High precision theory for the Rydberg P-states of helium and comparison with experiment up to principal quantum number $n = 102$

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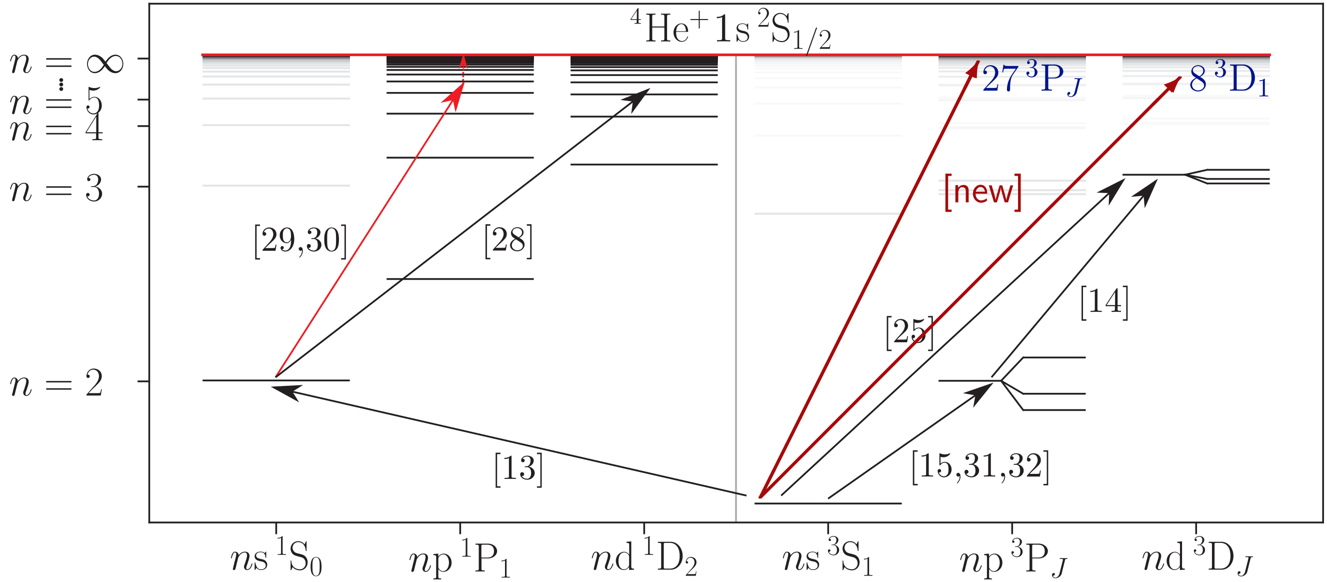
OUTLINE

- Motivation: measurements of Rydberg ^1P- and ^3P-states of helium up to $n = 102$ by the Zurich group (Gloria Clausen, Frédéric Merkt) in connection with an 9σ discrepancy between theory and experiment for the $1s2s\,^3S$ state
- New variational techniques: Triple basis sets in Hylleraas coordinates
- Variational results for Rydberg states of helium up to $n = 35$
- Quantum defect validity and extrapolation to $n = 102$
- Relativistic and QED corrections
- Comparison with experiment
- Summary and Discussion

G. Clausen et al., PRL **127**, 093001 (2021) and PRA **111**, 012817 (2025) measured absolute ionization energies down to $n = 24$ for the ^{1}P-states and $n = 27$ for ^{3}P states (F. Merkt, ETH).



<u>THEORY</u> (up to $O(m\alpha^7)$: 10σ discrepancy of 0.4 MHz for $2\,^3S_1$)

V. Patkos, V.A. Yerokhin, and K. Pachucki, Phys. Rev. A **103**, 042809 (2021)

[13] R.J. Rengelink et al., Nat. Phys. **14**, 1132 (2018)

[15] X. Zhang et al., Phys. Rev. Lett., **119**, 263002 (2017)

[25] C. Dorrer et al., Phys. Rev. Lett., **78**, 3658 (1997)

[new] M.H. Wu et al., Phys. Rev. A **111**, 052809 (2025); $2\,^3S_1 - 8\,^3D_1$

VIEWPOINT

Precision Spectroscopy Reaffirms Gap Between Theory and Experiment

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New physics may explain discrepant values for the ionization energy of a metastable state of helium.

Metrology in a two-electron atom: The ionization energy of metastable triplet helium $2\,^3S_1$

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Helium (He) is the ideal atom to perform tests of *ab initio* calculations in two-electron systems that consider all known effects, including quantum-electrodynamics and nuclear-size contributions. Recent state-of-the-art calculations and measurements of energy intervals involving the He $2\,^3S_1$ metastable state reveal discrepancies at the level of $7\,\sigma$ that require clarification both from the experimental and theoretical sides. We report on a new determination of the ionization energy $E_\mathrm{I}\,(2\,^3S_1)$ of the $(1s)(2s)\,^3S_1$ metastable state of He. The measurements rely on an approach combining interferometric laser-alignment control, SI-traceable frequency calibration, and imaging-assisted Doppler-free spectroscopy. With this approach we record spectra of the *np* Rydberg series in a highly collimated cold supersonic beam of metastable He generated by a cryogenic valve and an electric discharge. Extrapolation of the Rydberg series yields a new value of the ionization energy $[E_\mathrm{I}\,(2\,^3S_1)/h = 1\,152\,842\,742.7082(55)_\mathrm{stat}(25)_\mathrm{sys}$ MHz] that deviates by $9\,\sigma$ from the most precise theoretical result [1 152 842 742.231(52) MHz], reported by Patkóš *et al.* [Phys. Rev. A **103**, 042809 (2021)], confirming earlier discrepancies between experiment and theory in this fundamental system.

DOI: 10.1103/PhysRevA.111.012817

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

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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 $24 \leqslant n \leqslant 35$. 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 1 152 842 742.728(6) MHz, which agrees with but is larger than the experimental value by 14 ± 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 ± 17 kHz.

PHYSICAL REVIEW A **103**, 042809 (2021)

Complete $\alpha^7 m$ Lamb shift of helium triplet states

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We have derived the complete formula for the $\alpha^7 m$ contribution to energy levels of an arbitrary triplet state of the helium atom, performed numerical calculations for the $2\,^3S$ and $2\,^3P$ states, and thus improved the theoretical accuracy of ionization energies of these states by more than an order of magnitude. Using the nuclear charge radius extracted from the muonic helium Lamb shift, we obtain the theoretical prediction in excellent agreement with the measured $2\,^3S - 2\,^3P$ transition energy [X. Zheng *et al.*, Phys. Rev. Lett. **119**, 263002 (2017)]. At the same time, we observe significant discrepancies with experiments for the $2\,^3S - 3\,^3D$ and $2\,^3P - 3\,^3D$ transitions.

DOI: 10.1103/PhysRevA.103.042809

	$(m/M)^0$	$(m/M)^1$	$(m/M)^2$	$(m/M)^3$	Sum
$2\,^3S$:					
α^2	−1 152 953 922.384 (2)	164 775.354	−30.620	0.006	−1 152 789 177.644 (2)
α^4	−57 629.312	4.284	−0.001		−57 625.029
α^5	3 999.431	−0.800			3 998.632
α^6	65.235	−0.030			65.205
α^7	−6.168 (1)				−6.168 (1)
α^8	0.158 (52)				0.158 (52)
NS	2.616 (3)				2.616 (3)
NP	−0.001				−0.001
Total					−1 152 842 742.231 (52)

^{4}He 1s2s $^3S_1$ ionization energy

Theory 1 152 842 742.231(52)

Experiment 1 152 842 742.7082(55) (5 parts in 10^{12})

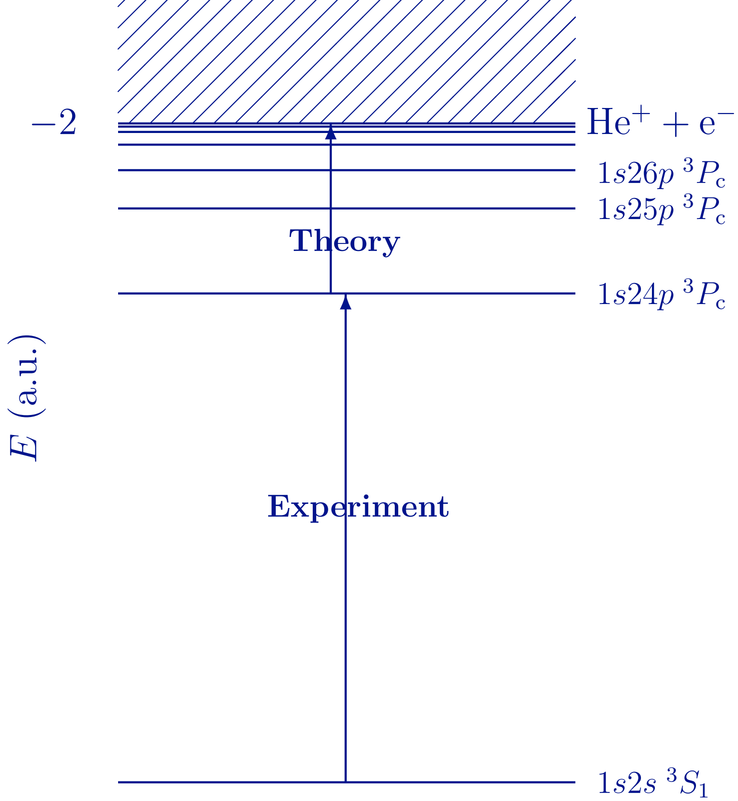
Difference -0.477(52) MHz

KEY POINT: QED terms decrease in proportion to $1/n^3$, and so are smaller by factor of $(2/24)^3 = 1/1728$ for n = 24.

Theoretical conributions to the ionization energy of 1s2p ^3P_c state of ^{4}He [Patkos et al., Phys. Rev. A 202, 042809 (2021)]

$2\,^3P$:					
α^2	−876 178 284.857 (2)	61 871.895	−25.840	0.006	−876 116 438.795 (2)
α^4	11 436.878	11.053	0.002		11 447.932
α^5	−1 234.732	−0.614			−1 235.346
α^6	−21.833	−0.001			−21.835
α^7	2.280 (1)				2.280 (1)
α^8	−0.048 (16)				−0.048 (16)
NS	−0.799 (1)				−0.799 (1)
NP	0.000				0.000
Total					−876 106 246.611 (16)

The α^6 term is the dominant source of uncertainty, but for high-n it is sppressed by a factor of $(2/n)^6$ =1/1728.


−2
He$^+$ + e$^-$
$1s26p\ ^3P_c$
$1s25p\ ^3P_c$
Theory
$1s24p\ ^3P_c$
E (a.u.)
Experiment
$1s2s\ ^3S_1$

Variational Calculations for Helium

- Helium is a fundamental atomic system, but very little is known about the higher-lying Rydberg states.
- The ground state is known to very high precision from the works of
  - C. Schwartz, Int. J. Mod. Phys. E **15**, 877 (2006).
  - Nakashima, Hijikata, and Nakatsuji J. Chem. Phys. **128**, 154108 (2008),
  - D. T. Aznabaev, A. K. Bekbaev, and Vladimir I. Korobov, Phys. Rev. A, **98**, 012510 (2018).
- The lower-lying excited states have been studied by G.W.F. Drake and Z.-C Yan, Phys. Rev. A, **46**, 2378 (1992) for all states up to $n = 10$ and $L = 7$.
- Aznabaev et al. have recently done high precision calculations up to $n = 4$ and $L = 3$
- Variational methods typically lose their accuracy with increasing principal quantum number n.

The present work does two things:

- Extends our previous double-basis-set method to triple basis sets in Hylleraas coordinates. This improves the accuracy by two or three orders of magnitude.
- Extends the calculations up to $n = 35$ for the P-states with little loss of accuracy.

Two principle kinds of basis sets are in current use:

- All exponential basis set with random coefficients (introduced by Korobov)

$$\Phi_i(r_1, r_2, r_{12}) = \exp(-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12}), \quad i = 1, 2, \cdots N$$

  where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the interelectron coordinate. This is more flexible for three-body molecular systems, but requires extended-precision arithmetic.

- The traditional Pekeris basis set with powers of r_1, r_2, and r_{12}

$$\Phi_{i,j,k}(r_1, r_2, r_{12}) = r_1^i\, r_2^j\, r_{12}^k \exp(-\alpha r_1 - \beta r_2), \quad i + j + k \leq \Omega$$

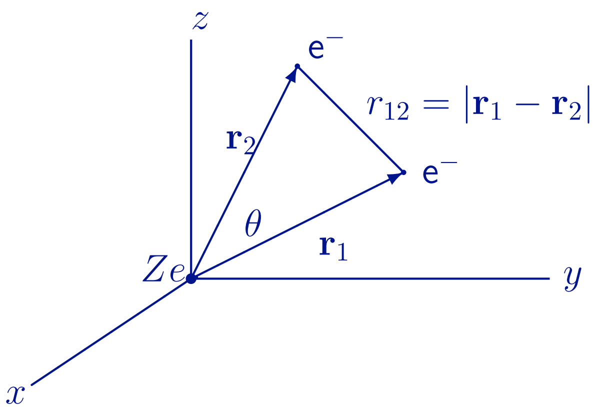
  where $\Omega = 1,\ 2,\ 3 \cdots$ defines a sequence of Pekeris shells with fixed α and β.

  Better suited to Rydberg states with many nodes.

The present work employs the traditional Pekeris basis sets, but doubled or tripled such that each combination of powers $i,\ j,\ k$ occurs two or three times with different nonlinear parameters α_p, β_p, $p = 1,\ 2,\ 3$, individually optimized to minimize the energy. Does not require extended-precision arithmetic up to $n = 15$.

$$\Phi_{i,j,k}^{(p)}(r_1, r_2, r_{12}) = r_1^i\, r_2^j\, r_{12}^k \exp(-\alpha_p r_1 - \beta_p r_2), \quad i + j + k \leq \Omega$$

Nonrelativistic Eigenvalues



Hylleraas coordinates

(Hylleraas, 1929)

The Hamiltonian in atomic units is

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

Expand

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i,j,k} a_{ijk}\, r_1^i\, r_2^j\, r_{12}^k\, e^{-\alpha r_1 - \beta r_2}\, \mathcal{Y}_{l_1 l_2 L}^M(\hat{\mathbf{r}}_\mathbf{1}, \hat{\mathbf{r}}_\mathbf{2}) \pm \text{exchange}$$

where $i + j + k \leq \Omega$ (Pekeris shell).

Diagonalize H in the

$$\phi_{ijk} = r_1^i\, r_2^j\, r_{12}^k\, e^{-\alpha r_1 - \beta r_2}\, \mathcal{Y}_{l_1 l_2 L}^M(\hat{\mathbf{r}}_\mathbf{1}, \hat{\mathbf{r}}_\mathbf{2}) \pm \text{exchange}$$

basis set.

to satisfy the variational condition

$$\delta \int \Psi\, (H - E)\, \Psi\, d\tau = 0.$$

New Variational Techniques

I. Old – Double the basis set

$$\text{If}\quad \phi_{i,j,k}(\alpha,\beta) = r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2}$$

$$\text{then}\quad \tilde{\phi}_{i,j,k} = a_1\phi_{i,j,k}(\alpha_1,\beta_1) + a_2\phi_{i,j,k}(\alpha_2,\beta_2)$$

asymptotic inner correlation

II. New – Triple the basis set

$$\text{If}\quad \phi_{i,j,k}(\alpha,\beta) = r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2}$$

$$\text{then}\quad \tilde{\phi}_{i,j,k} = a_1\phi_{i,j,k}(\alpha_1,\beta_1) + a_2\phi_{i,j,k}(\alpha_2,\beta_2) + a_3\phi_{i,j,k}(\alpha_3,\beta_3)$$

asymptotic intermediate inner correlation

III. Include the screened hydrogenic function

$$\phi_{\mathsf{SH}} = \psi_{1s}(Z)\psi_{nL}(Z-1)$$

explicitly in the basis set.

CORRELATED B-SPLINE METHOD

Useful results for P-states up to n = 37 have been obtained by the use of correlated B-spline basis sets, but at the expense of using much larger basis sets. See

PHYSICAL REVIEW A **113**, 012812 (2026)

Precise *ab initio* calculations of ^{4}He ($1snp\ ^3P_J$) fine structure of high Rydberg states

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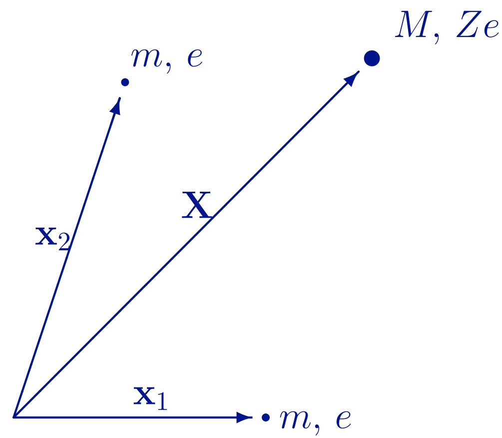
Mass Scaling



$$H = -\frac{\hbar^2}{2M}\nabla_X^2 - \frac{\hbar^2}{2m}\nabla_{x_1}^2 - \frac{\hbar^2}{2m}\nabla_{x_2}^2 - \frac{Ze^2}{|\mathbf{X}-\mathbf{x}_1|} - \frac{Ze^2}{|\mathbf{X}-\mathbf{x}_2|} + \frac{e^2}{|\mathbf{x_1}-\mathbf{x}_2|}$$

Transform to centre-of-mass plus relative coordinates $\mathbf{R}$, $\mathbf{r}_1$, $\mathbf{r}_2$

$$\begin{aligned}\mathbf{R} &= \frac{M\mathbf{X}+m\mathbf{x}_1+m\mathbf{x}_2}{M+2m}\\ \mathbf{r}_1 &= \mathbf{X}-\mathbf{x}_1\\ \mathbf{r}_2 &= \mathbf{X}-\mathbf{x}_2\end{aligned}$$

and ignore centre-of-mass motion. Then

$$H = -\frac{\hbar^2}{2\mu}\nabla_{r_1}^2 - \frac{\hbar^2}{2\mu}\nabla_{r_2}^2 - \frac{\hbar^2}{M}\nabla_{r_1}\cdot\nabla_{r_2} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|\mathbf{r_1}-\mathbf{r}_2|}$$

where $\mu = \dfrac{mM}{m+M}$ is the electron reduced mass.

Variational eigenvalues for the Rydberg $n\,^1P$ and $n\,^3P$ states of helium with $n > 10$ (a.u.).

n	$n\,^1P$ energy	$n\,^3P$ energy
10	-2.004 987 983 802 218 239 458 183(24)	-2.005 068 805 497 707 316 445 44(3)
11	-2.004 123 191 922 332 652 528 87(4)	-2.004 183 903 199 590 642 376 334(15)
12	-2.003 465 252 704 885 798 260 35(5)	-2.003 512 006 535 142 745 560 21(18)
13	-2.002 953 093 958 149 784 870 63(6)	-2.002 989 859 764 908 816 322 21(5)
14	-2.002 546 625 370 190 968 011 916(3)	-2.002 576 056 426 625 769 048 6(3)
15	-2.002 218 647 104 088 301 588 26(6)	-2.002 242 571 222 150 326 438 84(5)
16	-2.001 950 177 973 979 340 788 7(95)	-2.001 969 887 403 296 966 977 18(7)
17	-2.001 727 645 999 910 516 944 179(27	-2.001 744 075 191 087 356 004 98(14)
18	-2.001 541 138 760 913 624 708 318(8)	-2.001 554 976 940 232 726 651 82(4)
19	-2.001 383 280 102 341 609 780 599(16)	-2.001 395 044 604 295 124 987 6(3)
20	-2.001 248 489 450 687 613 108 87(11)	-2.001 258 574 692 820 423 808 93(9)
21	-2.001 132 481 733 017 529 517 338(5)	-2.001 141 192 656 477 678 691 390(23)
22	-2.001 031 922 552 162 285 435 5516(21)	-2.001 039 497 912 816 701 209 663(44)
23	-2.000 944 185 877 955 806 443957(7)	-2.000 950 814 760 962 146 314 69(6)
24	-2.000 867 180 846 170 111 282 23(6)	-2.000 873 014 566 616 659 392 40(9)
25	-2.000 799 226 024 103 063 045 555(6)	-2.000 804 386 829 929 070 608 458(13)
26	-2.000 738 956 837 741 719 217 65(4)	-2.000 743 544 360 330 295 812 81(17)
27	-2.000 685 256 528 882 402 121 453(18)	-2.000 689 352 623 570 976 558 76(3)
28	-2.000 637 204 047 170 837 143 041(29)	-2.000 640 876 467 041 024 093 026(20)
29	-2.000 594 034 290 981 601 789 1(1)	-2.000 597 339 504 545 631 854 5(2)
30	-2.000 555 107 462 372 974 259(24)	-2.000 558 092 835 757 975 283 2(5)
31	-2.000 519 885 224 314 856 988 9(1)	-2.000 522 590 726 604 946 168 6(1)
32	-2.000 487 911 987 756 799 324 1(1)	-2.000 490 371 534 947 756 033 9(3)
33	-2.000 458 800 104 867 467 859 0(2)	-2.000 461 042 627 369 818 585 4(4)
34	-2.000 432 218 063 626 956 609 8(4)	-2.000 490 371 534 947 756 033 9(3)
35	-2.000 407 881 008 092 820 968(2)	-2.000 409 760 435 014 704 045(2)

Screened hydrogenic energy is $E_{\rm SH} = -2 - \dfrac{1}{2n^2} = -2.000\,555\,555\cdots$ for $n = 30$.

QUANTUM DEFECT THEORY

Term energies for a quasi-hydrogenic atom (with $Z_{\text{eff}} = 1$):

$$E_n = -R_M \frac{1}{n*^2}$$

$$\begin{aligned} \text{where } R_M &= \frac{M}{m_e + M} R_\infty \text{ is the reduced mass Rydberg} \\ n* &= n - \delta(n*) \text{ is the effective principal quantum number} \end{aligned}$$

$\delta(n*)$ is the quantum defect defined by the Ritz expansion

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

containing only even powers.

QUESTION: Under what conditions is the quantum defect expansion exact?

– especially concerning the value of R_M and the Ritz expansion.

HARTREE'S PROOF:

For a Hamiltonian $H = H_C + \lambda V$

where H_C is a purely Coulombic Hamiltonian and V is a local short-range spherically symmetric correction potential, then the eigenvalues are given exactly by the Ritz expansion for the quantum defect.

RITZ DEFECT:

Defined to be a deviation from Hartree's proof – extensively studied in Drake, Adv. At. Mol. Opt. Phys. **32**, 93 (1994). No nonrelativistic Ritz defect found.

NEW RESULTS:

- Mass polarization due to the motion of the nucleus in the C. of M. frame modifies the correct value to use for R_M.
- Relativistic corrections violate the Ritz expansion.

$1/n^t$ expansion expansion coefficients for the first- and second-order mass polarization contribution to the energy for the $1snp\ ^1P$ and $1snp\ ^3P$ states of helium. Units are atomic units.

t	$c(\mathbf{p}_1\cdot\mathbf{p}_2)_t^{(1)}$	$c(\mathbf{p}_1\cdot\mathbf{p}_2)_t^{(2)}$
	$1snp\ ^1P$	
-2	0.0	-0.500000
-3	0.411 2423(26)	-0.168 636(14)
-4	-0.014 92(11)	-0.2474(7)
-5	-0.1109(19)	-0.378(12)
-6	0.027(15)	0.23(10)
-7	-0.19(6)	0.0(4)
-8	0.11(11)	0.2(8)
	$1snp\ ^3P$	
-2	0.0	-0.50000
-3	-0.452 876(8)	-0.165 32(8)
-4	-0.0929(4)	-0.335(4)
-5	-0.127(7)	-0.83(6)
-6	-0.02(6)	-0.7(5)
-7	0.23(23)	0.1(1.7)
-8	-0.3(5)	-3.(3)

SECOND-ORDER MASS POLARIZATION

$$E_{\rm MP}^{(2)} = R_M \left(\frac{\mu}{M}\right)^2 \left(-\frac{1}{n^2} + \frac{a_3}{n^3} + \cdots\right)$$

First discovered by Richard Drachman PRA **33**, 2680 (1986) in the asymptotic limit of high-L Rydberg states.

The corrected term energies are thus

$$E_n = -R_M \frac{1}{n{*}^2}\left[1 + \left(\frac{\mu}{M}\right)^2\right]$$

or equivalently

$$E_n = -R_M^{(+)} \frac{1}{n{*}^2}$$

with

$$R_M^{(+)} = R_\infty \frac{M + m_e}{M + 2m_e} \quad \text{in place of} \quad R_M = R_\infty \frac{M}{M + m_e}$$

Physically, this is the Rydberg for an electron outside a He^+ core instead of a bare He^{++} nucleus.

This provides a theoretical justification for what is commonly done on phenomenological grounds.

Note that

$$\frac{R_M^{(+)}}{R_M} = \frac{1}{1 - (\mu/M)^2} = 1 + \left(\frac{\mu}{M}\right)^2 + \left(\frac{\mu}{M}\right)^4 + \cdots$$

SECOND-ORDER RELATIVISTIC RECOIL

$$\tilde{\Delta}_2 = -\frac{Z\alpha^2}{2}\left\{\frac{1}{r_1}(\mathbf{p}_1+\mathbf{p}_2)\cdot\mathbf{p}_1 + \frac{1}{r_1^3}\mathbf{r}_1\cdot[\mathbf{r}_1\cdot(\mathbf{p}_1+\mathbf{p}_2)]\mathbf{p}_1 + \frac{1}{r_2}(\mathbf{p}_1+\mathbf{p}_2)\cdot\mathbf{p}_2 + \frac{1}{r_2^3}\mathbf{r}_2\cdot[\mathbf{r}_2\cdot(\mathbf{p}_1+\mathbf{p}_2)]\mathbf{p}_2\right\}$$

Write $\tilde{\Delta}_2 = \tilde{\Delta}_2^{(0)} + (\mu/M)\tilde{\Delta}_2^{(1)}$.
Then

$$(\mu/M)\tilde{\Delta}_2^{(1)} = -\frac{Z\alpha^2}{2}\left(\frac{\mu}{M}\right)^2\left(\frac{8}{3n^2} + O(n^{-3})\right)$$

From previous work (Drake & Yan, PRA **46**, 2378 (1992), there is an additional second-order $(\mu/M)^2$ recoil correction to the Breit interaction of

$$B^X = \frac{5}{3}\alpha^2\left(\frac{\mu}{M}\right)^2$$

and so the total is $(\frac{8}{3} - \frac{5}{3})\alpha^2(\mu/M)^2 = \alpha^2(\mu/M)^2$

The final quantum defect formula is thus

$$E_n = -R_M\left(\frac{1}{n*^2} + \frac{(\mu/M)^2}{n^2} - 2\alpha^2\frac{(\mu/M)^2}{n^2}\right)$$

Quantum defect parameters for the $n\,^1P$ and $n\,^3P$ states of helium.

t	$\delta_t(^1P) \times 10^6$	$\delta_t(^3P) \times 10^6$
	Infinite nuclear mass case	
0	-12 114.192 143 935 069 93(38)	68 293.614 172 491 0231(10)
2	7507.893 176 176 17(32)	-18 636.050 617 7460(14)
4	13 958.924 048 95(14)	-12 317.146 265 87(42)
6	4880.202 286(16)	-8064.197 353(37)
8	889.569 21(57)	-4612.819 8(12)
10	700.934 3(87)	-1423.315(18)
12	159.457(56)	-743.77(11)
14	-248.55(12)	-518.31(21)
	Finite nuclear mass case for ^{4}He	
0	-12 170.559 891 525 778(10)	68 355.695 242 244(65)
2	7 523.086 479 853 9(28)	-18 620.076 142(22)
4	13 981.956 941 91(21)	-12 331.288 9(23)
6	4 891.575 670 98(21)	-8083.805(83)
8	893.399 450(80)	-4618.8(1.2)
10	713.071 18(85)	-1452.5(7.6)
12	57.953 8(22)	-889.8(15.2)

EXTRAPOLATION STRATEGY

To extrapolate beyond $n = 35$ to $n = 102$:

- Use quantum defect theory only for the nonrelativistic energy where the Ritz expansion is well justified.
- Use simple $1/n$ expansions for all the relativistic and QED corrections, starting with $1/n^3$.

Relativistic Corrections

Relativistic corrections of $O(\alpha^2)$ and anomalous magnetic moment corrections of $O(\alpha^3)$ are (in atomic units)

$$\Delta E_{\rm rel} \;=\; \langle\Psi|H_{\rm rel}|\Psi\rangle_J\,, \tag{1}$$

where Ψ is a nonrelativistic wave function and $H_{\rm rel}$ is the Breit interaction defined by

$$\begin{aligned} H_{\rm rel} \;=\;& B_1 + B_2 + B_4 + B_{\rm so} + B_{\rm soo} + B_{\rm ss} + \frac{m}{M}(\tilde{\Delta}_2 + \tilde{\Delta}_{\rm so}) \\ &+ \gamma\left(2B_{\rm so} + \frac{4}{3}B_{\rm soo} + \frac{2}{3}B_{3e}^{(1)} + 2B_5\right) + \gamma\,\frac{m}{M}\tilde{\Delta}_{\rm so}\,. \end{aligned}$$

where $\gamma = \alpha/(2\pi)$ and

$$B_1 = \frac{\alpha^2}{8}(p_1^4 + p_2^4)$$

$$B_2 = -\frac{\alpha^2}{2}\left(\frac{1}{r_{12}}\mathbf{p}_1\cdot\mathbf{p}_2 + \frac{1}{r_{12}^3}\mathbf{r}_{12}\cdot(\mathbf{r}_{12}\cdot\mathbf{p}_1)\mathbf{p}_2\right)$$

$$B_4 = \alpha^2\pi\left(\frac{Z}{2}\delta(\mathbf{r}_1) + \frac{Z}{2}\delta(\mathbf{r}_2) - \delta(\mathbf{r}_{12})\right)$$

$$H_{\rm rel} = B_1 + B_2 + B_4 + B_{\rm so} + B_{\rm soo} + B_{\rm ss} + \frac{m}{M}(\tilde{\Delta}_2 + \tilde{\Delta}_{\rm so})$$
$$+ \gamma \left(2B_{\rm so} + \frac{4}{3}B_{\rm soo} + \frac{2}{3}B_{3e}^{(1)} + 2B_5\right) + \gamma \frac{m}{M}\tilde{\Delta}_{\rm so} \,.$$

Spin-dependent terms

$$B_{\rm so} = \frac{Z\alpha^2}{4}\left[\frac{1}{r_1^3}(\mathbf{r}_1 \times \mathbf{p}_1)\cdot\boldsymbol{\sigma}_1 + \frac{1}{r_2^3}(\mathbf{r}_2 \times \mathbf{p}_2)\cdot\boldsymbol{\sigma}_2\right]$$

$$B_{\rm soo} = \frac{\alpha^2}{4}\left[\frac{1}{r_{12}^3}\mathbf{r}_{12} \times \mathbf{p}_2 \cdot (2\boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2) - \frac{1}{r_{12}^3}\mathbf{r}_{12} \times \mathbf{p}_1 \cdot (2\boldsymbol{\sigma}_2 + \boldsymbol{\sigma}_1)\right]$$
$$B_{\rm ss} = \frac{\alpha^2}{4}\left[-\frac{8}{3}\pi\delta(\mathbf{r}_{12}) + \frac{1}{r_{12}^3}\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2 - \frac{3}{r_{12}^3}(\boldsymbol{\sigma}_1\cdot\mathbf{r}_{12})(\boldsymbol{\sigma}_2\cdot\mathbf{r}_{12})\right]$$

Relativistic recoil terms (A.P. Stone, 1961)

$$\tilde{\Delta}_2 = -\frac{Z\alpha^2}{2}\left\{\frac{1}{r_1}(\mathbf{p}_1 + \mathbf{p}_2)\cdot\mathbf{p}_1 + \frac{1}{r_1^3}\mathbf{r}_1\cdot[\mathbf{r}_1\cdot(\mathbf{p}_1 + \mathbf{p}_2)]\mathbf{p}_1\right.$$
$$\left. + \frac{1}{r_2}(\mathbf{p}_1 + \mathbf{p}_2)\cdot\mathbf{p}_2 + \frac{1}{r_2^3}\mathbf{r}_2\cdot[\mathbf{r}_2\cdot(\mathbf{p}_1 + \mathbf{p}_2)]\mathbf{p}_2\right\}$$

$$\tilde{\Delta}_{\rm so} = \frac{Z\alpha^2}{2}\left(\frac{1}{r_1^3}\mathbf{r}_1 \times \mathbf{p}_2\cdot\boldsymbol{\sigma}_1 + \frac{1}{r_2^3}\mathbf{r}_2 \times \mathbf{p}_1\cdot\boldsymbol{\sigma}_2\right)$$

QED Corrections

the QED shift for a $1snL\ {}^{1,3}L$ state of helium has the form form

$$E_{\rm QED} = E_{\rm L,1} + E_{\rm M,1} + E_{\rm R,1} + E_{\rm L,2}$$

where the main one-electron part is (in atomic units)

$$E_{\rm L,1} \;=\; \frac{4Z\alpha^3\langle\delta(\mathbf{r}_i)\rangle^{(0)}}{3}\left\{\ln(Z\alpha)^{-2} - \beta(n\,{}^{1,3}L) + \frac{19}{30} + \cdots\right\}$$

the mass scaling and mass polarization corrections are

$$E_{\rm M,1} = \frac{\mu\langle\delta(\mathbf{r}_i)\rangle^{(1)}}{M\langle\delta(\mathbf{r}_i)\rangle^{(0)}}E_{\rm L,1} + \frac{4Z\alpha^3\mu\langle\delta(\mathbf{r}_i)\rangle^{(0)}}{3M}\left[1 - \Delta\beta_{\rm MP}(n\,{}^{1,3}L)\right]$$

and the recoil corrections (including radiative recoil) are given by

$$E_{\rm R,1} \;=\; \frac{4Z^2\mu\alpha^3\langle\delta(\mathbf{r}_i)\rangle^{(0)}}{3M}\left[\frac{1}{4}\ln(Z\alpha)^{-2} - 2\beta(n\,{}^{1,3}L) - \frac{1}{12} - \frac{7}{4}a(n\,{}^{1,3}L)\right]$$

where $\beta(n\,{}^{1,3}L) = \ln(k_0/Z^2R_\infty)$ is the two-electron Bethe logarithm.

For the $1snp\ {}^1P$ states, $\beta(n\,{}^1P) = 2.984\,128\,556 - \frac{0.004\,920(5)}{n^3} + \frac{0.00412(3)}{n^4} + \frac{0.00103(3)}{n^5}$

(G.W.F. Drake, Phys. Scr. **T95**, 22 (2001).)

$1/n^t$ expansion coefficients $c(X)_t$ for the spin-independent matrix elements needed to calculate the relativistic and QED contributions to the energy for the $1snp\ ^1P$ and $1snp\ 3P$ states of helium, and corresponding mass polarization coefficients $c(X)_t^{(1)}$. Units are atomic units.

t	$c(p_1^4)_t$	$c(H_2)_t/\alpha^2$	$c(\delta(\mathbf{r}_1))_t$	$c(\delta(\mathbf{r}_{12}))_t$	$c(\tilde{\Delta}_2^\dagger)_t$	$c(Q)_t$	$c(Q_1)_t$
			$1snp\ ^1P$ matrix element expansions				
0	40.000000	0.000000	4.000000	0.000000	0.000000	0.000000	$\frac{16}{\pi}\ln 2$
-3	-0.437302(12)	-0.1950586(14)	0.01072794(14)	0.007599141(3)	-3.51472(7)	0.027129179(8)	-7.0603391
-4	0.3910(5)	0.00712(6)	-0.000390(8)	-0.00027613(15)	2.1286(25)	-0.0009861(5)	-0.000003(
-5	-0.024(6)	0.1023(9)	0.00178(15)	-0.006460(3)	0.47(3)	0.000767(10)	0.00009(2
-6	0.01(4)	-0.007(6)	0.0002(14)	0.00069(4)	-0.04(16)	0.00093(11)	-0.008(4)
-7	0.12(9)	0.051(16)	-0.027(7)	-0.00108(19)	0.5(4)	-0.0006(6)	0.013(22)
-8	0.15(7)	0.032(15)	0.005(14)	0.0010(5)	0.51(29)	0.0016(15)	-0.06(6)
			μ/M mass polarization coefficient $c(X)_t^{(1)}$, $X = p_1^4, \cdots$				
-3	-2.6901(15)	1.193803(20)	0.2972(7)	-0.027375(4)	1.509(5)	-0.0413522(27)	-0.9191(21
-4	0.60(5)	-0.8024(12)	-0.021(17)	-0.00832(22)	2.44(14)	-0.03181(15)	0.03(5)
-5	-1.5(3)	0.379(25)	0.13(7)	0.003(3)	-4.4(1.0)	-0.0339(26)	-0.36(18)
-6	0.4(5)	-0.19(19)		0.023(13)	-1.9(1.6)	0.029(19)	
-7		-0.44(28)				-0.04(6)	
-8						0.07(6)	
			$1snp\ ^3P$ matrix element expansions				
0	40.000000	0.000000	4.000000	0.000000	0.000000	0.000000	$\frac{16}{\pi}\ln 2$
-3	0.404605(6)	0.2625288(17)	-0.10271175(29)		0.683366(20)	0.02502589(9)	-7.0603388
-4	0.4580(3)	0.05380(9)	-0.021048(20)		2.1403(12)	0.005129(5)	-0.00003(3
-5	0.311(6)	0.0083(16)	-0.0167(5)		0.939(23)	0.01085(10)	0.0007(7)
-6	0.07(6)	-0.018(14)	0.003(5)		0.24(21)	0.0016(8)	0.328(6)
-7	-0.23(27)	-0.11(6)	0.023(24)		-1.(1)	-0.000(4)	0.113(21)
-8	0.4(6)	0.05(13)	-0.03(5)		1.1(2.1)	0.006(7)	-0.044(28)
			μ/M mass polarization coefficient $c(X)_t^{(1)}$, $X = p_1^4, \cdots$				
-3	2.157(6)	1.1921(5)	-0.229(4)		4.295(20)	0.0273384(10)	0.7431(22
-4	0.95(17)	-0.401(13)	-0.16(10)		0.0(6)	0.03963(6)	0.61(7)
-5	6.4(1.3)	0.70(12)	-1.0(5)		15.(5)	0.0477(13)	2.3(5)
-6	4.0(2.0)	0.4(4)			14.(7)	0.056(13)	1.5(1.1)
-7						0.00(6)	
-8						0.16(14)	

$1/n^t$ expansion coefficients $c(X)_t$ for the spin-dependent matrix elements needed to calculate the relativistic contributions to the energy for the $1snp\ ^3P$ states of helium, and corresponding μ/M mass polarization coefficients $c(X)_t^{(1)}$. Units are α^2 atomic units.

t	$c(H_{\rm so})$	$c(H_{\rm soo})$	$c(H_{\rm ss})$	$c(\tilde{\Delta}_3)$
		$1snp\ ^3P$ matrix element expansions		
-3	1.5256025(3)	-2.200288(13)	-0.894235(4)	-4.465063(12)
-4	0.312563(21)	-0.4509(6)	-0.18326(21)	-0.9149(8)
-5	0.0523(5)	-0.342(10)	-0.364(4)	-0.129(17)
-6	-0.136(6)	0.08(8)	-0.05(4)	0.35(18)
-7	-0.08(4)	0.4(3)	0.02(15)	1.5(9)
-8	-0.24(16)	-0.2(7)	-0.2(3)	-0.3(2.0)
	μ/M mass polarization coefficient $c(X)_t^{(1)}$, $X = H_{\rm so}, \cdots$			
-3	3.0663(17)	-3.9158(17)	-1.11972(17)	-5.684(10)
-4	2.66(5)	-3.78(5)	-1.454(6)	-7.0(3)
-5	4.3(4)	-5.6(5)	-1.63(7)	-15.4(2.5)
-6	1.0(7)	-3.8(1.2)	-2.64(25)	-5.(5)
-7			-0.17(27)	

The Electron-Electron Term

The electron-electron part is (Araki and Sucher)

$$\Delta E_{L,2} \quad = \quad \alpha^3 \Big(\frac{14}{3} \ln \alpha + \frac{164}{15} \Big) \langle \delta(\mathbf{r}_{ij}) \rangle - \frac{14}{3} \alpha^3 Q \,, \tag{4}$$

where the Q term is defined by

$$Q \quad = \quad (1/4\pi) \lim_{\epsilon \to 0} \langle r_{ij}^{-3}(\epsilon) + 4\pi(\gamma + \ln \epsilon) \delta(\mathbf{r}_{ij}) \rangle \,. \tag{5}$$

γ is Euler's constant, ϵ is the radius of a sphere about $r_{ij} = 0$ excluded from the integration.

Finite Nuclear Size Correction

In lowest order

$$\Delta E_{\rm nuc} = \frac{2\pi Z r_{\rm rms}^2}{3} \langle \delta(\mathbf{r}_i) \rangle \,, \tag{6}$$

where $r_{\rm rms} = R_{\rm rms}/a_{\rm Bohr}$, $R_{\rm rms}$ is the root-mean-square radius of the nuclear charge distribution, and $a_{\rm Bohr}$ is the Bohr radius.

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		
$E^{(4)}_{\rm c}$ [1]	8.8180	-21.8320	-21.8320	-21.8320	-21.8320
$\Delta E^{(4)}_J$ [2]	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

[1] K. Pachucki, V. Patkóš, and V. A. Yerokhin, Phys. Rev. A **95**, 062510 (2017).

[2] V. Patkóš, V.A. Yerokhin and K. Pachucki, Phys. Rev. A **103**, 042809 (2021).

Contributions to the $1s24p\ ^1P_1$ state ionization energies of ^{4}He

Contribution	Value (MHz)
Nonrelativistic (Enr)	5704 993.752 9760
1st. order mass pol. EM(1)	26.773 6188
2nd. order mass pol. EM(2)	–0.108 9075
Relativistic (Erel)	–13.292 1518
Singlet-triplet mixing (Est)	0.002 2762
Relativistic finite mass (ERR)M	–0.006 7915
Relativistic recoil (ERR)X	0.003 7235
Finite nuclear size (Enuc)	0.000 0433
electron-nucl. QED EL(1)	0.070 6936
electron-electron QED EL(2)	–0.040 2072
Higher-order QED	0.0015(15)
Total	5704 980.3477(15)

Contributions to the $1s27p\,^3P_J$ states ionization energies of ^{4}He (in MHz)

Contribution	$E(27\,^3P_0)$	$E(27\,^3P_1)$	$E(27\,^3P_2)$
Nonrelativistic (Enr)	4 535 100.640 7014	4 535 100.640 7014	: 4 535 100.640 7014
1st. order mass pol.	20.914 2858	20.914 2858	20.914 2858
2nd. order mass pol.	0.085 9051	0.085 9051	0.085 9051
Relativistic (Erel)	–10.027 2677	0.013 4362	0.839 8532
Anomalous mag. mom.	–0.011 6111	0.006 6171	–0.001 6481
Singlet-triplet mixing	–0.000 0000	0.001 5974	–0.000 0000
Relativistic finite mass	0.000 7562	–0.001 4172	–0.000 4852
Relativistic recoil	–0.003 7958(5)	–0.001 9981(5)	–0.001 8456(5)
Finite nuclear size	0.000 2914(3)	0.000 2914(3)	0.000 2914(3)
electron-nucl. QED	0.431 9203	0.431 9203	0.431 9203
electron-electron QED	0.022 9100	0.022 9100	0.022 9100
Higher-order QED	0.001 7(24)	–0.000 86(12)	–0.000 98(25)
Total	4 535 112.0550(24)	4 535 122.11264(12)	4 535 122.93017(25)
Centroid		4 535 121.44931(12)	

Ionization energy of the $1s2s\,^1S_0$ state of ^{4}He (in MHz)

$$I_{\rm tot}(2\,^1S_0) = \nu_{\rm exp}(2\,^1S_0 - n\,^1P_1) + I_{\rm theo}(n\,^1P_1)$$

n	$\nu_{\rm exp}(2\,^1S_0 - n\,^1P_1)$[a]	$I_{\rm theo}(n\,^1P_1)$	$I_{\rm tot}(2\,^1S_0)$
24	954 627 060.151(30)	5 704 980.348(1)	960 332 040.499(30)
25	955 074 118.614(26)	5 257 921.948(1)	960 332 040.562(26)
26	955 470 615.084(34)	4 861 425.438(1)	960 332 040.522(34)
28	956 140 022.429(21)	4 192 018.126(1)	960 332 040.555(21)
30	956 680 116.330(34)	3 651 924.176(1)	960 332 040.506(34)
32	957 122 179.519(22)	3 209 861.007(1)	960 332 040.526(23)
35	957 648 684.552(25)	2 683 355.970(1)	960 332 040.522(26)
40	958 277 418.204(42)	2 054 622.318(1)	960 332 040.522(42)
45	958 708 525.814(21)[b]	1 623 514.662(1)	960 332 040.476(21)
50	959 016 922.718(35)[b]	1 315 117.770(1)	960 332 040.488(35)
53	959 161 558.215(16)[b]	1 170 482.283(1)	960 332 040.498(16)
55	959 245 118.319(24)[b]	1 086 922.139(1)	960 332 040.458(24)
60	959 418 690.453(19)[b]	913 350.100(1)	960 332 040.553(19)
65	959 553 777.176(21)[b]	778 263.352(1)	960 332 040.528(21)
70	959 660 968.990(51)[b]	671 071.503(1)	960 332 040.493(51)
75	959 747 449.162(41)[b]	584 591.356(1)	960 332 040.518(41)
80	959 818 229.110(37)[b]	513 811.389(1)	960 332 040.499(37)
85	959 876 891.522(72)[b]	455 149.009(1)	960 332 040.531(72)
90	959 926 052.374(57)[b]	405 988.119(1)	960 332 040.493(57)
96	959 975 209.033(76)[b]	356 831.511(1)	960 332 040.544(76)
102	960 015 949.716(114)[b]	316 090.7461)	960 332 040.462(114)
	Average (weighted)		960 332 040.532(21)
	QDT Extrap.		960 332 040.501(32)
	Theory (Pachucki/Drake)		960 332 038.0(2.0)
	Difference		2.5(2.0)

[a] G. Clausen et.al. Phys. Rev. Lett. **127**, 093001 (2021).

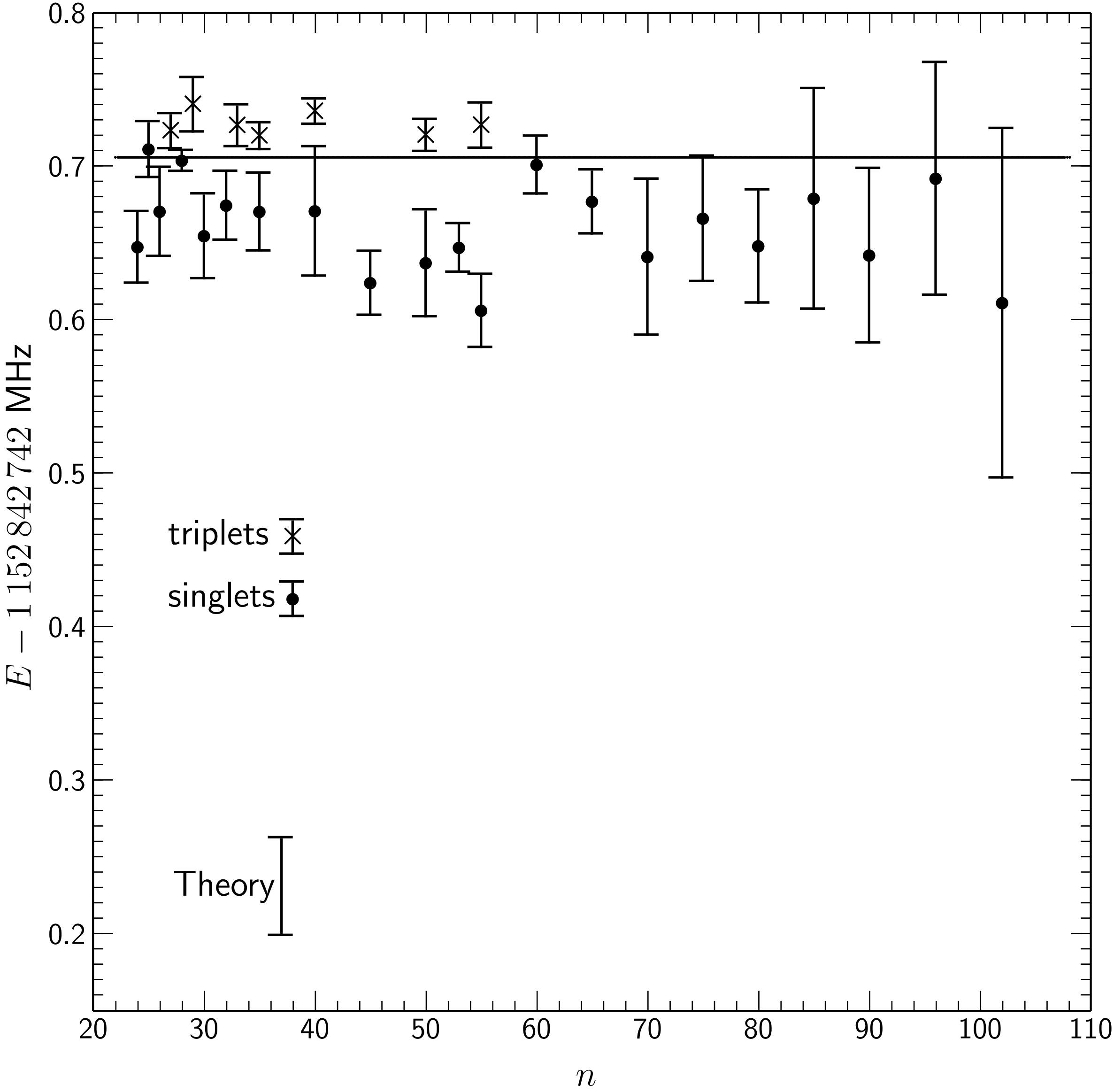
[b] Includes a Stark shift correction (G. Clausen and F. Merkt, private communication, 2026).

Ionization energy of the $1s2s\ ^3S_1$ state of ^{4}He (in MHz)

$$I_{\rm tot}(2\ ^3S_1) = \nu_{\rm exp}(2\ ^3S_1 - n\ ^3P_{\rm c}) + I_{\rm theo}(n\ ^3P_{\rm c})$$

n	$\nu_{\rm exp}(2\ ^3S_0 - n\ ^3P_{\rm c})^{\rm a}$	$I_{\rm theo}(n\ ^3P_{\rm c})$	$I_{\rm tot}(2\ ^3S_0)$
27	1148 307 621.274(11)	4535 121.449(2)	1152 842 742.723(11)
29	1148 912 959.549(18)	3929 783.192(2)	1152 842 742.740(18)
27	1148 307 621.274(11)	4535 121.449(2)	1152 842 742.723(12)
29	1148 912 959.549(17)	3929 783.192(2)	1152 842 742.740(18)
33	1149 809 632.367(13)	3033 110.360(2)	1152 842 742.727(14)
35	1150 147 008.567(08)	2695 734.153(2)	1152 842 742.720(09)
40	1150 779 829.987(07)	2062 912.749(1)	1152 842 742.736(08)
50	1151 523 381.730(10)	1319 360.990(1)	1152 842 742.720(11)
55	1151 752 633.012(14)	1090 109.715(1)	1152 842 742.727(15)
Average (weighted)			1152 842 742.727(11)
$I(2\ ^1S_0)+\nu(2\ ^1S_0-2\ ^3S_1)$			1152 842 742.680(21)
Grand average (weighted)			1152 842 742.705(16)
QDT Extrap.			1152 842 742.708(6) [a]
$2\ ^3S_1-8\ ^3D_1$			1152 842 742.652(54) [b]
Theory (Pachucki/Drake)			1152 842 742.231(52)
Difference			0.500(52)

[a] G. Clausen et al. Phys. Rev. A **111**, 012817 (2025).
[b] M. H. Wu et al., Phys. Rev. A **111**, 052809 (2025).



0.8
0.7
0.6
0.5
0.4
0.3
0.2
E − 1 152 842 742 MHz
triplets
singlets
Theory
20
30
40
50
60
70
80
90
100
110
n

Comparison of experimental and theoretical values for the ionization energies of the low-lying states of ^{4}He (MHz)

State	Experiment	Refs.	Theory	Refs.	Difference
$2\,^3S_1$	1152 842 742.708(6)	[1]	1152 842 742.231(52)	[9]	0.477(52)
$2\,^3S_1$	1152 842 742.705(16)	[2]	1152 842 742.231(52)	[9]	0.474(52)
$2\,^3P_1$	876 106 247.025(39)	[3,4,5,6]	876 106 246.611(16)	[9]	0.414(42)
$3\,^3D_1$	366 018 892.638(65)	[3,7]	366 018 892.691(23)	[10]	–0.053(69)
$3\,^1D_2$	365 917 748.688(34)	[8]	365 917 748.661(19)	[10]	0.027(38)

[1] G. Clausen et al., Phys. Rev. A **111**, 012817 (2025)

[2] Ref. [1] plus present theory.

[3] R.J. Rengelink et al., Nat. Phys. **14**, 1132 (2018)

[4] X. Zhang et al., Phys. Rev. Lett., **119**, 263002 (2017)

[5] P. Cansio Pastor et al., Phys. Rev. Lett., **92**, 023001 (2004)

[6] P. Cansio Pastor et al., Phys. Rev. Lett., **108**, 143001 (2012)

[7] C. Dorrer et al., Phys. Rev. Lett., **78**, 3658 (1997)

[8] Y.-J. Huang et al., Phys. Rev. A **97**, 032516 (2018)

[9] V. Patkos et al., Phys. Rev. A **103**, 042809 (2021)

[10] V.A. Yerokhin et al., Phys. Rev. A **102**, 012807 (2020)

SUMMARY AND DISCUSSION

- We have obtained the first high-precision eigenvalues for P-states with $n > 10$ up to $n = 35$, and quantum defect extrapolations to $n = 102$.
- There is excellent agreement from $n = 24$ to 102 with the Zurich measurements of Clausen et al., but a 9σ discrepancy of about 0.4 MHz remains for the $2\ ^3S$ state of helium.
- We have put the effective value of the Rydberg used in the quantum defect method on a firm theoretical foundation.

On-line resources are available at drake.sharcnet.ca.