Theory for the Rydberg states of helium: Results for $2 \le n \le 35$ and comparison with experiment for the singlet and triplet P-states

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(Dated: October 27, 2025)

High precision variational calculations in Hylleraas coordinates are presented for all singlet and triplet P-states of helium up to principal quantum number $n = 35$ with a uniform accuracy of 1 part in 10^{22} for the nonrelativistic energy. Mass polarization, relativistic and quantum electrodynamic effects are included to achieve a final accuracy of ± 1 kHz or better for the ionization energy of the Rydberg states of ^{4}He in the range $24 \le n \le 35$. The results are combined with 11 transition frequency measurements of Clausen et al. Phys. Rev. A **111**, 012817 (2025) to obtain complementary measurements of the ionization energy of the $1s2s\ ^3S_1$ state that do not depend on quantum defect extrapolations to the series limit. The result from the triplet spectrum yields an ionization energy of 1152 842 742.728(6) MHz, which agrees with but is larger than the experimental value by 14 $\pm$17 kHz. However, it confirms a much larger 9σ discrepancy of 0.468 ± 0.055 MHz with the theoretical ionization energy of Patkóš et al. Phys. Rev. A **103**, 042809 (2021). The results provide a test of the quantum defect extrapolation method at the level of $\pm$17 kHz. This revised version contains an additional table of spin-dependent matrix elements from the Breit interaction in the appendix for $n \le n \le 35$. The results are otherwise identical.

PACS numbers: 31.15.ap, 31.15.ac, 32.10.Dk

Recent work has revealed a 9σ disagreement between theory and experiment in the ionization energy of the metastable $1s2s\ ^3S_1$ state of helium [1, 2]. The origin of the discrepancy remains unexplained, even though helium is a fundamental three-body problem for which high precision calculations are available, including electron correlation, relativistic and quantum electrodynamic corrections for the $1s2s\ ^3S_1$ state [3–7]. The experiments of Clausen et al. [2] involve direct measurements of the ionization energy of the $1s2s\ ^3S_1$ state by extrapolation of the $1s2s\ ^3S_1 - 1snp\ ^3P_J$ ($J = 0, 1, 2$) transition frequencies to the series limit $n \to \infty$ by the use of quantum defect theory, beginning at $n = 27$. This experiment followed an earlier indirect measurement based on the $1s2s\ ^1S_0 - 1snp\ ^1P_1$ transition frequencies, beginning at $n = 24$, together with the high precision measurement of the $1s2s\ ^1S_0 - 1s2s\ ^3S_1$ transition frequency [8]. The two measurements agree with each other to within their statistical uncertainty (0.023 ± 0.035 MHz), and they confirm a discrepancy of 0.4774 ± 0.053 MHz, with experiment lying deeper than theory. Measurements on the ^{3}He isotope yield a parallel discrepancy of 0.482 ± 0.053 kHz [9]. The uncertainty of ± 0.053 MHz represents the theoretical uncertainty due to higher order QED contributions.

The measurements of Clausen et al. rely on the use of quantum defect theory to extrapolate to the series limit in order to find the ionization energy of the $1s2s\ ^3S_1$ state in question. Although quantum defect theory is well established and widely used, it is not an exact fundamental theory [10]. An alternative would be to perform a direct comparison between theory and experiment for transition frequencies to the high-n Rydberg states. The comparison would be meaningful because the QED uncertainties decrease approximately in proportion to $1/n^3$, and so become negligibly small at $n = 24$ and beyond. We showed in a previous publication [11] that it is indeed possible to perform high precision calculations for $n = 24$ by the use of triple basis sets in Hylleraas coordinates. This goes well beyond the previous limit of $n = 10$ [12], and represents a significant extension of the technology for high precision atomic theory into previously unexplored territory at the kHz level of accuracy (parts in 10^{12} for the total energy). In the present paper, these same techniques are applied to obtain ionization energies of all singlet and triplet P-states up to $n = 35$, including relativistic and QED corrections up to order α^3 Ry ($\alpha^5 mc^2$), and estimates of the α^4 Ry term based on exact calculations of the dominant part due to singlet-triplet mixing. The results enable direct determinations of the ionization energy of the $1s2s\ ^3S_1$ state without the need for extrapolation to the series limit.

The paper is organized as follows. The following section describes the triple basis set method of constructing nonrelativistic wave functions in Hylleraas coordinates for the Rydberg P-states of helium. Varational bounds are tabulated and compared with previous work. In Sect. II the formalism for relativistic and QED corrections is presented. The dominant terms of $O(\alpha^4)$ and $O(\alpha^5)$ are calculated directly, and the remainder estimated by a $1/n^3$ scaling from the known $n = 2$ case. Section VII presents a tabulation of the calculated ionization energies for the P-states up to $n = 35$. The ionization energy of the $1s2s\ ^1S_1$ state is calculated for each of the 11 measured $1s2s\ ^1S_0 - 1snp\ ^1P_1$ or $1s2s\ ^3S_1 - 1snp\ ^3P_c$ transition frequencies, and compared with the results of a quantum defect extrapolation. For the sake of brevity in the spectroscopic notation, the one-electron labels are

suppressed so that, for example, $2\,^1P_1$ denotes the state $1s2p\,^1P_1$. Units are atomic units throughout. The value of the reduced mass Rydberg constant used to convert from atomic units to MHz is

$$R_M = (1-\mu/M)R_\infty \tag{1}$$

with $R_\infty = 3289\,841\,960.250$ MHz, and $\mu/M = 1.370\,745\,6347\times10^{-4}$, where $\mu = Mm_{\rm e}/(M+m_{\rm e})$ is the reduced electron mass and M is the bare alpha-particle mass.

I. NONRELATIVISTIC WAVE FUNCTIONS

The primary obstacle to extending high precision calculations to the high-lying Rydberg states of helium is the difficulty of obtaining sufficiently accurate wave functions for the complete three body problem of a nucleus plus two electrons. Variational calculations typically suffer from a rapid decline in accuracy with increasing principal quantum number n, as is evident in the original ground-breaking calculations of Accad, Pekeris and Schiff [13] in Hylleraas coordinates. The basis functions involve powers of r_1, r_2 and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ for the radial coordinates of the two electrons. Their result for the $5\,^1P$ barely exceeds the accuracy of a simple screened hydrogenic approximation -2.02000 $\rm E_h$. Drake et al. [14–17] showed that much improved accuracy could be obtained by "doubling" the Hylleraas basis set so that it explicitly contains two variationally determined distance scales for the inner and outer electron. This served well for all states of helium up to $n = 10$ and $L = 7$ [17] (including relativistic and QED corrections). However, to reach the level of $n = 24$ and beyond, we have shown in our previous paper [11] that results of sufficient accuracy can be obtained by tripling the basis set so that each combination of powers is included three times with different exponential distance scales. In other calculations, Chi et al. [18] have recently obtained results of encouraging accuracy up to $n = 27$ for the nonrelativistic energy by the use of of correlated B-spline basis functions with up to 64000 terms, although the accuracy begins to deteriorate beyond $n = 20$. The only other calculations to go beyond $n = 10$ are the ICI calculations of Nakashima et al. [19] up to $n = 24$ for the nonelativistic energies of S-states. In addition, very high precision calculations have been performed by Aznabaev et al. [20] for the nonrelativistic energies for all states up to $n = 4$, using stochastic all-exponential basis functions with up to 22000 terms of the form $\exp(-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12})$.

As discussed previously [11, 21, 22], the heliumlike Hamiltonian is diagonalized in a basis set constructed from basis functions of the form (for P-states)

$$\begin{aligned}\phi_{i,j,k}(\alpha,\beta;\mathbf{r}_1,\mathbf{r}_2) &= r_1^i\, r_2^{j+1}\, r_{12}^k \exp(-\alpha r_1 - \beta r_2)\cos\theta_2 \\ &\quad \pm \text{ exchange}\end{aligned} \tag{2}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of electron 1 and electron 2 relative to the nucleus of charge Z, $\cos\theta_2$ gives the angular dependence on $\mathbf{r}_2$ appropriate to a p-electron, and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the inter-electron separation. The "exchange" term denotes an interchange of the labels 1 and 2, with the (+) sign for triplets and the (−) sign for singlets. A variational wave function in a triple basis set then has the form

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = \sum_{p=1}^{3} \sum_{i,j,k}^{i+j+k\le\Omega_p} c_{i,j,k}^{(p)} \phi_{i,j,k}(\alpha_p,\beta_p;\mathbf{r}_1,\mathbf{r}_2) \tag{3}$$

where the $c_{i,j,k}^{(p)}$ ar linear variational coefficients, and Ω_p controls the size of the basis set such that $i+j+k \le \Omega_p$ in each of the sectors labelled by p (with $\Omega_1 = \Omega$ being largest). The upper limit for the sum over p is 3 for a triple basis set. The six nonlinear variational parameters α_p, β_p are determined by minimizing the energy on a six-dimensional energy surface. This is accomplished by calculating analytically the derivatives $\partial E/\partial\alpha_p$, $\partial E/\partial\beta_p$ [16] and finding their zeros by Newton's method. The optimization produces a natural separation of the nonlinear parameters into short-range, intermediate, and asymptotic long-range sectors [23]. The basis set also includes the screened hydrogenic term $\psi_{1s}(\mathbf{r}_1;Z)\psi_{np}(\mathbf{r}_2;Z-1)\pm$ exchange for effective nuclear charges Z and $Z-1$ respectively.

The rationale for improved accuracy is that a point of diminishing returns (and numerical instability) is reached with increasing Ω, and so doubling or tripling the basis set allows more terms to be added without Ω becoming excessively large.

The principal computational step to obtain nonrelativistic wave functions and energies is to solve the generalized eigenvalue problem

$$\mathbf{H}\Psi = \lambda\mathbf{O}\Psi \tag{4}$$

where $\mathbf{H}$ is the Hamiltonian matrix with matrix elements $\langle\phi_{i',j',k'}|H|\phi_{i,j,k}\rangle$, $\mathbf{O}$ is the overlap matrix in the nonorthogonal basis set, and Ψ is the column vector of basis function coefficients $c_{i,j,k}^{(p)}$. The Hamiltonian in center-of-mass (CM) coordinates is given by (in atomic units with $4\pi\epsilon_0 = 1$)

$$H = \frac{p_1^2+p_2^2}{2\mu} + \frac{\mathbf{p}_1\cdot\mathbf{p}_2}{M} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \tag{5}$$

where $\mathbf{p}_1\cdot\mathbf{p}_2/M$ term is the mass polarization operator resulting from the motion of the nucleus in the CM frame. The correction due to the finite nuclear mass is obtained by comparison with the infinite nuclear mass case $M = \infty$. The power method is used to find the eigenvalue closest to an initial guess. The strategy is to perform a sequence of calculations with increasing values of Ω and assess the rate of convergence to determine the accuracy.

As discussed previously [11], the actual basis sets used in the calculations have two important modifications. First, for the special case of P-states, the rate of convergence can be improved for the finite nuclear mass case

TABLE I. Convergence table for the nonrelativistic energy of the $27\,^3P_1$ state assuming infinite nuclear mass. $D(\Omega) = [E(\Omega) - E(\Omega-1)] \times 10^{23}$ is the difference of successive entries, and $R(\Omega) = D(\Omega-1)/D(\Omega)$ is their ratio. $\Omega = (i+j+k)_{\max}$ for each Pekeris shell, and N is the number of terms in the triple basis set.

Ω	N	$E(\Omega)$ (E_h)	$D(\Omega)$	$R(\Omega)$
26	3168	−2.00068 93526 23570 97339 495		
27	3508	−2.00068 93526 23570 97591 082	251587	
28	3892	−2.00068 93526 23570 97620 998	29916	8.41
29	4284	−2.00068 93526 23570 97647 677	26679	1.12
30	4724	−2.00068 93526 23570 97652 802	5125	5.21
31	5172	−2.00068 93526 23570 97655 186	2384	2.15
32	5672	−2.00068 93526 23570 97655 585	399	5.98
33	6180	−2.00068 93526 23570 97655 816	231	1.72
34	6744	−2.00068 93526 23570 97655 851	34	6.77
∞		−2.00068 93526 23570 97655 876(3)		

by including a set of terms with the role of the s- and p-electrons interchanged. This is because the mass polarization operator has nonvanishing matrix elements of the form $\langle s(1)p(2)|\mathbf{p}_1\cdot\mathbf{p}_2/M|p(1)s(2)\rangle$ in the single-particle limit. Second, various truncations can be judiciously introduced to reduce the overall redundancy in the triple basis set [11].

Table I shows a typical convergence pattern for the $27\,^3P$ state for Ω in the range 26 to 34. $D(\Omega)$ denotes the difference between successive calculations, and $R(\Omega)$ is the ratio of successive differences. There is evidently and even-odd alternation in the ratios, with an additional significant figure of accuracy with every increase of Ω by 2. The extrapolated value, denoted by $\Omega = \infty$, is obtained by extending the ratios indefinitely. The convergence pattern is similar for the case of finite nuclear mass. This degree of accuracy for the energy is much more than what is needed in comparison with experiment, but other quantities typically converge much more slowly with to no more than half as many significant figures.

Table II presents a representative sample of comparisons between the nonrelativistic energies from the present work and previous calculations. The most accurate for states up to $n = 4$ are the all-exponential basis sets of Aznabaev et al.[20] with 22000 terms. Next in accuracy are the present calculations up to $n = 35$ with much smaller basis sets. A uniform standard of accuracy of at least 21 significant figures is maintained by progressively increasing the size of the basis set (as controlled by Ω) from less than 3000 terms below $n = 10$ to 7948 at $n = 35$. In contrast, the correlated B-spline calculations [18] require up to 64000 terms with declining accuracy beyond $n = 20$. The advantage of the B-spline method is that it has better numerical stability, and a lengthy optimization of nonlinear parameters is avoided. In most cases, the agreement with the present work is within the estimated uncertainty. Exceptions are the $2\,^1P$ state where there is an 8σ discrepancy, and a smaller discrepancy for the $3\,^1P$ state. A comprehensive tabulation of variational upper bounds and extrapolations for all P-states up to $n = 35$ is given in the Appendix.

II. RELATIVISTIC AND QED CORRECTIONS

With the nonrelativistic wave functions in hand, it is a straightforward matter to calculate the relativistic and QED corrections as expectation values using the standard methods of nrQED. Since all these terms decrease approximately in proportion to $1/n^3$, they are strongly suppressed for $n = 24$ and higher, relative to the low-lying states. To order α^2 Ry ($\alpha^4 mc^2$), the leading terms are the well-known Breit interaction terms (superscripts denote the power of α) (in atomic units) [17, 24]

$$E^{(2)}_{\rm rel} = \sum_{i=1}^{5} \langle B_i \rangle + \frac{\mu}{M}(\tilde{\Delta}_2 + \tilde{\Delta}_{3Z}) \tag{6}$$

where $B_1 = -(p_1^4 + p_2^4)/(8m^3c^2)$ arises from the relativistic variation of mass with velocity, B_2 is the orbit-orbit interaction defined by

$$B_2 = -\frac{e^2}{2(mc)^2}\left[\frac{\mathbf{p_1}\cdot\mathbf{p_2}}{r_{12}} + \frac{\mathbf{r}_{12}\cdot(\mathbf{r}_{12}\cdot\mathbf{p_1})\mathbf{p_2}}{r_{12}^3}\right] \tag{7}$$

$B_3 = B_{\rm so} + B_{\rm soo}$ contains the spin-orbit and spin-other-orbit interactions defined by

$$B_{\rm so} = \frac{Z\mu_{\rm B}e(1+2a_{\rm e})}{mc}\left[\frac{\mathbf{r}_1\times\mathbf{p}_1\cdot\mathbf{s}_1}{r_1^3} + \frac{\mathbf{r}_2\times\mathbf{p}_2\cdot\mathbf{s}_2}{r_2^3}\right] \tag{8}$$

$$B_{\rm soo} = -\frac{\mu_{\rm B}e}{2mcr_{12}^3}\mathbf{r}_{12}\times[(3+4a_{\rm e})\mathbf{p}_-\cdot\mathbf{s}_+ - \mathbf{p}_+\cdot\mathbf{s}_-] \tag{9}$$

where $\mathbf{p}_\pm = \mathbf{p}_1 \pm \mathbf{p_2}$, $\mathbf{s}_\pm = \mathbf{s}_1 \pm \mathbf{s_2}$, $\mu_{\rm B} = e\hbar/(2mc)$ is the Bohr magneton, and $a_{\rm e} \simeq \alpha/(2\pi) - 0.328\,429\alpha^2$ is the electron anomalous magnetic moment. B_5 is the spin-spin term $B_{\rm ss}$ defined by

$$B_{\rm ss}5 = 4\mu_e^2\left[\frac{8\pi}{3}\delta(r_{12})\mathbf{s}_1\cdot\mathbf{s}_2 + \frac{\mathbf{s}_1\cdot\mathbf{s}_2}{r_{12}^3} - \frac{3(\mathbf{s}_1\cdot\mathbf{r}_{12})\mathbf{s}_2\cdot\mathbf{r}_{12}}{r_{12}^5}\right], \tag{10}$$

where $\mu_e = \mu_{\rm B}(1+a_e)$, and the relativistic recoil terms are

$$\tilde{\Delta}_2 = -\frac{Ze^2}{2(mc)^2}\sum_{j=1}^{2}\left[\frac{1}{r_j}\mathbf{p}_+\cdot\mathbf{p}_j + \frac{1}{r_j^3}\mathbf{r}_j\cdot(\mathbf{r}_j\cdot\mathbf{p}_+)\mathbf{p}_j\right] \tag{11}$$

$$\tilde{\Delta}_{3Z} = \frac{2Z\mu_{\rm B}e}{mc}\sum_{i=1}^{2}\frac{1}{r_i^3}\mathbf{r}_i\times\mathbf{p}_+\cdot\mathbf{s}_i. \tag{12}$$

Finally B_4 contains the δ-function terms $B_4 = \alpha^2\pi[\frac{1}{2}\delta(r_1) + \frac{1}{2}\delta(r_2) - \delta(r_{12})]$. To each of these, there are finite nuclear mass corrections of order $\alpha^2\mu/M$ arising from (i) the mass scaling of each term, and (ii) cross terms between the B_i terms in $E^{(2)}_{\rm rel}$ and the mass polarization operator in Eq. (5). The relativistic recoil terms $\tilde{\Delta}_2$ and

TABLE II. Comparison of the nonrelativistic energies for the $n\,^1P$ and ^3P states of helium for the case of infinite nuclear mass.

n	N	Reference	$E(1snp\,^1P)$	$E(1snp\,^3P)$
2	22000	Aznabaev [20]	−2.12384 30864 98101 35924 73331 42374	−2.13316 41907 79283 20514 69927 63806
	2997	Present work	−2.12384 30864 98101 35924 1(22)	−2.13316 41907 79283 20514 0(8)
	64000	Chi [18]	−2.12384 30864 98101 343(2)	−2.13316 41907 79283 204(2)
3	22000	Aznabaev [20]	−2.05514 63620 91943 53692 83410 921	−2.05808 10842 74275 33134 26965 47203
	2617	Present work	−2.05514 63620 91943 53692 7(34)	−2.05808 10842 74275 33133 9(33)
	64000	Chi [18]	−2.05514 63620 91943 533(2)	−2.05808 10842 74275 3312(2)
4	22000	Aznabaev [20]	−2.03106 96504 50240 71475 89314 360941	−2.03232 43542 96630 33195 38824 67103
	2775	Present work	−2.03106 96504 50240 71474 2(12)	−2.03232 43542 96630 33195 6(9)
	64000	Chi [18]	−2.03106 96504 50240 713(2)	−2.03232 43542 96630 3319(2)
6	2622	Present work	−2.01383 39796 71740 10238 6(9)	−2.01420 95877 37505 91219(6)
	64000	Chi [18]	−2.01383 39796 71740 1020(2)	−2.01420 95877 37505 9133(4)
9	2864	Present work	−2.00615 63846 52853 81834 6(5)	−2.00626 72673 66409 03258 0(14)
	64000	Chi [18]	−2.00615 63846 52853 8182(2)	−2.00626 72673 66409 03258(2)
12	4868	Present work	−2.00346 52527 04885 79826 035(5)	−2.00351 20065 35142 74556 021(1 8)
	64000	Chi [18]	−2.00346 52527 04885 7982(2)	−2.00351 20065 35142 7456(2)
15	6160	Present work	−2.00221 86471 04088 30158 826(6)	−2.00224 25712 22150 32643 884(5)
	64000	Chi [18]	−2.00221 86471 04088 3016(4)	−2.00224 25712 22150 3264(2)
18	5518	Present work	−2.00154 11387 60913 62470 8318(8)	−2.00155 49769 40232 72665 182(4)
	64000	Chi [18]	−2.00154 11387 60913 625(4)	−2.00155 49769 40232 727(4)
21	6744	Present work	−2.00113 24817 33017 52951 738(2)	−2.00114 11926 56477 67869 1390(23)
	64000	Chi [18]	−2.00113 24817 33017 53(2)	−2.00114 11926 56477 68(2)
24	6744	Present work	−2.00086 71808 46170 11128 223(6)	−2.00087 30145 66616 65939 240(9)
	64000	Chi [18]	−2.00086 71808 46170 1(2)	−2.00087 30145 66616 7(2)
27	6744	Present work	−2.00068 52565 28882 40212 1453(18)	−2.00068 93526 23570 97655 876(3)
	64000	Chi [18]	−2.00068 52565 2888(2)	−2.00068 93526 2357(2)
30	6744	Present work	−2.00055 51074 62372 97425 91(24)	−2.00055 80928 35757 97528 32(5)
33	7948	Present work	−2.00045 88001 04867 46785 90(2)	−2.00046 10426 27369 81858 54(4)
35	7948	Present work	−2.00040 78810 08092 82096 8(2)	−2.00040 97604 35014 70404 5(2)

$\tilde{\Delta}_{3Z}$ arise from the transformation of the Breit interaction to CM plus relative coordinates [17, 25]. In the material to follow, the mass scaling and recoil terms taken together are denoted by $E^{(2)}_{\rm RR,M}$, and the cross terms (ii) by $E^{(2)}_{\rm RR,X}$.

The leading QED corrections of order α^3 Ry ($\alpha^5 mc^2$) due to electron self-energy and vacuum polarization can be divided into an electron-nucleus part ($E^{(3)}_{\rm L,1}$) [26] and an electron-electron part ($E^{(3)}_{\rm L,2}$) [27, 28] defined by

$$E^{(3)}_{\rm L,1} = \tfrac{4}{3} Z\alpha^3 [\tfrac{19}{30} - \ln(Z\alpha)^2 - \ln k_0] \langle \delta(r_1) + \delta(r_2) \rangle \quad (13)$$

$$E^{(3)}_{\rm L,2} = \alpha^3 [(\tfrac{89}{15} + \tfrac{14}{3} \ln\alpha - \tfrac{20}{3} \mathbf{s}_1 \cdot \mathbf{s}_2) \langle \delta(r_{12}) \rangle - \tfrac{14}{3} Q] \quad (14)$$

where k_0 is Bethe's mean excitation energy [24] in units of Z^2 Ry. The advantage of subtracting out the $\ln Z^2$ scaling of the Bethe logarithm and including it instead in the $\ln(Z\alpha)^2$ term is that the value is then close to the hydrogenic value 2.984 128 556 ($\pm 0.5\%$) for all states of all light atoms and ions studied [29–32]. Its value for the $27\,^1P$ and ^3P states of helium can be accurately estimated from the $1/n$ expansions of Drake [33] or Korobov [31] with the result

$$\ln k_0(27\,^1P) = 2.984\,128\,3136(3) - 0.000\,001\,25(7)\mu/M$$
$$\ln k_0(27\,^3P) = 2.984\,128\,2191(10) + 0.000\,003\,49(9)\mu/M$$

which is very close to the hydrogenic value. For $\Delta E^{(3)}_{\rm L,2}$, the Q term is defined by the improper integral

$$Q = \frac{1}{4\pi} \lim_{\epsilon \to 0} \langle r_{12}^{-3}(\epsilon) + 4\pi(\gamma + \ln\epsilon)\delta(\mathbf{r}_{12}) \rangle \quad (15)$$

where ϵ is the radius of an infinitesimal sphere that is excluded from the range of integration, and γ is Euler's constant.

Contributions of order α^4 Ry are more difficult to evaluate. They have been calculated in their entirety for the $2\,^1P_1$ state by Pachucki et al. [34]. Our strategy is to calculate the dominant parts that can be easily evaluated, subtract these from the results in Ref. [34], and estimate the remainder from its approximately $1/n^3$ scaling with n. For example, for the $2\,^1P_1$ state, the total contribution of order α^4 is 8.818 MHz [34]. The largest contribution comes from the $2\,^1P_1 - 2\,^3P_1$ second-order singlet-triplet mixing term induced by the spin-dependent terms in the Breit interaction acting twice of the form

$$E^{(4)}_{\rm st} = \sum_{n'=2}^{\infty} \frac{\langle 2\,^1P_1 | B | n'\,^3P_1 \rangle \langle n'\,^3P_1 | B | 2\,^1P_1 \rangle}{E(2\,^1P_1) - E(n'\,^3P_1)}\,, \quad (16)$$

including an integration over the continuum. The $n' = 2$ term $E^{(4)}_{\rm st,2}$ is largest (4.7549 MHz) [37], since the energy denominator is the smallest. In general, it is the $n' = n$

TABLE III. Evaluation of dominant and remainder terms of $O(\alpha^4)$ and $O(\alpha^5)$ Ry for the $2\,P$ states of helium for $1/n^3$ scaling of the remainder. Units are MHz.

Term	$2\,^1P_1$	$2\,^3P_0$	$2\,^3P_1$	$2\,^3P_2$	$2\,^3P_c$
			Partial sum of dominant terms		
$E^{(4)}_{\rm anom}$	0.0000	−0.0339	0.0178	−0.0004	0.0000
$E_{\rm R1}$	1.6634	−20.6548	−20.6548	−20.6548	−20.6548
$E_{\rm R2}$	0.0148	−0.1842	−0.1842	−0.1842	−0.1842
$E_{\rm e1}+E_{\rm e2}$	0.3246	0.0000	0.0000	0.0000	0.0000
$E^{(4)}_{\rm st,2}$	4.7550	0.0000	−4.7550	0.0000	−1.5850
$\alpha^4\ln(\alpha)$	0.2119	0.0000	0.0000	0.0000	0.0000
Subtotal	6.9697	−20.8729	−25.5762	−20.8430	−22.4240
			Complete $O(\alpha^4)$ totals for comparison		
$E^{(4)}_{\rm c}$ [34]	8.8180	−21.8320	−21.8320	−21.8320	−21.8320
$\Delta E^{(4)}_J$ [35]	0.0000	−4.9695	−3.4523	3.0653	0.0000
Total	8.8180	−26.8015	−25.2843	−18.7667	−21.8320
Difference	1.8483	−5.9286	0.2919	2.0763	0.5921
α^5	0.810	0.223	0.223	0.223	0.223
Total $=E_{\rm rmdr}$	2.658	−5.705	0.068	1.853	0.369

term that is largest for the $n\,^1P_1$ state, denoted by $E^{(4)}_{{\rm st},n}$, and equal but opposite sign for the $n\,^3P_1$ state.

There are also large radiative terms that come from a sum of one- and two-loop contributions denoted by $E_{\rm R1}$ and $E_{\rm R2}$ in Ref. [38] (1.995 MHz), electron-electron radiative terms $E_{\rm e1}$ and $E_{\rm e2}$ (0.3246 MHz), and an $\alpha^4\ln\alpha$ term (0.2120 MHz) [39]. The sum of these terms is 6.9697 MHz, leaving a remainder $E^{(4)}_{\rm rmdr}$ of $8.818-6.9697=1.848$ MHz that comes from a mixture of first- and second-order terms that are much more difficult to calculate, as discussed in detail in Refs. [38, 40]. However, all these terms scale roughly in proportion to $1/n^3$, so one can expect a corresponding contribution of approximately $1.848(2/27)^3=0.75$ kHz for the $27\,^1P_1$ state. These and the corresponding terms for the triplet states are summarized in Table III, along with a similar term of order α^5 [34]. The estimated remainders $E^{(4)}_{\rm rmdr}$ are included in the final results with the entire amount taken as the uncertainty. As a check, the scaling argument applied to the singlet-triplet mixing term $E^{(4)}_{{\rm st},n}$ reduces its value by a factor of 2460 for $n=27$ to 1.93 kHz, which is close to the correct value 1.597 kHz (see Table IV).

The last correction to be included is that due to finite nuclear size. To lowest order, the energy shift to sufficient accuracy is $E_{\rm nuc}=\frac{2}{3}\pi Z(R/a_0)^2\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle$ where a_0 is the Bohr radius and $R=1.6786(12)$ fm [42] is the radius of the nuclear charge distribution for ^{4}He.

As an example, the various calculated contributions to the ionization energy of the $27\,^1P_1$ and $27\,^3P_J$ states of ^{4}He relative to $^4{\rm He}^+(1s)$ are summarized in Table IV. For every entry, the corresponding hydrogenic value for the $^4{\rm He}^+(1s)$ ion is subtracted before converting from a.u. to MHz. The dominant source of uncertainty (±1 kHz) is the residual QED contribution of order α^4 Ry. However, this level of theoretical uncertainty is already much better than for the low-lying states of helium, and it establishes an absolute point of reference for transitions to low-lying states. Table V summarizes the calculated ionization energies for all the $n\,^1P_1$ and $n\,^3P_c$ (center of gravity) states of helium for $2\le n\le 35$, and Table VI lists separately the calculated fine-structure energy shifts relative to the center of gravity. As in Table IV, all the uncertainties are the entire amount of the residual QED contribution $E^{(4)}_{\rm rmdr}$ of order α^4 Ry. The results for $n=2$ are known much more accurately from the calculations of Patkóš et al. [34, 35]. They are included here to provide a consistent set of calculations over the entire range of n. The results for $n=3$ and higher are the most accurate in the literature. Tables of matrix elements for other $n\,P$ states are available at [36].

III. RESULTS

A direct comparison with experiment for the $2\,^1S_0-n\,^1P_1$ and $2\,^3S_1-n\,^3P_{\rm c}$ transition frequencies is complicated by the fact that the energies of the lower S-states is not known at this level of accuracy, and it is indeed the purpose of the experimental studies to determine it by use of quantum defect theory to extrapolate the series of measurements to the series limit. We therefore present instead the derived ionization energies of the lower $2\,^1S_0$ and $2\,^3S_1$ states obtained by adding the negative theoretical ionization frequencies $-I(n\,^1P)$ from Table IV to the measured $2\,S-n\,P$ transition frequencies from Refs. [1] and [2]. The results are shown in Table VII for the seven singlet measurements in the range $24\le n\le 35$, and the parallel four triplet measurements. In addition, the singlet measurements can be converted to triplet measurements of the $2\,^3S_1$ state by adding the highly accurate singlet-triplet transition frequency $\nu(2\,^1S_0-2\,^3S_1)=192\,510\,702.14872$ MHz [8], resulting in 11 independent

TABLE IV. Contributions to the $27\,^1P_1$ and $27\,^3P_J$ negative ionization frequencies of ^{4}He. $E^{(4)}_{\rm radiative}$ denotes the sum of radiative terms $E_{\rm R1}+ER_{\rm R2}+E_{\rm e1}+E_{\rm e2}$, and $E^{(4)}_{\rm rmdr}$ denotes the remainders from Table III scaled by a factor of $(2/n)^3$. Units are MHz.

Contribution	Order	$27\,^1P_1$	$27\,^3P_0$	$27\,^3P_1$	$27\,^3P_2$
Nonrelativistic $E_{\rm nr}$		−4508153.32664	−4535100.64070	−4535100.64070	−4535100.64070
1st. order mass pol. $E_{\rm M,1}$	μ/M	18.80897	−20.91429	−20.91429	−20.91429
2nd. order mass pol. $E_{\rm M,2}$	$(\mu/M)^2$	−0.08590	−0.08591	−0.08591	−0.08591
Relativistic $E^{(2)}_{\rm rel}$	α^2	−9.36849	10.02726	−0.01344	−0.83985
Relativ. finite mass $E^{(2)}_{\rm RR,M}$	$\alpha^2\mu/M$	−0.00478	−0.00076	0.00142	0.00049
Relativistic recoil $E^{(2)}_{\rm RR,X}$	$\alpha^2\mu/M$	0.00262	0.00380	0.00200	0.00185
Anomalous mag. mom.	$\alpha^3+\alpha^4$	0.0	0.01160	−0.00661	0.00165
$E^{(3)}_{\rm QED}$	α^3	0.02143	−0.44721	−0.44721	−0.44721
Singlet-triplet mixing $E^{(4)}_{\rm st,27}$	α^4	0.00160	0.00000	−0.00160	0.00000
$E^{(4)}_{\rm radiative}$	α^4	0.00107	−0.00762	−0.00762	−0.00762
$E^{(4)}_{\rm rmdr}$	α^4	0.0011(11)	−0.0023(23)	0.0010(10)	0.00013(13)
$E^{(5)}_{\rm QED}$	α^5	−0.0000	0.00075	0.00075	0.00074
Finite nuclear size $E_{\rm nuc}$	$(R/a_0)^2$	0.00003	−0.00029	−0.00029	−0.00029
Total		−4508143.9491(11)	−4535112.0557(23)	−4535122.1125(10)	−4535122.9310(7)
Center of gravity		−4508143.9491(11)		−4535121.4498(11)	
Experiment [a]		−4508143.903(78)		−4535121.435(20)	
Difference		0.046(78)		0.014(20)	

[a] From quantum defect fit [41].

measurements of the $2\,^3S_1$ ionization energy. The results are summarized in Fig. 1. First, the weighted average ionization energy of the $2\,^1S_0$ state (960 332 040.546(9) MHz) marginally agrees with the less accurately known theoretical value 960 332038.0(1.9) MHz. Second, the two sets of combined results for the $2\,^3S_1$ state (one from the singlets and one from the triplets) differ from each other by a similar amount (58 kHz from QDT exrapolation Ref. [2] and 30 kHz from the present work), so in this regard the results are consistent. Although the systematic uncertainty on the singlet side is large (±20 kHz), it is clear from Fig. 1 that there is a statistically meaningful difference between the two sets of results.

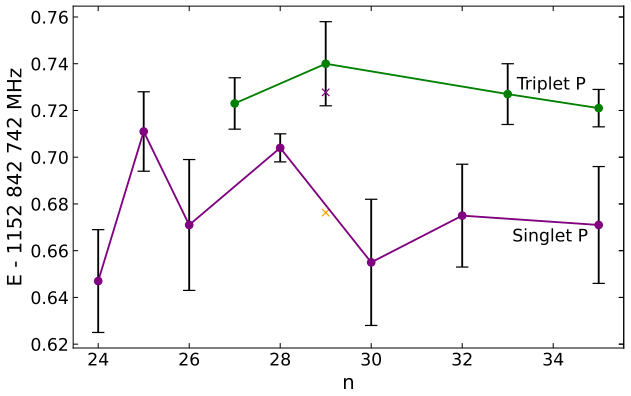

FIG. 1. Ionization energy of the $2\,^3S_1$ state of ^{4}He as determined by adding the calculated ionization frequency of the $n\,^3P_{\rm c}$ state to the measured $2\,^3S_1-n\,^3P_{\rm c}$ transition frequency [2], and similarly for the singlet case [1] together with the measured $2\,^1S_0-2\,^3S_1$ transition frequency [8].

The sharpest comparison between the present theory and the QDT extrapolations is provided by the four triplet-P measurements with $n=27,29,33$, and 35. The weighted average of the four measurements is 1152 842 742.7247(78) MHz, where the uncertainty of ±0.0078 MHz is the rms standard deviation of the four measurements divided by $\sqrt{3}$, and including the theoretical uncertainty added linearly. The result is larger than the QDT value $(1152\,842\,742.7082(55)_{\rm stat}(25)_{\rm sys}$ MHz) by 16 ± 10 kHz. The additional ± 20 kHz systematic uncertainty in the measurements is common to both sets of data and so is assumed to cancel. Similarly, our grand average over the two sets of measurements, weighted in proportion to the inverse square of the total uncertainties for the singlet and triplet data, is 1152 842 742.722(11) MHz. This agrees with, but lies 14±17 kHz deeper than the similarly weighted Clausen QDT value 1152 842 742.707(13) kHz. Taken together, the overall good agreement confirms a 9σ discrepancy of 0.471 ± 0.053 MHz with the theoretical value 1152 842 742.231(52) MHz. Further work on the theoretical side has not yielded any significant new results to resolve the discrepancy [43, 44]. As discussed by Clausen et al. [2], the discrepancy is even bigger (15σ) for the $2\,^3P$ state as derived from the $2\,^3P_J-3\,^3D_J$ transition frequency [45]. It is particularly significant that there is a nearly identical discrepancy of 0.482 ± 0.053 kHz for the ^{3}He isotope [9], despite the additional complications of hyperfine structure for this case.

TABLE V. Calculated negative ionization frequencies of the $n\,^1P_1$ and $n\,^3P_c$ states of ^{4}He. Units are MHz.

n	$I(n\,^1P_1)/h$	$I(n\,^3P_c)/h$
2	−814 709 146.5(2.7)	−876 106 246.6(2.3)
3	−362 787 967.3(8)	−382 117 481.1(7)
4	−204 397 210.37(33)	−212 661 130.22(29)
5	−130 955 541.64(17)	−135 204 995.78(15)
6	−91 009 810.41(10)	−93 472 929.86(8)
7	−66 901 127.43(6)	−68 453 141.74(5)
8	−51 242 587.32(4)	−52 282 461.860(35)
9	−40 501 246.341(29)	−41 231 541.911(24)
10	−32 814 665.275(21)	−33 346 972.326(18)
11	−27 125 436.770(16)	−27 525 292.385(13)
12	−22 797 031.709(12)	−23 104 960.774(10)
13	−19 427 674.895(10)	−19 669 820.901(8)
14	−16 753 624.158(8)	−16 947 462.118(6)
15	−14 595 939.724(6)	−14 753 507.979(5)
16	−12 829 749.819(5)	−12 959 559.3773(37)
17	−11 365 768.212(4)	−11 473 973.5454(29)
18	−10 138 783.8411(36)	−10 229 924.3219(23)
19	−9 100 271.0054(31)	−9 177 753.8936(19)
20	−8 213 516.6237(27)	−8 279 939.6243(15)
21	−7 450 330.3493(23)	−7 507 701.8588(12)
22	−6 788 776.0678(20)	−6 838 668.5736(12)
23	−6 211 577.8174(17)	−6 255 236.6672(11)
24	−5 704 980.3477(15)	−5 743 402.1284(11)
25	−5 257 921.9483(14)	−5 291 911.8055(11)
26	−4 861 425.4377(12)	−4 891 639.5603(10)
27	−4 508 143.9491(11)	−4 535 121.4498(10)
28	−4 192 018.1260(10)	−4 216 205.2379(10)
29	−3 908 014.5582(9)	−3 929 783.1919(10)
30	−3 651 924.1759(8)	−3 671 586.2926(10)
31	−3 420 205.3943(7)	−3 438 024.2366(9)
32	−3 209 861.0067(6)	−3 226 059.9508(9)
33	−3 018 340.7741(6)	−3 033 110.3603(9)
34	−2 843 463.7608(5)	−2 856 967.3194(9)
35	−2 683 355.9699(5)	−2 695 734.1549(9)

TABLE VI. Calculated fine structure shifts of the $n\,^3P_J$ states of ^{4}He, relative to the center of gravity. Units are MHz.

n	$\Delta I(n\,^3P_0)/h$	$\Delta I(n\,^3P_1)/h$	$\Delta I(n\,^3P_1)/h$
2	27599.1(2.3)	−2017.9(2.3)	−4309.1(2.3)
3	7577.8(7)	−535.5(7)	−1194.3(7)
4	3089.02(29)	−217.69(29)	−487.19(29)
5	1552.43(15)	−109.42(15)	−244.83(15)
6	888.15(8)	−62.63(8)	−140.05(8)
7	555.01(5)	−39.15(5)	−87.51(5)
8	369.767(35)	−26.093(35)	−58.298(35)
9	258.631(24)	−18.254(24)	−40.774(24)
10	187.941(18)	−13.267(18)	−29.628(18)
11	140.844(13)	−9.943(13)	−22.203(13)
12	108.262(10)	−7.644(10)	−17.066(10)
13	85.004(8)	−6.002(8)	−13.400(8)
14	67.961(6)	−4.799(6)	−10.713(6)
15	55.187(5)	−3.897(5)	−8.699(5)
16	45.4239(37)	−3.2074(37)	−7.1604(37)
17	37.8350(29)	−2.6715(29)	−5.9641(29)
18	31.8470(23)	−2.2486(23)	−5.0203(23)
19	27.0590(19)	−1.9104(19)	−4.2655(19)
20	23.1847(15)	−1.6368(15)	−3.6549(15)
21	20.0164(12)	−1.4134(12)	−3.1553(12)
22	17.3998(12)	−1.2282(12)	−2.7431(12)
23	15.2203(11)	−1.0742(11)	−2.3995(11)
24	13.3902(11)	−0.9450(11)	−2.1111(11)
25	11.8421(11)	−0.8356(11)	−1.8671(11)
26	10.5238(10)	−0.7425(10)	−1.6593(10)
27	9.3941(10)	−0.6627(10)	−1.4812(10)
28	8.4206(10)	−0.5939(10)	−1.3278(10)
29	7.5770(10)	−0.5343(10)	−1.1948(10)
30	6.8425(10)	−0.4824(10)	−1.0790(10)
31	6.1999(9)	−0.4370(9)	−0.9778(9)
32	5.6353(9)	−0.3971(9)	−0.8888(9)
33	5.1373(9)	−0.3620(9)	−0.8103(9)
34	4.6963(9)	−0.3308(9)	−0.7408(9)
35	4.3043(9)	−0.3031(9)	−0.6790(9)

IV. DISCUSSION

In summary, we have completed an extensive set of high precision variational calculations for all singlet and triplet P-states of ^{4}He up to $n = 35$, while maintaining a uniform standard of accuracy of 1 part in 10^{22} for the nonrelativistic energy. This is more than sufficient to determine the lowest-order α^2 relativistic and α^3 QED corrections at the 1 kHz level of accuracy. The dominant parts of the α^4 Ry are calculated directly for all n. The leading sources of uncertainty are the uncalculated terms of order α^4 Ry. These are estimated by assuming that the accurately known values for $n = 2$ [35] scale as $1/n^3$ with n, and taking the entire amount of the scaled value as the uncertainty. This procedure reduces the uncertainty to about 1 kHz at $n = 24$. A complete calculation of these α^4 terms for the Rydberg P-states is in progress and will be published separately.

The main significance of the results is that a direct comparison between theory and experiment for n in the range $24 \le n \le 35$ provides 11 independent measurements of the ionization frequency of the controversial $2\,^3S_1$ state. The grand average over singlets and triplets yields a 9σ disagreement between experiment and theory of 0.471 ± 0.053 MHz, in close agreement with the result obtained by quantum defect extrapolation to the series limit. However, QDT theory itself is a semiempirical fitting procedure that is not derivable from fundamental atomic physics. Although widely used and highly successful, it has never been tested at this high level of experimental accuracy. Especially the Ritz procedure of including only even powers in the quantum defect expansion may not remain valid in the presence of relativistic corrections [10]. It is therefore significant that the two methods of determining the ionization energy of the $2\,^3S_1$ state agree at the level of ±17 kHz from the Grand Average in Table VII.

Concerning theory for the $2\,^3S_1$ and $2\,^3P_1$ states, the calculation of Patkóš et al. [35] greatly reduced the uncertainty by a complete calculation of the QED terms of order α^5 Ry. They also estimated the contribution from the next higher-order α^6 Ry term, based on a hy-

drogenic approximation. The result of –0.158(52) MHz for the (positive) ionization energy of the $2\ ^3S_1$ state stands as the dominant source of theoretical uncertainty. In contrast, this uncertainty, and the entire α^4 Ry term, are suppressed to the 1 kHz level or below by the $1/n^3$ scaling at $n = 24$, thereby allowing a clear comparison with experiment for the singlet and triplet spectra ($\pm$95 kHz), uncomplicated by higher-order QED uncertainties, or the use of quantum defect theory for extrapolations to the series limit. This leaves unexplained a 9σ disagreement between theory and experiment for the ionization energy of the $2\,^3S_1$ state (0.471 ± 0.053 MHz)

ACKNOWLEDGMENTS

This research was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) and by the Digital Research Alliance of Canada/Compute Ontario. The authors are grateful to Frédéric Merkt for helpful advice and correspondence concerning the treatment of uncertainties in the experimental data reported in Table VII.

APPENDIX

This Appendix presents two supplementary tabulations. First, Table VIII presents a complete tabulation of the variational upper bounds and extrapolations for the nonrelativistic energies of the singlet and triplet P-states of helium with prncipal quantum number $4 \le n \le 35$. The number of terms N in the triple basis set gradually increases in order to maintain a consistent level of accuracy of approximately 22 significant figures.

Second, Table IX gives matrix elements of the spin-dependent operators $B'_{\rm so}$, $B'_{\rm soo}$, $B'_{\rm ss}$, and Δ'_{3Z}, where, for simplicity of comparison, the prime indicates that the anomalous magnetic moment correction is not included. For each n, the first entry is the matrix element $\langle n\,^3P_1|B_{X,\infty}|n\,^3P_1\rangle$ for the case of infinite nuclear mass, and the second entry is the complete mass polarization correction $\langle n\,^3P_1|B_{X,{\rm mp}'}|n\,^3P_1\rangle$ divided by μ/M for the case of ^{4}He, as defined in Ref. [12]. It is therefore the first-order perturbation correction due to mass polarization, plus higher-order terms in μ/M summed to infinity. The complete matrix element for the case of finite nuclear mass then corresponds to the operator

$$B'_X(M) = (1-\mu/M)^3[B'_{X,\infty} + (\mu/M)B'_{X,{\rm mp}}] \qquad (17)$$

For example, with $M/m_{\rm e} = 294.299\,541\,71(17)$ [46], and $\mu/M = 1/(1 + M/m_{\rm e})$, then $\langle 24\,^3P_1|B_X(M)'|24\,^3P_1\rangle = -1.854\,878\,538\,847(7)$. This agrees with the value $-1.854\,878\,538\,8401(2)$ calculated independently by Tang et al. [47] by the correlated B-spline method [18, 47].

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[1] G. Clausen, P. Jansen, S. Scheidegger, J. A. Agner, H. Schmutz, and F. Merkt, Ionization energy of the metastable $2\ ^1S_0$ state of ^{4}He from Rydberg-series extrapolation, Phys. Rev. Lett. **127**, 093001 (2021).

[2] G. Clausen, K. Gamlin, J. A. Agner, H. Schmutz, and F. Merkt, Metrology in a two-electron atom: The ionization energy of metastable triplet helium ($2\ ^3S_1$), Phys. Rev. A **111**, 012817 (2025).

[3] Z.-C. Yan and G. W. F. Drake, High Precision Calculation of Fine Structure Splittings in Helium and He-Like Ions, Phys. Rev. Lett. **74**, 4791 (1995).

[4] K. Pachucki, V. A. Yerokhin, and P. Cancio Pastor, Quantum electrodynamic calculation of the hyperfine structure of ^{3}He, Phys. Rev. A **85**, 042517 (2012).

[5] K. Pachucki and V. A. Yerokhin, Fine Structure of Heliumlike Ions and Determination of the Fine Structure Constant, Phys. Rev. Lett. **104**, 070403 (2010).

[6] X. Zheng, Y. R. Sun, J.-J. Chen, W. Jiang, K. Pachucki, and S.-M. Hu, Laser Spectroscopy of the Fine-Structure Splitting in the $2\ ^3P_J$ Levels of ^{4}He, Phys. Rev. Lett. **118**, 063001 (2017).

[7] K. Kato, T. D. G. Skinner, and E. A. Hessels, Ultrahigh-Precision Measurement of the $n = 2$ Triplet P_J Fine Structure of Atomic Helium Using Frequency-Offset Separated Oscillatory Fields, Phys. Rev. Lett. **121**, 143002 (2018).

[8] R. J. Rengelink, Y. van der Werf, R. P. M. J. W. Notermans, R. Jannin, K. S. E. Eikema, M. D. Hoogerland, and W. Vassen, Precision spectroscopy of helium in a magic wavelength optical dipole trap, Nat. Phys. **14**, 1132 (2018).

[9] G. Clausen and F. Merkt, Ionization Energy of Metastable ^{3}He ($2\,^3S_1$) and the Alpha- and Helion-Particle Charge-Radius Difference from Precision Spectroscopy of the *np* Rydberg Series, Phys. Rev. Lett. **134**, 223001 (2025).

[10] G. W. F. Drake, "Quantum defect theory and analysis of high precision helium term energies," in *Advances in Atomic, Molecular and Optical Physics* (Academic Press, 1993) Vol. 32, pp. 93–116.

[11] Aaron T. Bondy , G. W. F. Drake, C. McLeod, E. M. R. Petrimoulx, X.-Q. Qi, and Z.-X. Zhong, Theory for the Rydberg states of helium: Comparison with experiment for the $1s24p\ ^1P_1$ state ($n = 24$)

[12] G. W. F. Drake and Zong-Chao Yan, Energies and relativistic corrections for the Rydberg states of helium: Variational results and asymptotic analysis, Phys. Rev. A **46**, 2378 (1992).

[13] Y. Accad, C. L. Pekeris, and B. Schiff, S and P States of the Helium Isoelectronic Sequence up to $Z = 10$, Phys.

TABLE VII. Combined ionization energies I' of the $2\,^1S_0$ and $2\,^3S_1$ states of ^{4}He obtained by adding the theoretical ionization energy $I_{\rm theo.}(n\,^1P_1)$ or $I_{\rm theo.}(n\,^3P_{\rm c})$ to the experimental $2\,^1S_0 - n\,^1P_1$ or $2\,^3S_1 - n\,^3P_{\rm c}$ transition frequencies respectively, and compared with experimental ionization energies obtained by quantum defect extrapolation. The statistical and systematic uncertainties for the experimental data are shown in brackets. Units are MHz.

n	$I_{\rm theo.}(n\,P)/h$	$\nu_{\rm exp.}(2\,S - n\,P)$	$I'(2\,^1S_0)/h$	$I'(2\,^3S_1)/h$
		Singlets		
24	5704 980.3477(15)	954 627 060.151(22)	960 332 040.499(23)	1152 842 742.647(23) [a]
25	5257 921.9483(14)	955 074 118.614(17)	960 332 040.562(18)	1152 842 742.711(18) [a]
26	4861 425.4377(12)	955 470 615.084(28)	960 332 040.522(29)	1152 842 742.671(29) [a]
28	4192 018.1260(10)	956 140 022.429(6)	960 332 040.555(7)	1152 842 742.704(7) [a]
30	3651 924.1759(8)	956 680 116.330(27)	960 332 040.506(28)	1152 842 742.655(28) [a]
32	3209 861.0067(6)	957 122 179.519(22)	960 332 040.526(23)	1152 842 742.675(23) [a]
35	2683 355.9699(5)	957 648 684.552(25)	960 332 040.522(26)	1152 842 742.671(26) [a]
Weighted average			960 332 040.547(9)	$1152\,842\,742.694(10)_{\rm stat}(20)_{\rm sys}$
QDT Exp't. [1]				$1152\,842\,742.650(32)_{\rm stat}(20)_{\rm sys}$
Difference				$0.044(34)_{\rm stat}$
		Triplets		
27	4535 121.4498(10)	1148 307 621.274(11)		1152 842 742.723(12)
29	3929 783.1919(10)	1148 912 959.549(17)		1152 842 742.740(18)
33	3033 110.3603(9)	1149 809 632.367(13)		1152 842 742.727(14)
35	2695 734.1549(9)	1150 147 008.567(8)		1152 842 742.721(9)
Weighted average				$1152\,842\,742.7247(78)_{\rm stat}(25)_{\rm sys}$
QDT Exp't. [2]				$1152\,842\,742.7082(55)_{\rm stat}(25)_{\rm sys}$
Difference				$0.016(10)_{\rm stat}$
Grand average				1152 842 742.721(11)
QDT Exp't. [1, 2]				1152 842 742.707(13)
Difference				0.014(17)

[a] Obtained by adding $\nu(2\,^1S_0 - 2\,^3S_1) = 192\,510\,702.14872$ MHz [8] to $I'(2\,^1S_0)/h$.

Rev. A, **4**, 516 (1971).

[14] G. W. F. Drake, New variational techniques for the 1snd states of helium, Phys. Rev. Lett. **59**, 1549 (1987).

[15] G. W. F. Drake, High precision variational calculations for the $1s^2\ ^1S$ state of H^- and the $1s^2\ ^1S$, $1s2s\ ^1S$ and $1s2s\ ^3S$ states of helium, Nucl. Instrum. Methods Phys. Res. Sect. B, **31**, 7 (1988).

[16] G. W. F. Drake and A. J. Makowski, High Precision eigenvalues for the $1s2p\ ^1P$ and ^3P states of helium, J. Opt. Soc. Am. B, **5**, 2207 (1988).

[17] G. W. F. Drake and Z.-C. Yan, Energies and relativistic corrections for the Rydberg states of helium: Variational results and asymptotic analysis, Phys. Rev. A, **46**, 2378 (1992).

[18] J. Chi, H. Fang, Y.-H. Zhang, X.-Q. Qi, L.-Y. Tang and T.-Y. Shi, Accurate Nonrelativistic Energy Calculations for Helium $1snp\ ^{1,3}P$ ($n = 2to27$) States via Correlated B-Spline Basis Functions, Atoms **13**, 72 (2025).

[19] H. Nakashima, Y. Hijikata, and H. Nakatsuji, Solving the electron and electron-nuclear Schrödinger equations for the excited states of helium atom with the free iterative-complement-interaction method, J. Chem. Phys. **128**, 154108 (2008).

[20] D. T. Aznabaev, A. K. Bekbaev, and V. I. Korobov, Nonrelativistic energy levels of helium atoms, Phys. Rev. A **98**, 012510 (2018).

[21] G. W. F. Drake, M. M. Cassar and Razvan A. Nistor, Ground-state energies for helium, H^- and Ps^-, Phys. Rev. A **65**, 054501 (2002).

[22]

[23] E. M. R. Petrimoulx, A. T. Bondy, E. A. Ene, L. A. Sati, and G. W. F. Drake, Ground-state energy of H^-: a critical test of triple basis sets, Can. J. Phys. DOI10.1139/cjp-2023-0277 (2024).

[24] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms*, (Springer, New York, 1957), p. 181.

[25] A. P. Stone, Proc. Phys. Soc. **77**, 786 (1961); **81**, 868 (1963).

[26] P. K. Kabir and E. E. Salpeter, Radiative Corrections to the Ground-State Energy of the Helium Atom, Phys. Rev. **108**, 1256 (1957).

[27] H. Araki, Quantum-Electrodynamical Corrections to Energy-Levels of Helium, Prog. Theo. Phys. **17**, 619 (1957).

[28] J. Sucher, Energy Levels of the Two-Electron Atom to Order α^3 Ry; Ionization Energy of Helium Phys. Rev. **109**, 1010 (1958).

[29] Z.-C. Yan and G. W. F. Drake, Bethe Logarithm and QED Shift for Lithium, Phys. Rev. Lett. **91**, 113004 (2003).

[30] K. Pachucki and J. Komasa, Relativistic and QED Corrections for the Beryllium Atom, Phys. Rev. Lett. **92**, 213001 (2004).

[31] V. I. Korobov, Bethe logarithm for the helium atom, Phys. Rev. A **100**, 012517 (2019).

[32] M. Lesiuk and J. Lang, Atomic Bethe logarithm in the mean-field approximation, Phys. Rev. A **108**, 042817 (2023). The values obtained for $\ln(k_0/Z^2)$ for atoms heavier than Be are larger than the hydrogenic value by up to 4.7%.

[33] G. W. F. Drake, QED Effects in Helium and Compar-

isons with High Precision Experiment, Phys. Scr. **T95**, 22 (2001).

[34] K. Pachucki, V. Patkós, and V. A. Yerokhin, Testing fundamental interactions on the helium atom, Phys. Rev. A **95**, 062510 (2017).

[35] V. Patkóš, V.A. Yerokhin and K. Pachucki, Complete $m\alpha^7$ Lamb shift of helium triplet states, Phys. Rev. A **103**, 042809 (2021).

[36] Further tables of matrix elements for all $n\,P$ states of Helium with $2 \leq n \leq 35$ are available at DOI: 10.5061/dryad.cjsxksnkv.

[37] G. W. F. Drake in *Long-Range Casimir Forces : Theory and Recent Experiments on Atomic Systems*, Edited by Frank S. Levin and David A. Micha (Plenum Press, New York, 1993), p. 169 and TABLE XII.

[38] K. Pachucki, Helium energy levels including $m\alpha^6$ corrections, Phys. Rev. A **74**, 062510 (2006). His value for E_C of $0.201363\alpha^6 m$ (3.757 MHz) includes also mixing with higher $n\ ^3P_1$ states with $n > 2$. This reduces the value from our $E^{(4)}_{\rm st} = 4.755$ MHz.

[39] G. W. F. Drake, I. B. Khriplovich, A. I. Milstein and A. S. Yelkovsky, Energy corrections of order $mc^2\alpha^6 \ln\alpha$ in helium, Phys. Rev. A **48**, R15 (1993).

[40] K. Pachucki, $\alpha^4\mathcal{R}$ corrections to singlet states of helium, Phys. Rev. A **74**, 022512 (2006).

[41] G. Clausen and F. Merkt, Ref. [2] and private communication.

[42] K. Pachucki, V. Lensky, F. Hagelstein, S. S. L. Muli, S. Bacca, and R. Pohl, Comprehensive theory of the Lamb shift in light muonic atoms Rev. Mod. Phys. **96**, 015001 (2024).

[43] V. A. Yerokhin, V. Patkóš, and K. Pachucki, Relativistic Bethe logarithm for triplet states of helium-like ions, Eur. Phys. J. D **76**, 142 (2022).

[44] V. A. Yerokhin, V. Patkóš, and K. Pachucki, QED $m\alpha^7$ effects for triplet states of heliumlike ions, Phys. Rev. A **107**, 012810 (2023).

[45] P.-L. Luo, J.-L. Peng, J. Hu, Y. Feng, L.-B. Wang, and J.-T. Shy, Precision frequency measurements of ^{3,4}He $2\,^3P \to 3\,^3D$ transitions at 588 nm, Phys. Rev. A **94**, 062507 (2016).

[46] P. J. Mohr, D. B. Newell, B. N. Taylor, and E. Tiesinga, Codata recommended values of the fundamental physical constants: 2022, Rev. Mod. Phys. **97**, 025002 (2025).

[47] L.-Y. Tang, private communication (2025).

TABLE VIII. Variational upper bounds (first entry) and extrapolations (second entry) for the nonrelativistic energies of the $n\,^1P$ and $n\,^3P$ states of helium, assuming infinite nuclear mass. N is the number of terms in the basis set. Units are atomic units.

n	N	$E(n\,^1P)$	$E(n\,^3P)$
4	2775	−2.03106 96504 50240 71468 1	−2.03232 43542 96630 33188 0
		−2.03106 96504 50240 71474 2(12)	−2.03232 43542 96630 33195 6(9)
5	2775	−2.01990 59899 00846 44880 6	−2.02055 11872 56267 78819 2
		−2.01990 59899 00846 44884 8(7)	−2.02055 11872 56267 78824 6(11)
6	2622	−2.01383 39796 71740 10233 5	−2.01420 79587 73750 59118 0
		−2.01383 39796 71740 10238 6(9)	−2.01420 79587 73750 59121 9(6)
7	2949	−2.01016 93145 29388 98487 7	−2.01040 49600 07971 43124 2
		−2.01016 93145 29388 98489 8(3)	−2.01040 49600 07971 43126 2(5)
8	2839	−2.00778 91271 33235 89513 8	−2.00794 70137 71161 50524 9
		−2.00778 91271 33235 89515 6(3)	−2.00794 70137 71161 50526 2(5)
9	2864	−2.00615 63846 52853 81832 7	−2.00626 72673 66409 03255 4
		−2.00615 63846 52853 81834 6(5)	−2.00626 72673 66409 03258 0(14)
10	5303	−2.00498 79838 02218 23945 8138	−2.00506 88054 97707 31644 539
		−2.00498 79838 02218 23945 8183(24)	−2.00506 88054 97707 31644 544(3)
11	5821	−2.00412 31919 22332 65252 893	−2.00418 39031 99590 64237 6319
		−2.00412 31919 22332 65252 887(4)	−2.00418 39031 99590 64237 6334(1)
12	4868	−2.00346 52527 04885 79826 025	−2.00351 20065 35142 74556 011
		−2.00346 52527 04885 79826 035(5)	−2.00351 20065 35142 74556 021(18)
13	5588	−2.00295 30939 58149 78487 052	−2.00298 98597 64908 81632 212(11)
		−2.00295 30939 58149 78487 063(6)	−2.00298 98597 64908 81632 221(5)
14	5604	−2.00254 66253 70190 96801 19097	−2.00257 60564 26625 76904 83
		−2.00254 66253 70190 96801 19159(29	−2.00257 60564 26625 76904 86(3)
15	6160	−2.00221 86471 04088 30158 821	−2.00224 25712 22150 32643 875
		−2.00221 86471 04088 30158 826(6)	−2.00224 25712 22150 32643 884(5)
16	6160	−2.00195 01779 73979 34078 79	−2.00196 98874 03296 96697 712
		−2.00195 01779 73979 34078 87(95)	−2.00196 98874 03296 96697 718(7)
17	5518	−2.00172 76459 99910 51694 4161	−2.00174 40751 91087 35600 490
		−2.00172 76459 99910 51694 4179(27)	−2.00174 40751 91087 35600 498(14)
18	5518	−2.00154 11387 60913 62470 8305	−2.00155 49769 40232 72665 171
		−2.00154 11387 60913 62470 8318(8)	−2.00155 49769 40232 72665 182(4)
19	5870	−2.00138 32801 02341 60978 0542	−2.00139 50446 04295 12498 77
		−2.00138 32801 02341 60978 0599(16)	−2.00139 50446 04295 12498 76(3)
20	5624	−2.00124 84894 50687 61310 873	−2.00125 85746 92820 42380 855
		−2.00124 84894 50687 61310 887(11)	−2.00125 85746 92820 42380 893(9)
21	6744	−2.00113 24817 33017 52951 735	−2.00114 11926 56477 67869 1362
		−2.00113 24817 33017 52951 738(2)	−2.00114 11926 56477 67869 1390(23)
22	6744	−2.00103 19225 52162 28543 55462	−2.00103 94979 12816 70120 9912
		−2.00103 19225 52162 28543 55516(21	−2.00103 94979 12816 70120 9925(7)
23	6180	−2.00094 41858 77955 80644 3933	−2.00095 08147 60962 14631 450
		−2.00094 41858 77955 80644 3957(7)	−2.00095 08147 60962 14631 469(6)
24	6744	−2.00086 71808 46170 11128 219	−2.00087 30145 66616 65939 225
		−2.00086 71808 46170 11128 223(6)	−2.00087 30145 66616 65939 240(9)
25	6744	−2.00079 92260 24103 06304 5478	−2.00080 43868 29929 07060 8333
		−2.00079 92260 24103 06304 5555(6)	−2.00080 43868 29929 07060 8458(13)
26	6744	−2.00073 89568 37741 71921 753	−2.00074 35443 60330 29581 243
		−2.00073 89568 37741 71921 765(4)	−2.00074 35443 60330 29581 281(17)
27	6744	−2.00068 52565 28882 40212 1288	−2.00068 93526 23570 97655 851
		−2.00068 52565 28882 40212 1453(18)	−2.00068 93526 23570 97655 876(3)
28	6744	−2.00063 72040 47170 83714 2907	−2.00064 08764 67041 02409 2930
		−2.00063 72040 47170 83714 3041(29)	−2.00064 08764 67041 02409 3026(20)
29	6744	−2.00059 40342 90981 60178 88	−2.00059 73395 04545 63185 36
		−2.00059 40342 90981 60178 91(1)	−2.00059 73395 04545 63185 45(2)
30	6744	−2.00055 51074 62372 97425 66	−2.00055 80928 35757 97528 28
		−2.00055 51074 62372 97425 91(24)	−2.00055 80928 35757 97528 32(5)
31	7948	−2.00051 98852 24314 85698 88	−2.00052 25907 26604 94616 82
		−2.00051 98852 24314 85698 89(1)	−2.00052 25907 26604 94616 86(4)
32	7316	−2.00048 79119 87756 79932 35	−2.00049 03715 34947 75603 30
		−2.00048 79119 87756 79932 41(1)	−2.00049 03715 34947 75603 39(3)
33	7948	−2.00045 88001 04867 46785 88	−2.00046 10426 27369 81858 51
		−2.00045 88001 04867 46785 90(2)	−2.00046 10426 27369 81858 54(4)
34	7948	−2.00043 22180 63626 95660 94	−2.00043 42683 60440 67655 20
		−2.00043 22180 63626 95660 98(4)	−2.00043 42683 60440 67655 23(3)
35	7948	−2.00040 78810 08092 82096 5	−2.00040 97604 35014 70404 3
		−2.00040 78810 08092 82096 8(2)	−2.00040 97604 35014 70404 5(2)

TABLE IX. Matrix elements of the spin-dependent operators in the Breit interaction for the $n\,^1P$ and $n\,^3P$ states of helium, calculated for the case $J = 1$ [a]. For each pair, the first entry is $\langle n\,^3P_1|B'_{X,\infty}|n\,^3P_1\rangle$ and the second is the mass polarization correction coefficient $\langle n\,^3P_1|B'_{X,M}|n\,^3P_1\rangle$, in units of $10^{-5}\alpha^2$ a.u.

n	$\langle n\,^3P_1\|B'_{\rm so}\|n\,^3P_\|\rangle$	$\langle n\,^3P_1\|B'_{\rm soo}\|n\,^3P_\|\rangle$	$\langle n\,^3P_1\|B'_{\rm ss}\|n\,^3P_\|\rangle$	$\langle n\,^3P_1\|\Delta'_{3Z}\|n\,^3P_1\rangle$
24	−1.854352474671(9)	2.674998240246(7)	−1.0876431688957(15)	5.4271884889(18)
	−3.83779574(5)	4.92099467099(2)	−1.426091640(5)	7.233732(9)
25	−1.640050608267(9)	2.365817143049(9)	−0.9618981852881(32)	4.7999883364(5)
	−3.39005620(5)	4.34621403(5)	−1.258871388(19)	6.3850253(24)
26	−1.457538177043(19)	2.102506767458(24)	−0.854814797824(6)	4.26582611285(20)
	−3.00935205(10)	3.85758656(15)	−1.116808321(39)	5.6641036(13)
27	−1.3011326394968(16)	1.876866053129(9)	−0.7630553854971(8)	3.8080708978(9)
	−2.683591552(7)	3.43955493(5)	−0.9953436324(24)	5.047800(6)
28	−1.166328089046(7)	1.682392385106(22)	−0.683973821695(8)	3.4135353602(4)
	−2.40320799(5)	3.07981395(10)	−0.89087475(6)	4.5177234(29)
29	−1.049520545597(11)	1.5138849770276(27)	−0.6154539294841(11)	3.07167179(8)
	−2.160566619(11)	2.7685477611(34)	−0.8005302417(12)	4.0580(6)
30	−0.947804167335(10)	1.36715066900(7)	−0.555789670118(24)	2.773975696(11)
	−1.94952534(6)	2.4978561(5)	−0.72200070(18)	3.66098(8)
31	−0.8588184319796(30)	1.2387833248071(37)	−0.5035953168823(11)	2.51353855043(9)
	−1.765101303(13)	2.2613382989(28)	−0.6534165562(24)	3.31315810(27)
32	−0.7806323832762(37)	1.125996743532(7)	−0.457737428053(7)	2.28470903(5)
	−1.6032268020(27)	2.0537662962(7)	−0.59325170914(36)	3.00724(34)
33	−0.711656127544(10)	1.0264969147322(15)	−0.4172828436802(5)	2.08283398(11)
	−1.460557904(28)	1.87084326755(8)	−0.54025268262(11)	2.7381(8)
34	−0.65057257124(16)	0.9383834934(15)	−0.3814585816(8)	1.9040587(4)
	−1.3343283(12)	1.709018(11)	−0.493384(6)	2.5052(29)
35	−0.5962843365(25)	0.8600731859(6)	−0.34962065507060(6)	1.745171(4)
	−1.222212(18)	1.565333(4)	−0.4517884294(5)	2.263(29)

[a] excluding the anomalous magnetic moment correction.