

Review of High Precision Theory and Experiment for Helium

Gordon W. F. Drake

Department of Physics, University of Windsor, Windsor, Ontario N9B 3P4, Canada

Abstract. Progress in obtaining essentially exact solutions to the nonrelativistic Schrödinger equation for the entire singly-excited spectrum of helium and other three-body systems is reviewed, and a new upper bound for the ground state is presented. The calculation of relativistic and quantum electrodynamic corrections is discussed, including high precision values for the Bethe logarithm. The results are compared with high precision measurements of ionization energies in helium. Recent progress is reviewed in determining the fine structure intervals in helium with the objective of determining the fine structure constant to an accuracy of ± 1.7 parts in 10^8 or better. Extensions to lithium-like systems are briefly summarized.

1 Introduction

Hydrogen and other two-body systems have long been regarded as the ‘fundamental’ systems of atomic physics because the Schrödinger (or Dirac) equation can be solved exactly to give a lowest-order description of the system. The results to be reviewed here will show that helium (and other three-body systems) now stand on the same footing with hydrogen in that solutions to the Schrödinger equation that are essentially exact for all practical purposes are readily obtainable. The same is true for the lowest-order relativistic corrections. Interest therefore shifts to the higher order relativistic and QED corrections in helium, and especially the specifically two-electron effects that are not found in hydrogen. From an experimental point of view, helium has the advantage of being a monatomic gas that is easy to work with, and the triplet part of the spectrum has line widths that are narrower than in the case of hydrogen.

This paper gives a brief survey of the variational and asymptotic expansion methods used to solve the nonrelativistic problem, and the principal effects that must be taken into account in order to estimate the higher-order QED corrections. The lowest order QED shift can now be calculated to high precision, and there has been much recent progress on the next-to-lowest order terms.

There are two basic approaches to the theory of atomic helium, depending on whether the nuclear charge Z is small or large. For low- Z atoms and ions, the principal challenge is the accurate calculation of nonrelativistic electron correlation effects. Relativistic corrections can then be included by perturbation theory. For high- Z ions, relativistic effects become of dominant importance and must be taken into account to all orders via the one-electron Dirac equation. Corrections due to the electron-electron interaction can then be included by perturbation theory. The cross-over point between the two regimes is approximately $Z = 27$

where correlation effects (proportional to Z) are about the same size as relativistic effects (proportional to $\alpha^2 Z^4$). Both methods yield useful results over a substantial range of Z , leading to interesting comparisons between them. The main emphasis in this paper is on the region of low Z where an expansion of relativistic and QED effects in powers of αZ as well as α is useful.

The paper is organized as follows. Section 2 outlines the principal effects that must be taken into account, and summarizes the principal high precision measurements in helium and He-like ions. Then Sects. 3 and 5 describe the main ideas concerning the calculation of high precision nonrelativistic wave functions and energies, and the lowest-order relativistic corrections. These results are extended to Rydberg states with high angular momentum L by means of asymptotic expansion methods in Sect. 4. Since all of these contributions can be calculated to high precision, the central issue is the calculation of quantum electrodynamic (QED) effects as discussed in Sect. 6. The results are then compared with experiment in Sect. 7, including recent work on the determination of the fine structure constant from the helium fine structure splittings. The latter section also briefly reviews recent progress for the case of lithium. The aim throughout is to give the main ideas and results, together with appropriate references. This review is an update of an earlier conference proceeding published previously [1].

2 Principal Effects

The principal effects that must be taken into account, and their relative orders of magnitude, are as listed in Table 1. In the table, μ/M is the ratio of the reduced electron mass to the nuclear mass for ^4He , and α^2 is the square of the fine structure constant. Since these basic expansion parameters are about the same size for helium, the corresponding contributions to the energy are comparable in magnitude. The nonrelativistic energy refers to the energy for a hypothetical atom with infinite nuclear mass, and the mass polarization corrections (specific mass shift) arise from the fact that the dynamics of the actual nucleus in the center-of-mass frame must also be taken into account. The lowest-order relativistic corrections come from the Breit-Pauli interaction, and the relativistic recoil terms are finite nuclear mass corrections to these. The anomalous magnetic moment terms are simply taken into account as corrections to the basic Breit-Pauli interaction. All of these terms can be calculated to very high precision and subtracted from the observations, leaving the Lamb shift (QED) terms as the principal additional effect to be taken into account in comparing theory with experiment. This term gives by far the largest contribution to the theoretical uncertainty.

The types of information that can be extracted are illustrated by a typical experiment involving, say, transitions between the $1s2s\ ^3S$ state and the fine structure levels of the $1s2p\ ^3P_{0,1,2}$ manifold of states. The total transition frequency gives the QED shift, for which theory is not yet fully developed and experimental checks are very valuable. However, if one measures the $^3\text{He} - ^4\text{He}$ isotope shift for the same transition, then the QED uncertainty largely cancels, allowing the differential nuclear radius to be accurately determined. If one measures

Table 1. Contributions to the energy and their orders of magnitude. The expansion parameters are Z , $\mu/M = 1.370\,745\,620 \times 10^{-4}$, and $\alpha^2 = 0.532\,513\,6197 \times 10^{-4}$

Contribution	Magnitude
Nonrelativistic energy	Z^2
Mass polarization	$Z^2\mu/M$
Second-order mass polarization	$Z^2(\mu/M)^2$
Relativistic corrections	$Z^4\alpha^2$
Relativistic recoil	$Z^4\alpha^2\mu/M$
Anomalous magnetic moment	$Z^4\alpha^3$
Lamb shift	$Z^4\alpha^3 \ln \alpha + \dots$
Finite nuclear size	$Z^4\langle R_N/a_0 \rangle^2$

the isotope shift in the fine structure intervals, then the nuclear size correction also becomes negligible, providing an internal consistency check on both theory (especially for hyperfine structure) and experiment. Finally, a comparison with theory for the fine structure intervals themselves provides a measurement of the fine structure constant α .

The availability of high precision theory has stimulated a number of recent experiments of the above types, as summarized in Table 2. Most of these will not be discussed in detail here, but a few of them will be quoted as examples.

3 Nonrelativistic Wave Functions

The basic two-electron problem to be solved is illustrated in Fig. 1. A nucleus of charge Z is located at the origin, and the two electrons have position vectors \mathbf{r}_1 and \mathbf{r}_2 with an angle θ between them. The distance between the two electrons is $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. Assuming (for the moment) infinite nuclear mass, the Hamiltonian is (in atomic units)

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

and the Schrödinger equation to be solved is

$$H\Psi(\mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{r}_1, \mathbf{r}_2). \quad (2)$$

The presence of the $1/r_{12}$ Coulomb repulsion term in Eq. (1) makes the Schrödinger equation nonseparable, and so exact analytic solutions cannot be found. Early in the history of quantum mechanics, Hylleraas [23] suggested expanding the wave function in the form (generalized for states of arbitrary angular momentum L)

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2) = & \sum_{i,j,k}^{i+j+k \leq \Omega} a_{ijk} r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} \mathcal{Y}_{l_1, l_2, L}^M(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \\ & \pm \text{exchange term}, \end{aligned} \quad (3)$$

Table 2. Summary of high precision measurements for helium and He-like ions

Group		Measurements
Amsterdam ^a	He	$1s^2\ ^1S - 1s2p\ ^1P$
NIST ^b	He	$1s^2\ ^1S - 1s2p\ ^1P$
Harvard ^c	He	$1s2s\ ^3S - 1s2p\ ^3P$
North Texas ^d	He	$1s2s\ ^3S - 1s2p\ ^3P$
Florence ^e	He	$1s2s\ ^3S - 1s3p\ ^3P$
Paris ^f	He	$1s2s\ ^3S - 1s3d\ ^3D_1$
York ^g	He	$1s2p\ ^3P_1 - 1s2p\ ^3P_0$
York ^h	He	$1s2p\ ^3P_2 - 1s2p\ ^3P_1$
North Texas ⁱ	He	$1s2p\ ^3P_2 - 1s2p\ ^3P_1$
NIST ^j	He	$1s2s\ ^1S - 1snp\ ^1P$
Yale ^k	He	$1s2s\ ^1S - 1snd\ ^1D$
Colorado State ^l	He	$10\ ^{1,3}L - 10\ ^{1,3}(L+1)$
Colorado State ^m	He	$n = 7, 9, 10\ \text{G-H, H-I intervals}$
York ⁿ	He	$10\ ^{1,3}L - 10\ ^{1,3}(L+1)$
Strathclyde ^o	Li ⁺	$1s2s\ ^3S - 1s2p\ ^3P$
U. of Western Ontario ^p	Be ⁺⁺	$1s2s\ ^3S - 1s2p\ ^3P$
Argonne ^q	B ³⁺	$1s2s\ ^3S - 1s2p\ ^3P$
Florida State ^r	N ⁵⁺	$1s2s\ ^3S - 1s2p\ ^3P$
Oxford ^s	F ⁷⁺	$1s2p\ ^3P\ \text{fine structure}$
Florida State ^t	F ⁷⁺	$1s2p\ ^3P\ \text{fine structure}$
Florida State ^u	Mg ¹⁰⁺	$1s2p\ ^3P\ \text{fine structure}$

^aEikema *et al.* [2]^lClaytor, Hessels, and Lundeen [3]^bBergeson *et al.* [4]^mStevens and Lundeen [5]^cWen and Gabrielse [6]ⁿStorry, Rothery, and Hessels [7]^dShiner *et al.* [8]^oRiis *et al.* [9]^eMarin *et al.* [10]^pScholl *et al.* [11]^fDorrer *et al.* [12]^qDinneen *et al.* [13]^gStorry and Hessels [14]^rThompson *et al.* [15]^hStorry, George and Hessels [16]^sMyers *et al.* [17]ⁱCastilega *et al.* [18]^tMyers *et al.* [19]^jSansonetti and Gillaspay [20]^uMyers and Tarbutt [21]^kLichten *et al.* [22]

where the a_{ijk} are linear variational coefficients, and $\mathcal{Y}_{l_1, l_2, L}^M(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$ represents a vector-coupled product of spherical harmonics with angular momenta l_1 and l_2 to form a state with total angular momentum L . α and β are additional nonlinear scale factors that can be separately adjusted to optimize the energy. The usual procedure is to include all powers i, j, k such that $i + j + k \leq \Omega$, and to study the convergence as the integer Ω is progressively increased. If all powers are included, the number of terms in the basis set is

$$N = \frac{1}{6}(\Omega + 1)(\Omega + 2)(\Omega + 3) \quad (4)$$

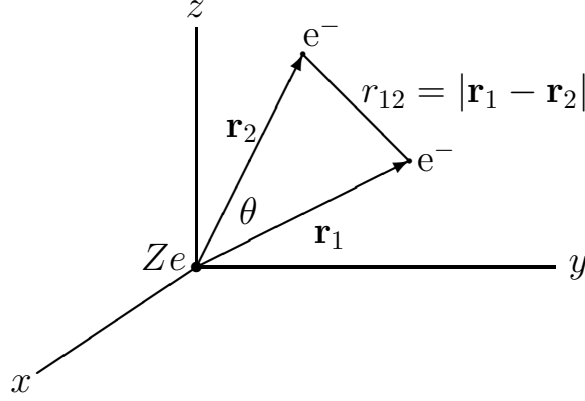


Fig. 1. Geometry of the two-electron helium problem

and so grows rapidly with Ω .

The principal computational step is to diagonalize the \mathbf{H} matrix in the nonorthogonal basis set defined by

$$\begin{aligned} \varphi_{ijk}(\alpha, \beta) = & r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} \mathcal{Y}_{l_1, l_2, L}^M(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \\ & \pm \text{exchange term.} \end{aligned} \quad (5)$$

This is equivalent to satisfying the variational condition

$$\delta \int \Psi^* (H - E) \Psi d\tau = 0. \quad (6)$$

The first several variational eigenvalues are then upper bounds to the true eigenvalues, provided only that the correct *number* of variational eigenvalues lies below (Hylleraas-Undheim-MacDonald Theorem [24]), and the eigenvector coefficients are the optimum values of the a_{ijk} coefficients in Eq. (3). For fixed α and β , all the eigenvalues move inexorably downward toward the exact energies as Ω is progressively increased.

Early calculations with small basis sets containing just a few powers of r_{12} easily recovered nearly all the correlation energy (see Bethe and Salpeter [25] for a review). These results demonstrated the great efficiency of Hylleraas-type basis sets in describing electron correlation.

Further Hylleraas-type calculations with basis sets of increasing size and sophistication, culminating with the work of Pekeris and coworkers in the 1960's (see Accad, Pekeris, and Schiff [26]) showed that nonrelativistic energies accurate to a few parts in 10^9 could be obtained by this method, at least for the low-lying states of helium and He-like ions. However, these calculations also revealed two serious numerical problems. First, it is difficult to improve upon this accuracy of a few parts in 10^9 without using extremely large basis sets where roundoff error and numerical linear dependence become a problem. Second, as

is typical of variational calculations, the accuracy is best for the lowest state of each symmetry, but rapidly deteriorates with increasing n .

3.1 Recent Advances

Over the past 15 years, both of the above limitations on accuracy have been resolved by “doubling” the basis set so that each combination of powers i, j, k is included twice with different exponential scale factors [27,28,29]. Explicitly, each basis function $\varphi_{ijk}(\alpha, \beta)$ defined by Eq. (5) is replaced by

$$\tilde{\varphi}_{ijk} = a_A \varphi_{ijk}(\alpha_A, \beta_A) + a_B \varphi_{ijk}(\alpha_B, \beta_B) \quad (7)$$

where a_A and a_B are independent variational parameters, and $(\alpha_A, \beta_A), (\alpha_B, \beta_B)$ are two sets of exponential scale factors that are common to all the basis set members. A complete optimization with respect to all the exponential scale factors leads to a natural partition of the basis set into two distinct distance scales—one appropriate to the long-range asymptotic behavior of the wave function, and one appropriate to the complex correlated motion near the nucleus. The greater flexibility in the available distance scales allows a much better physical description of the atomic wave function, especially for the higher-lying Rydberg states where two sets of distance scales are clearly important. However, the multiple distance scales also greatly improve the accuracy for the low-lying states. With care, the basis set size can be reduced by omitting some of the powers i, j, k from one of the two sectors (see Ref. [28] for further details).

As a final subtlety, the screened hydrogenic wave function $\psi_{1s}^Z(\mathbf{r}_1)\psi_{nL}^{Z-1}(\mathbf{r}_2) \pm \text{exchange}$ is included as an additional independent member of the basis set. Without this term, rather large basis sets are required just to recover the screened hydrogenic energy $-2 - (Z-1)^2/(2n^2)$ for Rydberg states.

The $1s^2\ ^1S$ ground state of helium has been particularly intensively studied by many authors as a classic example of the three-body problem. For this case, we have found that for very large basis sets, it is advantageous to introduce a triple basis set with three sets of nonlinear parameters representing the asymptotic, intermediate and short range behavior of the wave function. Fig. 2 shows the systematic way in which the optimized α_i and β_i vary with Ω in each of the three sectors. Standard quadruple precision (32 decimal digit) arithmetic is sufficient to maintain numerical stability, provided that the nonlinear parameters are allowed to continue increasing with Ω as shown in Fig. 2. Table 3 shows the convergence pattern for the energy. The quantity $R(\Omega)$ in the last column is the ratio of successive differences defined by

$$R(\Omega) = \frac{E(\Omega - 1) - E(\Omega - 2)}{E(\Omega) - E(\Omega - 1)}. \quad (8)$$

If $R(\Omega)$ were a constant, then the series could be extrapolated to $\Omega = \infty$ as a geometric series. The tabulated values are not quite constant, but the variation with Ω is sufficiently smooth that a reliable extrapolation can be made. The results are in good agreement with other recent calculations using entirely different

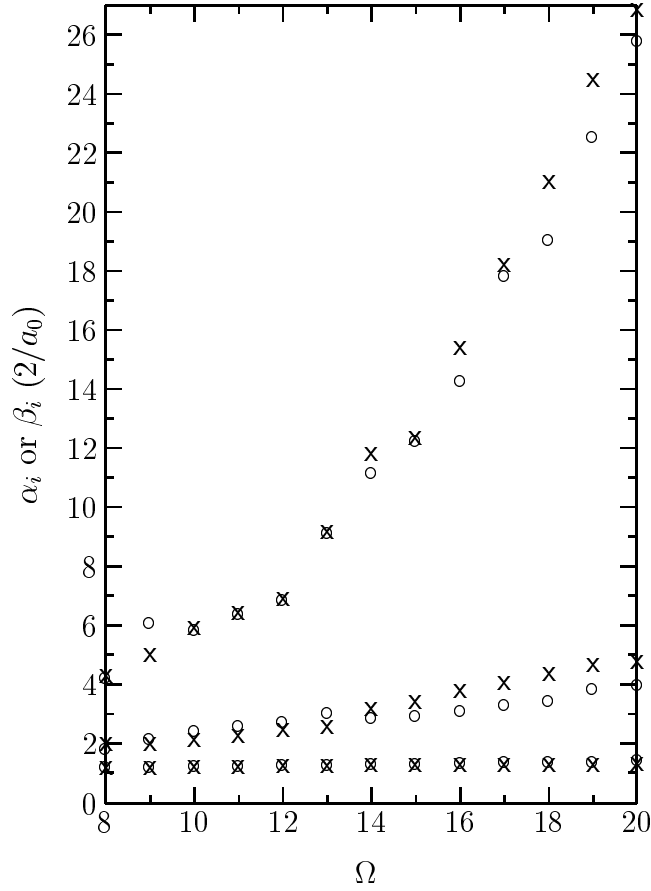


Fig. 2. Variation of the exponential scale factors with basis set size for the helium $1s^2\ ^1S$ state. The three pairs of curves are for a triple basis set with \circ for α and \times for β in each of the three sectors. $\Omega = i + j + k$ is the sum of powers in each sector

basis set methods, suggesting that the indicated accuracy of 3 parts in 10^{22} is meaningful. The results in Table 3 are an update of those presented in Ref. [34]. The variational bound for the 2358 term basis set in Table 3 is the best upper bound in the literature. It surpasses the one obtained recently by Korobov [30] using a basis set consisting entirely of terms with complex nonlinear parameters chosen in a quasi-random manner.

4 Asymptotic Expansions

Results of similar accuracy are now available for all the higher-lying $1snl\ ^{1,3}L$ Rydberg states of helium up to $n = 10$ and $L = 7$ (see Drake [35] and earlier references therein). One might object that these long strings of figures are just

Table 3. Convergence study for the ground state energy of helium, using a triple basis set (in atomic units). $R(\Omega)$ is the ratio of successive differences between the tabulated energies

Ω	$N_{\text{tot}}(\Omega)$	$E(\Omega)$	$R(\Omega)$
8	269	-2.903 724 377 029 560 058 400	
9	347	-2.903 724 377 033 543 320 480	
10	443	-2.903 724 377 034 047 783 838	7.90
11	549	-2.903 724 377 034 104 634 696	8.87
12	676	-2.903 724 377 034 116 928 328	4.62
13	814	-2.903 724 377 034 119 224 401	5.35
14	976	-2.903 724 377 034 119 539 797	7.28
15	1150	-2.903 724 377 034 119 585 888	6.84
16	1351	-2.903 724 377 034 119 596 137	4.50
17	1565	-2.903 724 377 034 119 597 856	5.96
18	1809	-2.903 724 377 034 119 598 206	4.90
19	2067	-2.903 724 377 034 119 598 286	4.44
20	2358	-2.903 724 377 034 119 598 305	4.02
Extrapolation	∞	-2.903 724 377 034 119 598 311(1)	
Korobov [30]	2200	-2.903 724 377 034 119 598 296	
Korobov extrap.	∞	-2.903 724 377 034 119 598 306(10)	
Goldman [31]	8066	-2.903 724 377 034 119 593 82	
Bürgers <i>et al.</i> [32]	24 497	-2.903 724 377 034 119 589(5)	
Baker <i>et al.</i> [33]	476	-2.903 724 377 034 118 4	

Table 4. Variational energies for the $n = 10$ singlet and triplet states of helium

State	Singlet	Triplet
10 S	-2.005 142 991 747 919(79)	-2.005 310 794 915 611 3(11)
10 P	-2.004 987 983 802 217 9(26)	-2.005 068 805 497 706 7(30)
10 D	-2.005 002 071 654 256 81(75)	-2.005 002 818 080 228 84(53)
10 F	-2.005 000 417 564 668 80(11)	-2.005 000 421 686 604 88(26)
10 G	-2.005 000 112 764 318 746(22)	-2.005 000 112 777 003 317(21)
10 H	-2.005 000 039 214 394 532(17)	-2.005 000 039 214 417 416(17)
10 I	-2.005 000 016 086 516 1947(3)	-2.005 000 016 086 516 2194(3)
10 K	-2.005 000 007 388 375 8769(0)	-2.005 000 007 388 375 8769(0)

numerology with little physical content. However, with increasing L , one can give a full physical account of the variational results by means of a simple (in concept) core polarization model largely developed by Drachman [36] (see also Drake [29]). An examination of the eigenvalues for the $n = 10$ Rydberg states listed in Table 4 reveals two significant features. First, with increasing L , the

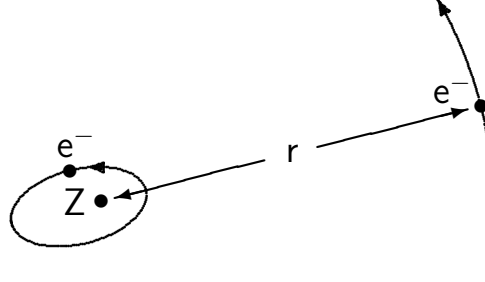


Fig. 3. Illustration of the physical basis for the asymptotic expansion method in which the Rydberg electron moves in the field generated by the polarized core

first several figures are accounted for by the screened hydrogenic energy

$$E_{\text{SH}} = -\frac{Z^2}{2} - \frac{(Z-1)^2}{2n^2} \quad (9)$$

$$= -2.005 \quad \text{for } Z = 2, n = 10$$

corresponding to the energy of the inner $1s$ electron with the full nuclear charge Z , and the outer nl electron with the screened nuclear charge $Z-1$. Second, the singlet-triplet splitting goes rapidly to zero with increasing L . This suggests that for sufficiently high L , one can treat the Rydberg electron as a distinguishable particle moving in the field of the polarizable core consisting of the nucleus and the tightly bound $1s$ electron. As illustrated in Fig. 3, the various multipole moments of the core then give rise to an asymptotic potential of the form

$$\Delta V(r) = \frac{c_4}{r^4} + \frac{c_6}{r^6} + \frac{c_7}{r^7} + \dots \quad (10)$$

where r is the coordinate of the Rydberg electron. In first order, the correction to the energy is then $\langle \Delta V(r) \rangle$, where the expectation value is with respect to the Rydberg electron. Since the core is a hydrogenic system, all the c_i coefficients and expectation values can be calculated analytically. For example, c_4 is related to the core polarizability $\alpha_1 = (9/32)a_0^3$ by $c_4 = -\alpha_1/2$ (a_0 is the Bohr radius), and c_6 is related to the quadrupole polarizability $\alpha_2 = (15/64)a_0^5$ and a nonadiabatic correction to the dipole polarizability $\beta_1 = (43/512)a_0^5$ by $c_6 = -\alpha_2/2 + 3\beta_1$. Detailed expressions for the higher order terms up to c_{10} have been derived (see Drachman [36] for further discussion). Each term can be calculated analytically by repeated use of the perturbation methods of Dalgarno and Lewis [37]. However, the expansion must be terminated at $i = 2(L+1)$ because the expectation values $\langle r^{-i} \rangle$ diverge beyond this point. In this sense, the series must be regarded as an asymptotic expansion.

As an example, Table 5 shows that the terms up to c_{10} , together with a second-order perturbation correction [38], account for the variationally calculated energy of the $1s10k$ state to within an accuracy of only a few Hz. All the entries can be expressed analytically as rational fractions. For example, the $c_4\langle r^{-4} \rangle$ contribution is exactly (in atomic units)

$$\begin{aligned} c_4\langle r^{-4} \rangle &= -\frac{3 \times 61}{2^{10} \times 5^6 \times 7 \times 13 \times 17} \\ &= -7.393\,341\,95 \cdots \times 10^{-9}. \end{aligned} \quad (11)$$

Since the accuracy of the asymptotic expansion rapidly gets even better with increasing L , there is clearly no need to perform numerical solutions to the Schrödinger equation for $L > 7$. The entire singly excited spectrum of helium is covered by a combination of high precision variational solutions for small n and L , quantum defect extrapolations for high n , and asymptotic expansions based on the core polarization model for high L . The complete asymptotic expansion for helium up to $\langle r^{-10} \rangle$ is [36,29]

$$\begin{aligned} E_{nL} = & -2 - \frac{1}{2n^2} + \frac{1}{2} \left\{ -\frac{9}{32}\langle r^{-4} \rangle + \frac{69}{256}\langle r^{-6} \rangle + \frac{3833}{7680}\langle r^{-7} \rangle \right. \\ & - \left[\frac{55923}{32768} + \frac{957}{5120}L(L+1) \right] \langle r^{-8} \rangle - \frac{908185}{344064}\langle r^{-9} \rangle \\ & + \left. \left[\frac{3824925}{524288} + \frac{33275}{14336}L(L+1) \right] \langle r^{-10} \rangle \right\} \\ & + e_{2,0}^{1,1} - \frac{23}{20}e_{2,0}^{1,2}. \end{aligned} \quad (12)$$

The last two terms are small second-order dipole-dipole and dipole-quadrupole perturbation corrections. The numerical values of all these terms for the example of the $1s10k$ state are as listed in Table 5.

5 Relativistic Corrections

The lowest order relativistic corrections are given by expectation values of the well-known Breit interaction [25]

$$\begin{aligned} H_{\text{rel}} = & B_1 + B_2 + B_{3Z} + B_{3e} + B_5 \\ & + \frac{Z\pi\alpha^2}{2} \sum_{i=1}^2 \delta(\mathbf{r}_i) - \pi\alpha^2 \left(1 + \frac{8}{3} \mathbf{s}_1 \cdot \mathbf{s}_2 \right) \delta(\mathbf{r}_{12}) \end{aligned} \quad (13)$$

where $B_1 = -(\alpha^2/8) \sum_{i=1}^2 \nabla_i^4$, B_2 is the orbit-orbit interaction, B_{3Z} is the spin-orbit interaction, B_{3e} is the spin-other-orbit interaction proportional to the spin sum $s_1 + 2s_2$, and B_5 is the spin-spin interaction. In addition, finite-nuclear-mass corrections of $O(\alpha^2\mu/M)$ au come from the mass scaling of these terms, cross terms with the mass polarization operator, and the relativistic recoil terms $\tilde{\Delta}_2$

Table 5. Asymptotic expansion for the energy of the 1s10k state of helium

Quantity	Value
$-Z^2/2$	-2.000 000 000 000 000 00
$-1/(2n^2)$	-0.005 000 000 000 000 00
$c_4\langle r^{-4} \rangle$	-0.000 000 007 393 341 95
$c_6\langle r^{-6} \rangle$	0.000 000 000 004 980 47
$c_7\langle r^{-7} \rangle$	0.000 000 000 000 278 95
$c_8\langle r^{-8} \rangle$	-0.000 000 000 000 224 33
$c_9\langle r^{-9} \rangle$	-0.000 000 000 000 002 25
$c_{10}\langle r^{-10} \rangle$	0.000 000 000 000 003 73
Second order	-0.000 000 000 000 070 91
Total	-2.005 000 007 388 376 30(74)
Variational	-2.005 000 007 388 375 8769(0)
Difference	-0.000 000 000 000 000 42(74)

and $\tilde{\Delta}_3$ first derived by Stone [39]. All of these effects can be calculated to high precision and included in the final results as described in Refs. [27,28,29,35]. Asymptotic expansions analogous to those discussed in Sect. 4 are also known for all these terms [27,28,29]. As with the nonrelativistic energy, they provide accurate numerical values for $L \geq 7$.

6 Quantum Electrodynamic Corrections

All the terms up to this point can be calculated to high precision, leaving a finite residual piece due to higher order relativistic and quantum electrodynamic effects which lie at the frontier of current theory.

6.1 Electron-Nucleus Terms

The leading QED term of $O(\alpha^3)$ is the first term to present new computational challenges. It contains contributions coming from both the electron-nucleus interactions of leading order $\alpha^3 Z^4$, and the electron-electron interaction of leading order $\alpha^3 Z^3$. As derived by Kabir and Salpeter [40], the general form of the electron-nucleus part $\Delta E_{L,1}^{(3)}$ for helium is simply obtained from the corresponding hydrogenic case by inserting the correct electron density at the nucleus in place of the hydrogenic quantity $\langle \delta(\mathbf{r}) \rangle = Z^3/(\pi n^3)$. The lowest-order QED shift is then

$$\Delta E_{L,1}^{(3)} = \frac{4\alpha^3 Z}{3} \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle \left[\ln(Z\alpha)^{-2} + \frac{19}{30} - \beta(nLS) \right]. \quad (14)$$

This part is easily done, but the Bethe logarithm $\beta(nLS)$, representing the emission and absorption of virtual photons, is much more difficult to calculate. It is

Table 6. $1/n$ expansion coefficients b_i for the Bethe logarithms of helium. The coefficients d_1 and d_2 give the finite mass correction due to mass polarization effects on the wave function. See Eqs. (16) and (17)

State	b_1	b_2	b_3	d_1	d_2
n^1S	-0.030 979(7)	-0.022 48(4)	0.040 55(5)	0.151 3(5)	-0.0188(9)
n^3S	-0.033 80(2)	-0.053 4(1)	0.037 6(1)	0.008 3(6)	0.060(1)
n^1P	-0.004 920(5)	0.004 12(3)	0.001 03(3)	-0.028(1)	—
n^3P	-0.006 71(2)	0.002 05(12)	0.008 76(15)	0.068(1)	—
n^1D	-0.000 621(2)	0.000 93(1)	0.000 52(2)	—	—
n^3D	-0.000 329(3)	0.001 24(2)	-0.001 40(4)	—	—

defined in terms of a sum over virtual two-electron intermediate states by

$$\beta(nLS) = \frac{\sum_m |\langle 0 | \mathbf{p}_1 + \mathbf{p}_2 | m \rangle|^2 (E_m - E_0) \ln[2Z^{-2}(E_m - E_0)]}{\sum_m |\langle 0 | \mathbf{p}_1 + \mathbf{p}_2 | m \rangle|^2 (E_m - E_0)}. \quad (15)$$

The accurate calculation of $\beta(nLS)$, until recently regarded as one of the most challenging problems in atomic structure theory, is now solved. The computational difficulty is that the sum in the numerator is very nearly divergent, and so the dominant contribution comes from states lying high in the scattering continuum (both one- and two-electron). In monumental calculations based on explicit numerical integrations over intermediate photon momenta as originally proposed by Schwartz [41], Baker *et al.* [42] and Korobov and Korobov [43] have obtained accurate values of $\beta(nLS)$ for the low-lying S-states of helium (1^1S , 2^1S , and 2^3S). However, Drake and Goldman [44] have recently shown that Bethe logarithms can be calculated to high accuracy much more efficiently by introducing basis sets whose spectrum of pseudostates spans a huge range of energies (up to 10^{40} eV). The sums in Eq. (15) can then be performed by summing directly over the spectrum of pseudostates. The result for the $1s^2^1S$ ground state of helium is $\beta(1^1S) = 2.983\,865\,857(3)$ for infinite nuclear mass, and the correction due to mass polarization in the wave function is $\Delta\beta_M(1^1S) = 0.09438(1)\mu/M$. The results for the higher lying S-, P-, and D-states can all be accurately represented by the $1/n$ expansions

$$\beta(n^{1,3}L) = \beta(1s) + b_1/n^3 + b_2/n^4 + b_3/n^5, \quad (16)$$

$$\Delta\beta_M(n^{1,3}L) = (d_1/n^3 + d_2/n^4) \mu/M, \quad (17)$$

where $\beta(1s) = 2.984\,128\,556$ is the Bethe logarithm for the $1s$ state of hydrogen. The coefficients b_i and d_i are listed in Table 6.

For higher values of L , one may use instead an asymptotic expansion for the Bethe logarithm similar to that for the energy discussed in Sect. 4. In this picture, the Rydberg electron induces corrections to the Bethe logarithm for the $1s$ electron corresponding to the various multipole moments of the core, with the leading term being the dipole term $0.316\,205(6)\langle x^{-4} \rangle / Z^6$ [45,46]. The complete

expression is

$$\beta(1snl) = \beta(1s) + \left(\frac{Z-1}{Z}\right)^4 \frac{\beta(nl)}{n^3} + \frac{0.316\,205(6)}{Z^6} \langle x^{-4} \rangle + \Delta\beta(1snl) \quad (18)$$

where the $\beta(nl)$ are hydrogenic Bethe logarithms [47], and $\Delta\beta(1snl)$ takes into account contributions from the higher multipole moments. A least squares fit to direct calculations up to $L = 6$ and $n = 6$ for helium yields the results

$$\Delta\beta(1snl \ ^1L) = 95.8(8)\langle r^{-6} \rangle - 845(19)\langle r^{-7} \rangle + 1406(50)\langle r^{-8} \rangle, \quad (19)$$

$$\Delta\beta(1snl \ ^3L) = 95.1(9)\langle r^{-6} \rangle - 841(23)\langle r^{-7} \rangle + 1584(60)\langle r^{-8} \rangle. \quad (20)$$

These formulas give about the same accuracy as the original calculations. For example, for the $1s4f \ ^1F$ state, $\beta(4 \ ^1F) = 2.984\,127\,1493(3)$. A full account will be given in a future publication.

The above results are of pivotal importance because they allow the QED part of the D-state energies to be calculated to sufficient accuracy that these states can be taken as absolute points of reference in the interpretation of measured transition frequencies. In particular, the much larger S-state QED shift can then be extracted from measured $nS - n'D$ transition frequencies by subtraction of the other known terms.

6.2 Electron-Electron Terms

The corresponding QED shift coming from the electron-electron interaction is [48,49]

$$\Delta E_{L,2}^{(3)} = \alpha^3 \left(\frac{14}{3} \ln \alpha + \frac{164}{15} \right) - \frac{14}{3} \alpha^3 Q \quad (21)$$

where

$$Q = \left(\frac{1}{4\pi} \right) \lim_{\epsilon \rightarrow 0} \langle r_{ij}^{-3}(\epsilon) + 4\pi(\gamma + \ln \epsilon) \delta(\mathbf{r}_{12}) \rangle \quad (22)$$

γ is Euler's constant, and ϵ is the radius of a sphere centered about $r_{12} = 0$ that is excluded from the range of integration. The above is the sum of several contributions coming from one- and two-photon exchange, vertex terms, vacuum polarization terms, Coulomb corrections, and the anomalous magnetic moment of the electron. Since all the terms in Eq. (21) can be accurately calculated, they do not introduce additional sources of uncertainty.

6.3 Higher Order Terms

Relativistic and QED terms of order α^4 a.u. and α^5 a.u. are also important in the comparison with experiment. Until recently, a complete theory for these terms did not exist, except for the spin-dependent parts of $O(\alpha^4)$ and $O(\alpha^5)$ a.u. discussed below in Sect. 7.1. For the spin-independent part, the dominant term comes from the one-loop QED shift due to the electron-nucleus interaction of

$O(\alpha^4 Z^5)$ a.u. In the corresponding hydrogenic case, this term is just proportional to the electron density at the nucleus (i.e. matrix element of the delta-function). The corresponding two-electron generalization is thus easily calculated from [50]

$$\Delta E_{L,1}^{(4)} = \frac{4\alpha^4 Z^2}{3} \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle 3\pi \left(\frac{427}{384} - \frac{\ln 2}{2} \right), \quad (23)$$

including electron self-energy and vacuum polarization contributions. For example, this contributes -771.1 MHz, -51.995 MHz, and -67.634 MHz respectively, to the (positive) ionization energies of the helium $1s^2\ ^1S$, $1s2s\ ^1S$, and $1s2s\ ^3S$ states, while the experimental uncertainties are more than an order of magnitude smaller. There would be large discrepancies between theory and experiment without this QED term. The corresponding two-loop term from the hydrogenic Lamb shift is

$$\Delta E_{2L,1}^{(4)} = \frac{4\alpha^4 Z}{3\pi} \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle 0.404\,206. \quad (24)$$

This term also makes a significant contribution. For singlet states, the $O(\alpha^4 \ln \alpha)$ electron-electron QED term

$$V_{e-e}^s = \pi\alpha^4 \ln(\alpha^{-1}) \delta(r_{12}) \quad (25)$$

has been identified and calculated [51]. It contributes -30.67 MHz and -2.494 MHz respectively to the ionization energies of the helium $1\ ^1S$ and $2\ ^1S$.

However, there still remain QED corrections to the electron-electron interaction and purely relativistic corrections of order $\alpha^4 Z^6$ corresponding to the one-electron Dirac energies of this order and their two-electron corrections. In a recent series of papers, Pachucki [52,53,54] has made important progress in the derivation of effective operators for the relativistic corrections for triplet states. The results can be expressed in the form

$$\Delta E_B^{(4)} = \alpha^4 \langle H_{e-n}(1) + H_{e-n}(2) + H_V \rangle + \sum_I \alpha^4 \left\langle B_I \frac{1}{(E-H)^I} B_I \right\rangle \quad (26)$$

where

$$H_{e-n}(i) = \frac{p_i^6}{16} - \frac{1}{8} \left[\mathbf{p}_i, \frac{Z}{r_i} \right]^2 - \frac{5}{128} \left[p_i^2, \left[p_i^2, \frac{Z}{r_i} \right] \right] - \frac{3}{32} p_i^2 \left[\mathbf{p}_i, \left[\mathbf{p}_i, \frac{Z}{r_i} \right] \right] \quad (27)$$

is the electron-nucleus part of the correction to the lowest order Breit interaction, H_V is a lengthy expression for the corresponding electron-electron part (see Ref. [54]), and the last term in Eq. (26) represents the second-order perturbation correction due to the Breit interaction terms in (13). The second-order correction is not convergent as it stands because of the cross term between the delta-functions in Eq. (13). Pachucki has shown that this divergence cancels other divergences occurring in the evaluation of $\langle H_{e-n}(i) \rangle$, leaving a finite residual piece that can be evaluated by finite basis set methods, as described by Yan and Drake [55]. The result is a relativistic shift of $3.00(1)$ MHz for the ionization energy of the $2\ ^3S$ state of helium, in addition to the QED terms (23) and (24).

Table 7. Contributions to the total ionization energies for the S-states of helium. The values used for the physical constants are $R_\infty = 3\,289\,841\,960.389$ MHz, $\alpha^{-1} = 137.035\,9895$ and $\mu/M = 1.370\,745\,620 \times 10^{-4}$. Units are MHz

Quantity	$1s^2\,^1S$	$1s2s\,^1S$	$1s2s\,^3S$
E_{NR}	5 945 405 676.78	960 331 428.619	1 152 795 881.779
μ/M	-143 446.25	-8 570.430	-6 711.192
$(\mu/M)^2$	58.15	16.722	7.107
α^2	-16 901.71	11 969.813(1)	57 621.420
$\alpha^2 \mu/M$	101.39	4.987	3.617
$\alpha^3 + \dots$ QED	-41 233(91)	-2 806.7(25.0)	-4 058.9(6.0)
Nuclear size	-29.59(2)	-1.995(1)	-2.596(2)
Total	5 945 204 226(91)	960 332 041.0(25.0)	1 152 842 741.2(6.0)
Expt.	5 945 204 238(45) ^a 5 945 204 356(48) ^b	960 332 041.01(15) ^c	1 152 842 742.87(6) ^d
Difference	12(102) 130(103)	0.0(25.0)	1.7(6.0)

^aEikema *et al.* [2]. ^cLichten *et al.* [22].
^bBergeson *et al.* [4]. ^dDorrer *et al.* [12].

Theory is now complete, at least for the triplet states, up to terms of $O(\alpha^4)$ a.u. Ionization energies for all the states of helium up to $n = 10$ and $L = 7$ have been tabulated by Drake and Martin [50], and Drake and Goldman [44]. These results can be extended to states of higher n by the use of quantum defect methods, as discussed by Drake [35,56].

7 Comparison with Experiment

Accurate experimental data are now available for the ionization energies of most of the low-lying states of helium, as reviewed by Drake and Martin [50]. All these results were obtained by taking the more accurately known theoretical energies for the higher-lying P- and D-states as known points of reference and taking differences. As discussed by Drake and Goldman [44], the use of the new Bethe logarithms given in Sect. 6.1 markedly improves the agreement between theory and experiment, leaving residual discrepancies that are typically one or two MHz or less. The one exception is the $3\,^1S$ state, which evidently lies higher than theory by 18 ± 14 MHz. A remeasurement of this state would be desirable.

The low-lying S-states are of particular interest because of the large QED contributions to their ionization energies. Table 7 summarizes the various contributions, and Table 8 gives the QED part in greater detail. For the $1s^2\,^1S$ state, theory and experiment agree at the ± 100 MHz level (1.7 parts in 10^8) out of a total ionization energy of 5 945 204 226(100) MHz. The total QED contribution is -41 233(100) MHz. For the $1s2s\,^1S$ state, the agreement is spectacularly good. The difference between theory and the experimental average [20,22] is less than 0.1 MHz (1.2 parts in 10^{10}) out of a total theoretical ionization energy of

Table 8. Details of QED and higher-order relativistic contributions to the ionization energies of helium. Units are MHz

Quantity	$1s^2\ ^1S$	$1s2s\ ^1S$	$1s2s\ ^3S$
Electron-nucleus QED			
$\alpha^3 Z^4$	-44708.756	-3085.814	-4035.803
$\alpha^4 Z^5$	-771.109	-51.995	-67.634
$\alpha^5 Z^6 \ln^2(\alpha)$	83.628	5.639	7.335
$\alpha^5 Z^6 \ln(\alpha)$ (est.)	-52(52)	-4.9(4.9)	-6.0(6.0)
$\alpha^5 Z^6$ (est.)	37(37)	2.5(2.5)	3.3(3.3)
2-loop	-6.876	-0.464	-0.603
2-loop binding	3.948	0.266	0.346
finite mass	4.051	0.145	0.215
Subtotal	-45410(52)	-3134.6(4.5)	-4098.8(6.0)
Electron-electron QED			
α^3 e-e	4208.058	330.359	36.883
$\alpha^4 \ln(\alpha)$ e-e	-30.666	-2.494	0.0
α^4 relativistic	± 75	± 24	3.00(1)
Total	-41233(91)	-2806.7(25.0)	-4058.9(6.0)

960 332 040.9(25) MHz. Here, the total QED contribution is -2807(25) MHz. In view of the large ± 25 MHz uncertainty assigned to the uncalculated relativistic correction of $O(\alpha^4)$ a.u. (the $\Delta E_B^{(4)}$ term), the agreement for the $1s2s\ ^1S$ state is much better than what one might expect.

For the $1s2s\ ^3S$ state, the theoretical uncertainty of ± 6 MHz is considerably less due to Pachucki's calculation of $\Delta E_B^{(4)}$. Its contribution of 3.00(1) MHz to the ionization energy reduces the difference between theory and experiment to 1.7 ± 6 MHz. The ± 6 MHz theoretical uncertainty is conservatively taken to be the entire amount of the $\alpha^5 Z^6 \ln(\alpha)$ a.u. term in Table 8. Since the n -dependence of this term is more complicated than a simple $1/n^3$ dependence, it is at best an approximation to replace a factor of $Z^3/(\pi n^3)$ by $\langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle$ to form the two-electron generalization [see Eq. (14)]. For each term of $O(\alpha^5)$ a.u. in Table 8, the two-electron coefficient $C(1sns)$ multiplying $\langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle$ is calculated from the corresponding one-electron coefficients according to

$$C(1sns) = \frac{C(1s) + C(ns)/n^3}{1 + 1/n^3}. \quad (28)$$

The factor in the demoninator ensures that the correct leading term in a $1/Z$ expansion is recovered in the limit of large Z .

The experimental uncertainty of ± 0.06 MHz for the $2\ ^3S$ state corresponds to an accuracy of ± 15 parts per million (ppm) in the total QED shift. This considerably exceeds the accuracy of the best microwave resonance measurement of the Lamb shift in the He^+ hydrogenic ion (± 86 ppm) [57], and it matches the accuracy of the recent anisotropy measurement by van Wijngaarden *et al.* [58].

7.1 Measurement of the Fine Structure Constant

A comparison between theory and experiment for the fine structure intervals in helium holds the promise of providing a measurement of the fine structure constant α that would provide a significant test of other methods such as the ac Josephson effect and the quantum Hall effect. The latter two differ by 15 parts in 10^8 and are not in good agreement with each other [59].

The helium $1s2p\ ^3P$ manifold of states has three fine-structure levels labeled by the total angular momentum $J = 0, 1$, and 2 . If the largest $J = 0 \rightarrow 1$ interval of about 29 617 MHz could be measured to an accuracy of ± 1 kHz, this would determine α to an accuracy of ± 1.7 parts in 10^8 , provided that the interval could be calculated to a similar degree of accuracy. In lowest order, the dominant contribution of order α^2 a.u. comes from the spin-dependent terms $B_{3Z} + B_{3e} + B_5$ of the Breit interaction (13). This part is known to an accuracy of 2 parts in 10^{10} , and the corrections of order α^3 a.u. and α^4 a.u. have similarly been calculated to the necessary accuracy [55]. At each stage, the principal challenge is to find the equivalent nonrelativistic operators whose expectation value in terms of Schrödinger wave functions gives the correct coefficient of the corresponding power of α . This analysis, as originally done by Douglas and Kroll for the α^4 terms [60], has been completed for the next higher order $\alpha^5 \ln \alpha$ and α^5 terms by Zhang [61,62,63], and numerical results obtained for the former [64]. Recent work by Pachucki [65] has verified Tao Zhang's derivation of the terms of order $\alpha^5 \ln \alpha$, and Pachucki and Sapirstein [66] have evaluated the electron-nucleus and spin-dependent 'Bethe logarithm' parts of the pure $O(\alpha^5)$ terms. However, there remain electron-electron terms, some of which are known to contribute at the ± 10 kHz level of accuracy [61]. For example, the term

$$\Delta E_{13} = \frac{15\alpha^5}{16\pi} \langle p_1^2 \phi_0 | \frac{1}{r^5} \boldsymbol{\sigma}_1 \cdot \mathbf{r} \boldsymbol{\sigma}_2 \cdot \mathbf{r} | \phi_0 \rangle \quad (29)$$

contributes -10.7 and 4 kHz to the intervals $\nu_{0,1}$ and $\nu_{1,2}$ respectively. A full evaluation of 24 other terms of this type, together with finite mass corrections to the Douglas and Kroll terms [60], is in progress and will be completed in the near future. The residual uncertainty due to higher order terms will then be less than 1 kHz.

Table 9 presents a summary of the known contributions to the fine structure intervals, and a comparison with several recent experiments. The theoretical uncertainty will remain at ± 15 kHz until the calculations described above have been completed. However, the present result is in remarkably good agreement with the measurement of Minardi *et al.* [67], which is within a factor of two of reaching the 1 kHz level for the larger $\nu_{0,1}$ interval. The measurements of Storry *et al.* [16] and Castilega *et al.* [18] at the ± 1 kHz level for the $\nu_{1,2}$ interval are not as sensitive to α , but they provide an important check on the theory. Once both theory and experiment are in place to the necessary accuracy, a new value for α can be derived.

Table 9. Comparison of theory and experiment for the fine structure splittings of helium $2\ ^3P_J$. Units are MHz

Contribution	$\nu_{0,1}$	$\nu_{1,2}$
α^2	29 564.600 02	2 317.232 22
$\alpha^2 \mu/M$	-0.830 97	3.009 64
$\alpha^2 (\mu/M)^2$	0.000 80	-0.000 08
α^3	54.707 87	-22.548 22
$\alpha^3 \mu/M$	-0.003 82	0.003 21
α^4 2nd. order	1.727 63(5)	-8.040 26(38)
α^4 D.K.	-3.335 19(3)	1.533 93(5)
$Z\alpha^5 \ln(Z\alpha)^{-2}$	0.031 82	0.063 64
$Z\alpha^5 \ln(Z\alpha)^{-2}$ 2nd. order	0.042 50	-0.043 80
$\alpha^5 \ln(\alpha)^{-2}$ s.o.o.	-0.011 09	-0.022 19
$\alpha^5 \ln(\alpha)^{-2}$ s.s.	0.032 27	-0.012 91
α^5 electron-nucl. ^a	-0.012 28(16)	-0.001 55(27)
α^5 electron-electron (est.)	± 0.015	± 0.015
Total	29 616.949 57(17)	2 291.173 64(39)
	± 0.015	± 0.015
Experiment		
Storry <i>et al.</i> [16]		2 291.174 0(14)
Castilleja <i>et al.</i> [18]		2 291.175 9(10)
Minardi <i>et al.</i> [67]	29 616.9497(20)	2 291.174(15)
Shiner <i>et al.</i> [8]	29 616.962(3)	2 291.173(3)
Wen and Gabrielse [6]	29 616.962(3)	2 291.198(8)
Storry and Hessels [14]	29 616.966(13)	
Hughes <i>et al.</i> [68]	29 616.911(27)	2 291.196(5)

^aElectron-nucleus terms calculated by Pachucki and Sapirstein [66]

7.2 Applications to Lithium

The methods described in Sect. 3 for the calculation of accurate nonrelativistic wave functions and energies can in principle be applied to more complex atoms and molecules. The principal difficulties are that the number of terms required in the basis set to reach a given level of accuracy grows extremely rapidly with the number of particles, and the correlated integrals become much more difficult to evaluate. Only in the case of lithium (and Li-like ions) have results of spectroscopic accuracy been obtained (see Ref. [69] for a review). However, the demand on computer resources increases by about a factor of 6000 to reach the same level of accuracy.

The evaluation of matrix elements of the Breit interaction requires the calculation of even more difficult singular integrals, and this remained an unsolved problem until the recent development of new algorithms [70,71]. With these results in hand, it is now possible to include all the relativistic and QED terms as in the helium case. The resulting theoretical ionization energy for the $1s^2 2s\ ^2S$ ground state of 0.198 142 09(2) a.u. is larger than the experimental value by

only $0.000\,000\,06(3)$ a.u. (0.013 ± 0.07 cm $^{-1}$). The fine structure splitting for the $1s^2p^2\,^2P$ also agrees with experiment at the $\pm 0.000\,05$ cm $^{-1}$ level of accuracy [72].

Also as in the case of helium, asymptotic expansion methods can be applied to the Rydberg states of lithium and compared with high precision measurements [73,74]. This case is more difficult because the Li^+ core is a nonhydrogenic two-electron ion for which the multipole moments cannot be calculated analytically, and variational basis set methods must be used instead. However, the method is in principle capable of the same high accuracy as for helium.

Finally, for all of these cases, once accurate wave functions are available, they can be used to calculate a wide variety of atomic properties, such as oscillator strengths, multipole moments, long range interactions, etc. A great deal of work has been done in this area, some of which is reviewed in various chapters throughout the *Atomic, Molecular, and Optical Physics Handbook* [35]. A particularly fascinating example is the use of the lithium isotope shift to determine the nuclear radius of exotic ‘halo’ nuclei such as ^6Li [75]

8 Concluding Remarks

A principal objective of this review was to show that helium can now take its place alongside hydrogen as a fundamental system of atomic physics. The Schrödinger equation has been solved and lowest order relativistic corrections calculated to much better than spectroscopic accuracy. To a somewhat lesser extent, accurate solutions also exist for lithiumlike systems, but here theory is much less well developed. The residual discrepancies between theory and experiment determine the higher order relativistic and QED (Lamb shift) contributions to nearly the same accuracy as in the corresponding hydrogenic systems. Interest therefore shifts to the calculation of these contributions, for which theory is far from complete for atoms more complicated than hydrogen. Each theoretical advance provides a motivation for parallel advances in the state-of-the-art for high precision measurement. The results obtained to date provide unique tests of both theory and experiment at the highest attainable levels of accuracy, and they provide a new tool for the determination of other quantities such as the fine structure constant and the radii of exotic nuclei.

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