
\end{pmatrix}
\]

kHz,

\[
\alpha^{-1} = 137.035999243(20)
\]
where the zeros correspond to a parameter having no effect on the predicted transition. The covariance matrix output by the fitting software is omitted here for brevity. The result for the error estimate using (B2) is

\[(\sigma_{\Delta \nu})_{RR210} = 20 \text{ kHz}.\]  

(B7)

The analysis may then be repeated with the other seven models, RR220, RR310, RR320, RR211, RR221, RR311, and RR321, which are adjacent to RR210 in the 3-dimensional model space with coordinates \((O_S, O_P, O_D)\). Given all eight model predictions and error estimates, a model-averaged value and unconditional error estimate is obtained in the manner described in Section A2. The result is

\[\Delta \nu(2S_{1/2} \rightarrow 4P_{1/2}) = 616.520.017.542(24) \text{ kHz}.\]  

(B8)

An identical analysis predicts

\[\Delta \nu(2S_{1/2} \rightarrow 4P_{3/2}) = 616.521.388.669(27) \text{ kHz}.\]  

(B9)

TABLE XV. Table of second-order Akaike criteria (AICc) for the exploratory analysis of \(S, P,\) and \(D\) transitions. \(O_D = 0.\) Bolded values identify the models used for averaging.

| \(O_S\) | 0 | 1  | 2  | 3  | 4  |
|--------|---|----|----|----|----|
| \(O_P\) | -1107.0 | -1165.3 | -1160.1 | -1154.4 | -1148.2 |
| 1 | -1474.1 | -1492.4 | -1498.3 | -1496.3 | -1491.2 |
| 2 | -1471.4 | **-1500.4** | **-1497.3** | -1495.2 | -1490.0 |
| 3 | -1471.8 | **-1498.1** | **-1495.3** | -1494.3 | -1488.7 |
| 4 | -1469.2 | -1495.6 | -1492.4 | -1492.1 | -1485.3 |

TABLE XVI. Table of second-order Akaike criteria (AICc) for the exploratory analysis of \(S, P,\) and \(D\) transitions. \(O_D = 1.\) Bolded values identify the models used for averaging.

| \(O_S\) | 0 | 1  | 2  | 3  | 4  |
|--------|---|----|----|----|----|
| \(O_P\) | -1137.6 | -1257.2 | -1252.2 | -1246.2 | -1239.7 |
| 1 | -1479.5 | -1487.8 | -1493.4 | -1490.8 | -1485.3 |
| 2 | -1477.1 | **-1499.7** | **-1497.1** | -1494.7 | -1489.1 |
| 3 | -1475.0 | **-1498.2** | **-1495.0** | -1493.5 | -1487.6 |
| 4 | -1472.4 | -1495.4 | -1491.9 | -1491.2 | -1483.9 |
TABLE XVII. Table of second-order Akaike criteria (AICc) for the exploratory analysis of $S, P,$ and $D$ transitions. $O_D = 2$.

| $O_S$ | 0   | 1   | 2   | 3   | 4   |
|-------|-----|-----|-----|-----|-----|
| 0     | -1136.3 | -1269.9 | -1264.7 | -1258.4 | -1251.5 |
| 1     | -1489.6 | -1492.4 | -1499.2 | -1497.5 | -1491.7 |
| 2     | -1486.7 | -1499.2 | -1498.1 | -1496.3 | -1490.1 |
| 3     | -1483.7 | -1497.0 | -1495.3 | -1493.8 | -1487.4 |
| 4     | -1481.3 | -1494.1 | -1493.2 | -1491.2 | -1483.8 |

TABLE XVIII. Table of second-order Akaike criteria (AICc) for the exploratory analysis of $S, P,$ and $D$ transitions. $O_D = 3$.

| $O_S$ | 0   | 1   | 2   | 3   | 4   |
|-------|-----|-----|-----|-----|-----|
| 0     | -1149.8 | -1480.2 | -1485.6 | -1483.0 | -1477.0 |
| 1     | -1494.2 | -1490.3 | -1497.5 | -1495.6 | -1489.5 |
| 2     | -1502.8 | -1497.5 | -1496.7 | -1494.7 | -1488.2 |
| 3     | -1500.7 | -1495.3 | -1493.9 | -1495.9 | -1489.2 |
| 4     | -1497.7 | -1492.0 | -1491.3 | -1493.5 | -1486.7 |