
Atomic, Molecular, & Optical Physics Handbook

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Atomic, Molecular, & Optical Physics HANDBOOK

Editor

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High Precision Calculations for Helium

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11.1 INTRODUCTION

Exact analytic solutions to the Schrödinger equation are known only for atomic hydrogen, and other equivalent two-body systems (see Chap. 9). However, very high precision approximations are now available for helium, which are essentially exact for all practical purposes. This chapter summarizes the computational methods and tabulates numerical results for the ground state and several singly excited states. Similar methods can be applied to other three-body problems.

11.2 THE THREE-BODY SCHRÖDINGER EQUATION

The Schrödinger equation for a three-body system consisting of a nucleus of charge Ze , and mass M , and

two electrons of charge $-e$ and mass m_e is

$$\left[\frac{1}{2M} P_N^2 + \frac{1}{2m_e} \sum_{i=1}^2 P_i^2 + V(\mathbf{R}_N, \mathbf{R}_i) \right] \Psi = E\Psi, \quad (11.1)$$

where $\mathbf{P}_i = (\hbar/i)\nabla_i$ and

$$V(\mathbf{R}_N, \mathbf{R}_i) = -\frac{Ze^2}{|\mathbf{R}_N - \mathbf{R}_1|} - \frac{Ze^2}{|\mathbf{R}_N - \mathbf{R}_2|} + \frac{e^2}{|\mathbf{R}_1 - \mathbf{R}_2|} \quad (11.2)$$

depends only on the relative particle separations. Since the center of mass (c.m.) is then an ignorable coordinate, it can be eliminated by defining the relative particle coordinates

$$\mathbf{r}_i = \mathbf{R}_i - \mathbf{R}_N$$

to obtain

$$\left[\frac{1}{2\mu} \sum_{i=1}^2 P_i^2 + \frac{1}{M} \mathbf{p}_1 \cdot \mathbf{p}_2 + V(\mathbf{r}_1, \mathbf{r}_2) \right] \Psi = E\Psi, \quad (11.3)$$

where $\mu = m_e M / (m_e + M)$ is the electron reduced mass and the term $H_{\text{mp}} = \mathbf{p}_1 \cdot \mathbf{p}_2 / M$ is called the mass polarization operator. For computational purposes, it is usual to measure distance in units of $a_\mu = (m_e/\mu)a_0$ and energies in units of $e^2/a_\mu = 2(\mu/m_e)R_\infty$ so that Eq. (11.3) assumes the dimensionless form

$$\left[-\frac{1}{2} \sum_{i=1}^2 \nabla_{\rho_i}^2 - \frac{\mu}{M} \nabla_{\rho_1} \cdot \nabla_{\rho_2} + V(\rho_1, \rho_2) \right] \Psi = \varepsilon\Psi, \quad (11.4)$$

where $\rho_i = \mathbf{r}_i/a_\mu$, $\varepsilon = E/(e^2/a_\mu)$, and

$$V(\rho_1, \rho_2) = -\frac{Z}{\rho_1} - \frac{Z}{\rho_2} + \frac{1}{|\rho_1 - \rho_2|}. \quad (11.5)$$

The limit $\mu/M \rightarrow 0$ defines the infinite nuclear mass problem with eigenvalue ε_0 and eigenfunction Ψ_0 . If the mass polarization term is treated as a small perturbation, then the total energy assumes the form

$$E = \left[\varepsilon_0 + \frac{\mu}{M} \varepsilon_1 + \left(\frac{\mu}{M} \right)^2 \varepsilon_2 + \dots \right] \frac{\mu}{m_e} \frac{e^2}{a_0}, \quad (11.6)$$

where $\varepsilon_1 = -\langle \Psi_0 | \nabla_{\rho_1} \cdot \nabla_{\rho_2} | \Psi_0 \rangle$ determines the first-order specific mass shift and ε_2 is the second-order coefficient. The common $(\mu/m_e)\varepsilon_0$ mass scaling of all eigenvalues determines the normal mass shift. Since $\mu/m = 1 - \mu/M$, the shift is $-(\mu/M)\varepsilon_0$.

11.2.1 Formal Mathematical Properties

Two-Particle Coalescences. The exact nonrelativistic wave function for any many-body system contains discontinuities or cusps in the spherically averaged radial derivative with respect to r_{ij} as $r_{ij} \rightarrow 0$, where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is any interparticle coordinate. If the masses and charges are m_i and q_i respectively, then the discontinuities are given by the Kato cusp condition [1]

$$\hbar^2 \left(\frac{\partial \bar{\Psi}}{\partial r_{ij}} \right)_{r_{ij}=0} = \mu_{ij} q_i q_j \bar{\Psi}(r_{ij}=0), \quad (11.7)$$

where $\mu_{ij} = m_i m_j / (m_i + m_j)$ and $\bar{\Psi}$ denotes the wave function averaged over a sphere centered at $r_{ij} = 0$. If Ψ vanishes at $r_{ij} = 0$, then its leading dependence on r_{ij} is of the form $r_{ij}^l Y_{lm}(\mathbf{r}_{ij})$ for some integer $l > 0$ [2]. Equation (11.7) applies to any Coulombic system. The electron-nucleus cusp in the wave functions for hydrogen provides a simple example.

Three-Particle Coalescences. Three-particle coalescences are described by the Fock expansion [3], as recently discussed by Myers *et al.* [4]. For the S -states of He-like ions, the expansion has the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{j=0}^{\infty} \sum_{k=0}^{[j/2]} \mathcal{R}^j (\ln \mathcal{R})^k \phi_{j,k}, \quad (11.8)$$

where $[]$ denotes "greatest integer in", and $\mathcal{R} = (r_1^2 + r_2^2)^{1/2}$ is the hyperradius. The leading coefficients are

$$\begin{aligned} \phi_{0,0} &= 1, \\ \phi_{1,0} &= -(Zr_1 + Zr_2 - \frac{1}{2}r_{12})/\mathcal{R}, \\ \phi_{2,1} &= -2Z \left(\frac{\pi-2}{3\pi} \right) \frac{\mathbf{r}_1 \cdot \mathbf{r}_2}{\mathcal{R}^2}. \end{aligned} \quad (11.9)$$

The next term $\phi_{2,0}$ is known in terms of a lengthy expression [4, 5], but higher terms have not yet been obtained in closed form. The Fock expansion has been proved convergent for all $\mathcal{R} < \frac{1}{2}$ [6], and extended to pointwise convergence for all \mathcal{R} [7, 8].

Asymptotic Form. The long range behavior of many-electron wave functions has been studied from several points of view [9–11]. The basic result of Ref. [12] is that at large distances, the one-electron density behaves as

$$\rho^{1/2}(r) \sim r^{Z^*/t-1} e^{-tr}, \quad (11.10)$$

where $t = (2I_1)^{1/2}$, I_1 is the first ionization potential (in a.u.), and $Z^* = Z - N + 1$ is the screened nuclear charge seen by the outer most electron. For hydrogenic systems with principal quantum number n , $I_1 = (Z^*)^2/2n^2$.

11.3 COMPUTATIONAL METHODS

11.3.1 Variational Methods

Most high precision calculations for the bound states of three-body systems such as helium are based on the Rayleigh-Ritz variational principle. For any normalizable trial function Ψ_{tr} , the quantity

$$E_{\text{tr}} = \frac{\langle \Psi_{\text{tr}} | H | \Psi_{\text{tr}} \rangle}{\langle \Psi_{\text{tr}} | \Psi_{\text{tr}} \rangle} \quad (11.11)$$

satisfies the inequality $E_{\text{tr}} \geq E_1$, where E_1 is the true ground state energy. Thus E_{tr} is an upper bound to E_1 . The inequality is easily proved by expanding Ψ_{tr} in the complete basis set of eigenfunctions $\Psi_1, \Psi_2, \Psi_3, \dots$ of H with eigenvalues $E_1 < E_2 < E_3 < \dots$, so that

$$\Psi_{\text{tr}} = \sum_{i=1}^{\infty} c_i \Psi_i, \quad (11.12)$$

where the c_i are expansion coefficients. This can always be done in principle, even though the exact Ψ_i are not

actually known. If Ψ_{tr} is normalized so that $\langle \Psi_{\text{tr}} | \Psi_{\text{tr}} \rangle = 1$, then $\sum_{i=1}^{\infty} |c_i|^2 = 1$ and

$$\begin{aligned} E_{\text{tr}} &= |c_1|^2 E_1 + |c_2|^2 E_2 + |c_3|^2 E_3 + \dots \\ &= E_1 + |c_2|^2 (E_2 - E_1) + |c_3|^2 (E_3 - E_1) + \dots \\ &\geq E_1, \end{aligned} \quad (11.13)$$

which proves the theorem.

The basic idea of variational calculations then is to write Ψ_{tr} in some arbitrarily chosen mathematical form with variational parameters (subject to normalizability and boundary conditions at the origin and infinity), and then adjust the parameters to obtain the minimum value of E_{tr} .

The minimization problem for the case of *linear* variational coefficients can be solved algebraically. For example, let

$$\chi_p(\alpha, \beta) = r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} \quad (11.14)$$

denote the members of a basis set, where p is an index labeling distinct triplets of nonnegative integer values for the powers $\{i, j, k\}$, and α, β are (for the moment) fixed constants determining the distance scale.

If Ψ_{tr} is expanded in the form

$$\Psi_{\text{tr}} = \sum_{p=1}^N c_p \chi_p(\alpha, \beta), \quad (11.15)$$

then the solution to the system of equations $\partial E_{\text{tr}} / \partial c_p = 0$, $p = 1, \dots, N$, is exactly equivalent to solving the N -dimensional generalized eigenvalue problem

$$\mathbf{H}\mathbf{c} = \lambda\mathbf{O}\mathbf{c}, \quad (11.16)$$

where \mathbf{c} is a column vector of coefficients c_p ; and \mathbf{H} and \mathbf{O} have matrix elements $H_{pq} = \langle \chi_p | H | \chi_q \rangle$ and $O_{pq} = \langle \chi_p | \chi_q \rangle$. There are N eigenvalues $\lambda_1, \lambda_2, \dots, \lambda_N$, of which the lowest is an upper bound to E_1 .

Extension to Excited States. By the Hylleraas-Undheim-MacDonald (HUM) theorem [13,14], the remaining eigenvalues $\lambda_2, \lambda_3, \dots$ are also upper bounds to the exact energies E_2, E_3, \dots , provided that the spectrum is bounded from below. The HUM theorem is a consequence of the matrix eigenvalue interleaving theorem, which states that as the dimensions of \mathbf{H} and \mathbf{O} are progressively increased by adding an extra row and column, the N old eigenvalues λ_p fall between the $N+1$ new ones. Consequently, as illustrated in Fig. 11.1, all eigenvalues numbered from the bottom up must move inexorably downward as N is increased. Since the exact spectrum of bound states is obtained in the limit $N \rightarrow \infty$, no λ_p can cross the corresponding exact E_p on its way down. Thus $\lambda_p \geq E_p$ for every finite N .

11.3.2 Construction of Basis Sets

Since the Schrödinger equation (11.4) is not separable in the electron coordinates, basis sets which incorporate

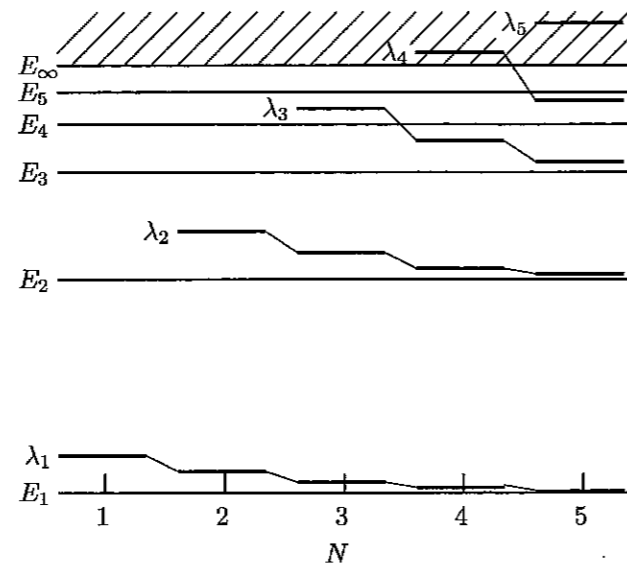


Figure 11.1. Diagram illustrating the Hylleraas-Undheim-MacDonald Theorem. The λ_p , $p = 1, \dots, N$ are the variational eigenvalues for an N -dimensional basis set, and the E_i are the exact eigenvalues of H . The highest λ_p lie in the continuous spectrum of H .

the $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ interelectron coordinate are most efficient. The necessity for r_{12} terms also follows from the Fock expansion (11.8). A basis set constructed from terms of the form (11.14) is called a Hylleraas basis set [15].¹

With $\chi_p(\alpha, \beta)$ defined as in (11.14), the general form for a state of total angular momentum L is

$$\begin{aligned} \Psi_{\text{tr}} &= \sum_{l_1=0}^{[L/2]} \sum_p C_{p,l_1} \chi_p(\alpha, \beta) r_1^{l_1} r_2^{l_2} \mathcal{Y}_{l_1 l_2 L}^M(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \\ &\pm \text{exchange}, \end{aligned} \quad (11.17)$$

where

$$\begin{aligned} \mathcal{Y}_{l_1 l_2 L}^M(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) &= \sum_{m_1, m_2} Y_{l_1 m_1}(\hat{\mathbf{r}}_1) Y_{l_2 m_2}(\hat{\mathbf{r}}_2) \\ &\times \langle l_1 l_2 m_1 m_2 | LM \rangle \end{aligned} \quad (11.18)$$

is the vector coupled product of angular momenta l_1, l_2 for the two electrons. The sum over p in (11.17) typically includes all terms in (11.14) with $i + j + k \leq \Omega$, where Ω is an integer determining a so-called *Pekeris shell* of terms, and the exchange term denotes the interchange of r_1 and r_2 with (+) for singlet states and (-) for triplet states. Convergence is studied by progressively increasing Ω . The number of terms is

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

¹The basis set is often expressed in terms of the equivalent variables $s = r_1 + r_2$, $t = r_1 - r_2$, $u = r_{12}$.

Basis sets of this type were used by many authors, culminating in the extensive high precision calculations of Pekeris and coworkers [16] for low-lying states, using as many as 1078 terms. Their accuracy is not easily surpassed because of the rapid growth of N with Ω , and because of numerical linear dependence in the basis set for large Ω . Recently, their accuracy has been surpassed by two principal methods. The first explicitly includes powers of logarithmic and half-integral terms in χ_p , as suggested by the Fock expansion [17-19]. This is particularly effective for S -states. The second focuses directly on the multiple distance scales required for an accurate representation of the wave function by writing the trial function in terms of the double basis set [20]

$$\begin{aligned} \Psi_{\text{tr}} &= \sum_{l_1=0}^{[L/2]} \sum_p \left[C_{p,l_1}^{(1)} \chi_p(\alpha_1, \beta_1) + C_{p,l_1}^{(2)} \chi_p(\alpha_2, \beta_2) \right] \\ &\times r_1^{l_1} r_2^{l_2} \mathcal{Y}_{l_1 l_2 L}(r_1, r_2) \pm \text{exchange}, \end{aligned} \quad (11.19)$$

where each $\chi_p(\alpha, \beta)$ is of the form (11.14), but with different values for the distance scales α_1, β_1 and α_2, β_2 in the two sets of terms. They are determined by a complete minimization of E_{tr} with respect to all four parameters, producing a natural division of the basis set into an asymptotic sector and a close-range correlation sector. The method produces a dramatic improvement in accuracy for higher-lying Rydberg states (where variational methods typically deteriorate rapidly in accuracy) and is also effective for low-lying S -states [21,22]. Nonrelativistic energies accurate to 1 part in 10^{16} are obtainable with modest computing resources.

11.3.3 Calculation of Matrix Elements

The three-body problem has the unique advantage that the full six-dimensional volume element (in the c.m. frame) can be transformed to the product of a three-dimensional angular integral (ang) and a three-dimensional radial integral (rad) over r_1, r_2 , and r_{12} . The transformation is

$$\begin{aligned} \iint d\mathbf{r}_1 d\mathbf{r}_2 &= \int_0^{2\pi} d\phi \int_0^{2\pi} d\varphi_1 \int_0^\pi \sin\theta_1 d\theta_1 \\ &\times \int_0^\infty r_1 dr_1 \int_0^\infty r_2 dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r_{12} dr_{12}, \end{aligned} \quad (11.20)$$

where θ_1, φ_1 are the polar angles of \mathbf{r}_1 and ϕ is the angle of rotation of the triangle formed by $\mathbf{r}_1, \mathbf{r}_2$, and \mathbf{r}_{12} about the \mathbf{r}_1 direction. The polar angles θ_2, φ_2 are then dependent variables. The basic angular integral is

$$\begin{aligned} \langle Y_{l_1 m_1}^*(\theta_1, \varphi_1) Y_{l_2 m_2}(\theta_2, \varphi_2) \rangle_{\text{ang}} \\ = 2\pi \delta_{l_1 l_2} \delta_{m_1 m_2} P_{l_1}(\cos\theta), \end{aligned} \quad (11.21)$$

where $\cos\theta \equiv \hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2$ denotes the radial function

$$\cos\theta = \frac{r_1^2 + r_2^2 - r_{12}^2}{2r_1 r_2}, \quad (11.22)$$

and $P_L(\cos\theta)$ is a Legendre polynomial. The angular integral over vector-coupled spherical harmonics is [23]

$$\begin{aligned} \langle \mathcal{Y}_{l_1' l_2' L'}^{M'}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \mathcal{Y}_{l_1 l_2 L}^M(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \rangle_{\text{ang}} \\ = \delta_{L, L'} \delta_{M, M'} \sum_{\Lambda} C_{\Lambda} P_{\Lambda}(\cos\theta), \end{aligned} \quad (11.23)$$

where

$$\begin{aligned} C_{\Lambda} &= \frac{1}{2} [(2l_1 + 1)(2l_1' + 1)(2l_2 + 1)(2l_2' + 1)]^{1/2} \\ &\times (-1)^{L+\Lambda} (2\Lambda + 1) \\ &\times \begin{pmatrix} l_1' & l_1 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2' & l_2 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L & l_1 & l_2 \\ \Lambda & l_2' & l_1' \end{Bmatrix}, \end{aligned} \quad (11.24)$$

and the sum over Λ includes all nonvanishing terms. This can be extended to general matrix elements of tensor operators by further vector coupling [23].

Radial Integrals. Table 11.1 lists formulas for the radial integrals arising from matrix elements of H , as well as those from the Breit interaction (see Sect. 21.1). Although they can all be written in closed form, some have been expressed as infinite series in order to achieve good numerical stability. The exceptions are formulas 5 and 10 in the Table, which became unstable as $\alpha \rightarrow \beta$. More elaborate techniques for these are discussed in Ref. [24]. Other cases can be derived by use of the formula

$$\begin{aligned} \langle r_1^{-1} r_2^{-1} f(r_{12}) e^{-\alpha r_1 - \beta r_2} \rangle_{\text{rad}} \\ = \frac{2}{\alpha^2 - \beta^2} \int_0^\infty (e^{-\beta r} - e^{-\alpha r}) r f(r) dr, \end{aligned} \quad (11.25)$$

and then differentiating or integrating with respect to α or β to raise or lower the powers of r_1 and r_2 .

Total Integral. The angular integral (11.23) combined with the radial integrals from Table 11.1 yields the total integral

$$\langle \mathcal{Y}_{l_1' l_2' L'}^{M'} \mathcal{Y}_{l_1 l_2 L}^M f(a, b, c; \alpha, \beta) \rangle = \sum_{\Lambda} C_{\Lambda} I_{\Lambda}(a, b, c; \alpha, \beta), \quad (11.26)$$

where

$$\begin{aligned} I_{\Lambda}(a, b, c; \alpha, \beta) &= \langle f(a, b, c; \alpha, \beta) P_{\Lambda}(\cos\theta) \rangle_{\text{rad}}, \\ f(a, b, c; \alpha, \beta) &= r_1^{\alpha} r_2^{\beta} r_{12}^c e^{-\alpha r_1 - \beta r_2}. \end{aligned}$$

Starting from I_0 and I_1 , the general I_{Λ} can be efficiently calculated from the recursion relations [23]

Table 11.1. Formulas for the radial integrals $I_0(a, b, c; \alpha, \beta) = \langle r_1^a r_2^b r_{12}^c e^{-\alpha r_1 - \beta r_2} \rangle_{\text{rad}}$ and $I_0^{\text{log}}(a, b, c; \alpha, \beta) = \langle r_1^a r_2^b r_{12}^c \ln r_{12} e^{-\alpha r_1 - \beta r_2} \rangle_{\text{rad}}$. $\psi(n) = -\gamma + \sum_{k=1}^{n-1} k^{-1}$ is the digamma function, ${}_2F_1(a, b; c; z)$ is the hypergeometric function, and $s = a + b + c + 5$. Except as noted, the formulas apply for $a \geq -1$, $b \geq -1$, $c \geq -1$.

1. $I_0(-2, -2, -1; \alpha, \beta) = \frac{2}{\alpha} \ln \left(\frac{\alpha + \beta}{\beta} \right) + \frac{2}{\beta} \ln \left(\frac{\alpha + \beta}{\alpha} \right)$
2. $I_0(a, b, c; \alpha, \beta) = \frac{2}{c+2} \sum_{i=0}^{[(c+1)/2]} \binom{c+2}{2i+1} [F_{a+2i+2, b+c-2i+2}(\alpha, \beta) + F_{b+2i+2, a+c-2i+2}(\beta, \alpha)]$
($c \geq -1, s \geq 0$)
where $F_{p,q}(\alpha, \beta) = \begin{cases} \frac{q!}{(\alpha + \beta)^{p+1} \beta^{q+1}} \sum_{j=1}^q \frac{(p+j)!}{j!} \left(\frac{\beta}{\alpha + \beta} \right)^j & q \geq 0, p \geq 0 \\ \frac{p!}{\alpha^{p+q+2}} \sum_{j=p+q+1}^{\infty} \frac{j!}{(j-q)!} \left(\frac{\alpha}{\alpha + \beta} \right)^{j+1} & q < 0, p \geq 0 \\ 0^a & p < 0 \end{cases}$
3. $I_0(a, b, c; \alpha, \alpha) = \frac{2^{c+3} s!}{(c+2)(2\alpha)^{s+1}} \left\{ \sum_{j=0}^{a+1} \binom{a+1}{j} (b+1)! \left[\frac{j!}{(j+b+2)!} - \frac{(j+c+2)!}{(j+b+c+4)!} \right] + (a \leftrightarrow b) \right\}$
5. $I_0(a, b, -2; \alpha, \beta) = \frac{(a+1)!}{\alpha^{a+2}} \sum_{j=0}^{a+1} \frac{(b+1+j)!}{j!} \left[\frac{\alpha^j}{(\alpha + \beta)^{b+2+j}} - \frac{(-\alpha)^j}{(\beta - \alpha)^{b+2+j}} \right]$
 $\times \left[\ln \left(\frac{2\alpha}{\alpha + \beta} \right) - \psi(a+2-j) + \psi(1) \right] + \left(\frac{a \leftrightarrow b}{\alpha \leftrightarrow \beta} \right)$
6. $I_0(a, b, -2; \alpha, \alpha) = \frac{2s!(a+1)(b+1)!}{(2\alpha)^{s+1}} \left[\sum_{j=0}^{a+1} \frac{\psi(s+1-j) - \psi(a+2-j)}{j!(s-j)!} + (a \leftrightarrow b) \right]$
7. $I_0(-1, -1, -3; \alpha, \beta) = \frac{2(\beta \ln \beta - \alpha \ln \alpha)}{\alpha^2 - \beta^2} + \frac{2[\psi(2) - \ln \epsilon]^b}{\alpha + \beta}$
8. $I_0(a, b, -3; \alpha, \beta) = \left[\frac{(a+1)!}{\alpha^{a+1}(\alpha + \beta)^{b+2}} \sum_{j=0}^a \frac{(b+1+j)!}{j!(a+1-j)!} \left(\frac{\alpha}{\alpha + \beta} \right)^j + \left(\frac{a \leftrightarrow b}{\alpha \leftrightarrow \beta} \right) \right] - \frac{s! [\ln(\alpha\beta\epsilon^2) - \psi(1)]}{(\alpha + \beta)^{s+1}}$
 $- \frac{(a+1)!(b+1)!}{(s+1)\alpha^{a+2}\beta^{b+1}} {}_2F_1(a+2, 1; s+2; \frac{\alpha-\beta}{\alpha})$, $a \geq -1, b \geq -1$
9. $I_0^{\text{log}}(-1, -1, c; \alpha, \beta) = \frac{2(c+1)!}{\alpha^2 - \beta^2} \left[\frac{\ln \alpha - \psi(c+2)}{\alpha^{c+2}} - \frac{\ln \beta - \psi(c+2)}{\beta^{c+2}} \right]$
10. $I_0^{\text{log}}(a, b, c; \alpha, \beta) = \frac{(a+1)!}{(c+2)\alpha^{a+c+4}} \sum_{j=0}^{a+1} \frac{(b+1+j)!(a+c+3-j)!}{j!(a+1-j)!} \left[\frac{\alpha^j}{(\alpha + \beta)^{b+2+j}} - \frac{(-\alpha)^j}{(\beta - \alpha)^{b+2+j}} \right]$
 $+ \left(\frac{a \leftrightarrow b}{\alpha \leftrightarrow \beta} \right)$
11. $I_0^{\text{log}}(a, b, c; \alpha, \alpha) = \frac{2^{c+3} s!(b+1)!}{(c+2)(2\alpha)^{s+1}} \sum_{j=0}^{a+1} \binom{a+1}{j} \left\{ \left[\frac{j!}{(j+b+2)!} - \frac{(j+c+2)!}{(j+b+c+4)!} \right] \left[\psi(s+1) - \ln \alpha - \frac{1}{c+2} \right] \right.$
 $\left. + \frac{(a+c+3-j)!}{(s+1-j)!} [\psi(s+1-j) - \psi(a+c+4-j)] \right\} + (a \leftrightarrow b)$

^a Terms with $p < 0$ represent divergent parts which cancel from convergent differences between integrals with the same α and β .
^b ϵ is the radius of an infinitesimal sphere about $r_{12} = 0$ which is omitted from the range of integration.

$$I_{\Lambda+1}(a, b, c; \alpha, \beta) = \frac{2\Lambda+1}{c+2} I_{\Lambda}(a-1, b-1, c+2; \alpha, \beta) - I_{\Lambda-1}(a, b, c; \alpha, \beta), \quad c \neq -2 \quad (11.27)$$

$$I_{\Lambda+1}(a, b, -2; \alpha, \beta) = (2\Lambda+1) I_{\Lambda}^{\text{log}}(a-1, b-1, 0; \alpha, \beta) - I_{\Lambda-1}(a, b, -2; \alpha, \beta), \quad c = -2 \quad (11.28)$$

where

$$I_{\Lambda}^{\text{log}}(a, b, c; \alpha, \beta) = \langle f(a, b, c, \alpha, \beta) \ln r_{12} P_{\Lambda}(\cos \theta) \rangle_{\text{rad}}.$$

The I_{Λ}^{log} integrals follow the recursion relation

$$I_{\Lambda+1}^{\text{log}}(a, b, c; \alpha, \beta) = \frac{(2\Lambda+1)}{c+2} \left[I_{\Lambda}^{\text{log}}(a-1, b-1, c+2; \alpha, \beta) - \frac{1}{c+2} I_{\Lambda}(a-1, b-1, c+2; \alpha, \beta) \right] + I_{\Lambda-1}^{\text{log}}(a, b, c; \alpha, \beta). \quad (11.29)$$

Hamiltonian Matrix Elements. The general form of the Laplacian operator in terms of r_1, r_2, r_{12} variables is

$$\nabla_1^2 = \frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left(r_1^2 \frac{\partial}{\partial r_1} \right) + \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{l_1^2}{r_1^2} + \frac{2(r_1 - r_2 \cos \theta)}{r} \frac{\partial^2}{\partial r_1 \partial r} - 2(\nabla_1^Y \cdot \mathbf{r}_2) \frac{1}{r} \frac{\partial}{\partial r}, \quad (11.30)$$

and similarly for ∇_2^2 with subscripts 1 and 2 interchanged. The term ∇_1^Y is understood to act only on the $\mathcal{Y}_{l_1 l_2 L}^M(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$ part of the wave function. This term in ∇_1^2 can be easily evaluated by means of the effective operator replacement

$$\langle \mathcal{Y}_{l_1 l_2 L}^{M*} | \nabla_1^Y \cdot \mathbf{r}_2 | \mathcal{Y}_{l_1 l_2 L}^M \rangle_{\text{ang}} \frac{1}{r_{12}} \frac{\partial g(r_{12})}{\partial r_{12}} \rightarrow \frac{g(r_{12})}{2r_1 r_2} \sum_{\Lambda} \tilde{C}_{\Lambda} P_{\Lambda}(\cos \theta) \quad (11.31)$$

for the angular part of the total integral, where

$$\tilde{C}_{\Lambda} = [l_1'(l_1' + 1) - l_1(l_1 + 1) - \Lambda(\Lambda + 1)] C_{\Lambda}. \quad (11.32)$$

The replacement (11.31) becomes an equality after radial integration with any function $g(r_{12})$ in the integrand. The matrix elements of H between arbitrary basis functions defined by

$$\chi = r_1^a r_2^b r_{12}^c e^{-\alpha r_1 - \beta r_2} \mathcal{Y}_{l_1 l_2 L}^M(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2), \\ \chi' = r_1^{a'} r_2^{b'} r_{12}^{c'} e^{-\alpha' r_1 - \beta' r_2} \mathcal{Y}_{l_1' l_2' L}^M(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2),$$

can then be written in the explicitly Hermitian form (for infinite nuclear mass)

$$\langle \chi' | H | \chi \rangle = \frac{1}{8} \sum_{\Lambda} C_{\Lambda} \sum_{i=0}^2 \left[A_i^{(1)} I_{\Lambda}(a_+ - i, b_+, c_+; \alpha_+, \beta_+) + A_i^{(2)} I_{\Lambda}(a_+, b_+ - i, c_+; \alpha_+, \beta_+) + A_i^{(3)} I_{\Lambda}(a_+, b_+, c_+ - i; \alpha_+, \beta_+) \right] \quad (11.33)$$

where $a_{\pm} = a' \pm a$, $\alpha_{\pm} = \alpha' \pm \alpha$ etc., and

$$A_0^{(1)} = -\alpha_+^2 - \alpha_-^2 + 2\alpha_- \alpha_+ (c_-/c_+), \\ A_1^{(1)} = 2\{\alpha_+(a_+ + 2) + \alpha_- a_- - [\alpha_+ a_- + \alpha_-(a_+ + 2)](c_-/c_+)\} - 8Z, \\ A_2^{(1)} = -a_+^2 - a_-^2 + 2a_+ + 2a_-(a_+ + 1)(c_-/c_+) + 2l_1(l_1 + 1)(1 - c_-/c_+) + 2l_1'(l_1' + 1)(1 + c_-/c_+), \\ A_0^{(3)} = 0, \quad A_1^{(3)} = 8, \\ A_2^{(3)} = 2(c_+^2 - c_-^2),$$

with $(c_-/c_+) = 0$ for $c_+ = 0$. The $A_i^{(2)}$ are defined similarly to $A_i^{(1)}$ with the replacements $a \rightarrow b$, $\alpha \rightarrow \beta$, $l_1 \rightarrow l_2$. The overlap integral is

$$\langle \chi' | \chi \rangle = \sum_{\Lambda} C_{\Lambda} I_{\Lambda}(a_+, b_+, c_+; \alpha_+, \beta_+). \quad (11.34)$$

11.3.4 Other Computational Methods

Although not yet at the same level of accuracy as variational methods, certain nonvariational methods, such as finite element methods [25], solutions to the Faddeev equations [26], and the correlated-function hyperspherical-harmonic method [27], have their own advantages of flexibility and/or generality. A characteristic feature of these methods is that they provide direct numerical solutions to the three-body problem which in principle converge pointwise to the exact solution, rather than depending upon a globally optimized solution. Other methods particularly suited to doubly-excited states are discussed in Chap. 25.

11.4 VARIATIONAL EIGENVALUES

High precision variational eigenvalues are available for all states of helium up to $n = 10$ and $L = 7$ [21, 22]. The nonrelativistic values of ϵ_0, ϵ_1 and ϵ_2 [see Eq. (11.6)] are listed in Tables 11.2 and 11.3. The ϵ_0 are the eigenvalues for infinite nuclear mass, and ϵ_1 and ϵ_2 , together with Eq. (11.6) give the finite mass corrections for the isotopes ${}^3\text{He}$ and ${}^4\text{He}$. The values of μ/M can be calculated from

$$\frac{\mu}{M} = \left[\frac{M_A}{5.485799015(130) \times 10^{-4}} - N + 1 \right]^{-1} \quad (11.35)$$

Table 11.2. Nonrelativistic eigenvalue coefficients ε_0 and ε_1 for helium.

State	$\varepsilon_0(n^1L)$	$\varepsilon_1(n^1L)$	$\varepsilon_0(n^3L)$	$\varepsilon_1(n^3L)$
1 S	-2.903 724 377 034 119 5	0.159 069 475 085 84		
2 S	-2.145 974 046 054 419(6)	0.009 503 864 419 28	-2.175 229 378 236 791 30	0.007 442 130 706 04
2 P	-2.123 843 086 498 093(2)	0.046 044 524 937(1)	-2.133 164 190 779 273(5)	-0.064 572 425 024(4)
3 S	-2.061 271 989 740 911(5)	0.002 630 567 097 7(1)	-2.068 689 067 472 457 19	0.001 896 211 617 81
3 P	-2.055 146 362 091 94(3)	0.014 548 047 097(1)	-2.058 081 084 274 28(4)	-0.018 369 001 636(2)
3 D	-2.055 620 732 852 246(6)	-0.000 249 399 992 1(1)	-2.055 636 309 453 261(4)	0.000 025 322 839(1)
4 S	-2.033 586 717 030 72(1)	0.001 073 641 226 6(1)	-2.036 512 083 098 236 30(2)	0.000 742 661 516 18
4 P	-2.031 069 650 450 24(3)	0.006 254 923 554 3(1)	-2.032 324 354 296 62(2)	-0.007 555 178 98(1)
4 D	-2.031 279 846 178 687(7)	-0.000 129 175 188 7(8)	-2.031 288 847 501 795(3)	0.000 029 442 651(2)
4 F	-2.031 255 144 381 749(1)	-0.000 010 024 269 4(2)	-2.031 255 168 403 245 6(6)	-0.000 009 669 639 6
5 S	-2.021 176 851 574 363(5)	0.000 538 860 360 5(1)	-2.022 618 872 302 312 27(1)	0.000 363 697 136 49
5 P	-2.019 905 989 900 83(2)	0.003 230 021 84(2)	-2.020 551 187 256 25(1)	-0.003 810 911 035(1)
5 D	-2.020 015 836 159 984(4)	-0.000 071 883 131(6)	-2.020 021 027 446 911(5)	0.000 019 568 85(1)
5 F	-2.020 002 937 158 742 7(5)	-0.000 005 704 294 6(4)	-2.020 002 957 377 369 4(4)	-0.000 005 406 490 0(5)
5 G	-2.020 000 710 898 584 71(1)	-0.000 001 404 413 6	-2.020 000 710 925 343 92(1)	-0.000 001 404 001 3
6 S	-2.014 563 098 446 60(1)	0.000 307 704 277(1)	-2.015 377 452 992 862 19(3)	0.000 204 329 479 10
6 P	-2.013 833 979 671 73(2)	0.001 878 058 536(1)	-2.014 207 958 773 74(1)	-0.002 184 346 463(1)
6 D	-2.013 898 227 424 286(5)	-0.000 043 412 268 9(9)	-2.013 901 415 453 792(7)	0.000 012 742 22(3)
6 F	-2.013 890 683 815 549 7(3)	-0.000 003 482 257(7)	-2.013 890 698 348 532 0(2)	-0.000 003 268 458 6(8)
6 G	-2.013 889 345 387 313 22(3)	-0.000 000 898 579 9(7)	-2.013 889 345 416 952 96(3)	-0.000 000 898 123 7(7)
6 H	-2.013 889 034 754 279 72	-0.000 000 290 347 1	-2.013 889 034 754 301 55	-0.000 000 290 346 7
7 S	-2.010 625 776 210 87(2)	0.000 191 925 025(1)	-2.011 129 919 527 626 21(4)	0.000 125 981 736 89
7 P	-2.010 169 314 529 35(2)	0.001 186 152 30(1)	-2.010 404 960 007 94(2)	-0.001 366 500 8(3)
7 D	-2.010 210 028 457 98(1)	-0.000 028 027 840(2)	-2.010 212 105 955 595(2)	0.000 008 563 121(3)
7 F	-2.010 205 248 074 013(1)	-0.000 002 262 00(4)	-2.010 205 258 374 865(1)	-0.000 002 110 58(3)
7 G	-2.010 204 386 224 772 55(7)	-0.000 000 598 396 3(3)	-2.010 204 386 250 217 93(6)	-0.000 000 598 005(1)
7 H	-2.010 204 182 806 482 04(2)	-0.000 000 201 097 8	-2.010 204 182 806 512 04(1)	-0.000 000 201 097 3
7 I	-2.010 204 120 606 191 32	-0.000 000 077 775 5	-2.010 204 120 606 191 340	-0.000 000 077 775 5
8 S	-2.008 093 622 105 61(4)	0.000 127 650 436(1)	-2.008 427 122 064 721 42(6)	0.000 083 070 552 34
8 P	-2.007 789 127 133 22(2)	0.000 796 195 83(5)	-2.007 947 013 771 12(1)	-0.000 911 053 5(3)
8 D	-2.007 816 512 563 811(7)	-0.000 019 076 181(1)	-2.007 817 934 711 706(3)	0.000 005 971 123 4(3)
8 F	-2.007 813 297 115 014 1(6)	-0.000 001 545 48(1)	-2.007 813 304 535 090 8(5)	-0.000 001 436 452(2)
8 G	-2.007 812 711 494 024 1(1)	-0.000 000 415 004 0(1)	-2.007 812 711 514 424 82(9)	-0.000 000 414 690 4
8 H	-2.007 812 571 828 655 81(1)	-0.000 000 142 649 2(3)	-2.007 812 571 828 685 73(1)	-0.000 000 142 648 7(2)
8 I	-2.007 812 528 549 584 59	-0.000 000 056 935 9	-2.007 812 528 549 584 61	-0.000 000 056 935 9
8 K	-2.007 812 512 570 229 31	-0.000 000 025 111 3	-2.007 812 512 570 229 306	-0.000 000 025 111 3
9 S	-2.006 369 553 107 85(3)	0.000 089 149 638 7(7)	-2.006 601 516 715 010 67(3)	0.000 057 628 311 52
9 P	-2.006 156 384 652 86(5)	0.000 559 978 028(2)	-2.006 267 267 366 41(4)	-0.000 637 531 359(6)
9 D	-2.006 175 671 437 641(6)	-0.000 013 542 185(3)	-2.006 176 684 884 697(2)	0.000 004 306 538(6)
9 F	-2.006 173 406 897 324 6(8)	-0.000 001 099 967 1(3)	-2.006 173 412 365 043 0(7)	-0.000 001 019 651(2)
9 G	-2.006 172 991 627 586 3(2)	-0.000 000 298 267 2(1)	-2.006 172 991 643 665 0(3)	-0.000 000 298 019 8(1)
9 H	-2.006 172 891 903 619 14(2)	-0.000 000 104 002 2	-2.006 172 891 903 645 88(2)	-0.000 000 104 001 9
9 I	-2.006 172 860 732 382 57	-0.000 000 042 313 6	-2.006 172 860 732 382 60	-0.000 000 042 313 6(1)
9 K	-2.006 172 849 096 329 78	-0.000 000 019 151 6	-2.006 172 849 096 329 780	-0.000 000 019 151 6
10 S	-2.005 142 991 748 00(8)	0.000 064 697 214(3)	-2.005 310 794 915 611 3(2)	0.000 041 598 811 52
10 P	-2.004 987 983 802 22(4)	0.000 408 649 426 3	-2.005 068 805 497 8(1)	-0.000 463 433 718(8)
10 D	-2.005 002 071 654 250(6)	-0.000 009 947 506 0(6)	-2.005 002 818 080 232(8)	0.000 003 198 298(8)
10 F	-2.005 000 417 564 668 2(9)	-0.000 000 809 442(9)	-2.005 000 421 686 603 6(7)	-0.000 000 748 926 4(2)
10 G	-2.005 000 112 764 318 0(3)	-0.000 000 220 982(2)	-2.005 000 112 777 003 1(4)	-0.000 000 220 785(3)
10 H	-2.005 000 039 214 394 52(2)	-0.000 000 077 806 7	-2.005 000 039 214 417 41(2)	-0.000 000 077 806 2
10 I	-2.005 000 016 086 516 19	-0.000 000 032 059 0(1)	-2.005 000 016 086 516 22	-0.000 000 032 058 9(2)
10 K	-2.005 000 007 388 375 88	-0.000 000 014 751 4	-2.005 000 007 388 375 88	-0.000 000 014 751 4

Table 11.3. Eigenvalue coefficients ε_2 for helium.

State	$\varepsilon_2(n^1L)$	$\varepsilon_2(n^3L)$
1 S	-0.470 391 870(1)	
2 S	-0.135 276 864(1)	-0.057 495 847 9(2)
2 P	-0.168 271 22(7)	-0.204 959 88(1)
3 S	-0.058 599 3124(4)	-0.040 455 850 5(5)
3 P	-0.066 047 859(3)	-0.070 292 710(2)
3 D	-0.057 201 299(9)	-0.054 737 73(1)
4 S	-0.032 522 293(2)	-0.025 628 633 8(1)
4 P	-0.035 159 71(6)	-0.036 129 973(2)
4 D	-0.032 150 91(2)	-0.030 747 891(7)
4 F	-0.031 274 336(4)	-0.031 277 992 1(3)
5 S	-0.020 647 26(9)	-0.017 322 734 96
5 P	-0.021 847 6(3)	-0.022 166 61(9)
5 D	-0.020 510 1(2)	-0.019 706 2(2)
5 F	-0.020 013 498(6)	-0.020 016 561(4)
5 G	-0.020 003 560 8	-0.020 003 564 6
6 S	-0.014 261 796(4)	-0.012 411 399 1(3)
6 P	-0.014 902 86(9)	-0.015 033 58(5)
6 D	-0.014 199 4(2)	-0.013 707 27(1)
6 F	-0.013 896 984(2)	-0.013 899 22(3)
6 G	-0.013 891 179(6)	-0.013 891 184(8)
6 H	-0.013 889 619 1	-0.013 889 619 0
7 S	-0.010 438 2(2)	-0.009 304 443 3(3)
7 P	-0.010 818 6(2)	-0.010 879(2)
7 D	-0.010 405 09(3)	-0.010 085 212(1)
7 F	-0.010 209 2(3)	-0.010 210 7(3)
7 G	-0.010 205 61(5)	-0.010 205 61(5)
7 H	-0.010 204 590(2)	-0.010 204 587(2)
7 I	-0.010 204 276 7	-0.010 204 276 8
8 S	-0.007 968 944(3)	-0.007 224 770 5(3)
8 P	-0.008 211 7(5)	-0.008 248 7(6)
8 D	-0.007 950 7(4)	-0.007 731 59(2)
8 F	-0.007 815 9(3)	-0.007 817 0(2)
8 G	-0.007 813 563(1)	-0.007 813 568(3)
8 H	-0.007 812 855(4)	-0.007 812 859(5)
8 I	-0.007 812 642 9	-0.007 812 642 9
8 K	-0.007 812 563 0	-0.007 812 563 0
9 S	-0.006 282 5136(1)	-0.005 768 028 5(1)
9 P	-0.006 445 7(2)	-0.006 464 936 9(1)
9 D	-0.006 270 99(7)	-0.006 115 2(1)
9 F	-0.006 175 20(1)	-0.006 176 025 4(7)
9 G	-0.006 173 579 6(1)	-0.006 173 592(4)
9 H	-0.006 173 104(2)	-0.006 173 101(2)
9 I	-0.006 172 945 9(1)	-0.006 172 946 0(2)
9 K	-0.006 172 887 6	-0.006 172 887 6
10 S	-0.005 079 8362(8)	-0.004 709 453 0(1)
10 P	-0.005 197(1)	-0.005 206 7(1)
10 D	-0.005 072 4(4)	-0.004 958 0(8)
10 F	-0.005 001 76(2)	-0.005 002 386(2)
10 G	-0.005 000 55(2)	-0.005 000 55(2)
10 H	-0.005 000 193 5(2)	-0.005 000 193 5(1)
10 I	-0.005 000 080 3(4)	-0.005 000 081(1)
10 K	-0.005 000 036 9	-0.005 000 036 8

Table 11.4. Values of the reduced electron mass ratio μ/M .

Isotope	$\mu/M \times 10^4$
¹ H	5.443 205 67(11)
² D	2.723 695 02(6)
³ He	1.819 212 04(3)
⁴ He	1.370 745 62(3)
⁶ Li	0.912 167 73(11)
⁷ Li	0.782 020 31(9)
⁹ Be	0.608 820 44(3)

where M_A is the atomic mass (in amu, see Ref. [28] for a tabulation)² and N is the number of electrons. For ⁴He, one can use directly the accurately known value of m_e/m_α to calculate $\mu/M = 1/(m_\alpha/m_e + 1)$. Values of μ/M for the first several isotopes are listed in Table 11.4, and the corresponding energy coefficients for the $1s^2 \ ^1S$ ground state are given in Table 11.5.

11.4.1 Expectation Values of Operators and Sum Rules

Expectation values for various powers of the radial coordinates, together with operators appearing in the Breit interaction, are listed in Table 11.6 for the ground state of helium and He-like ions. Included are all terms required to calculate $\langle V^2 \rangle$, and the oscillator strength sum rules [29]

$$S(-1) = \frac{2}{3} \langle (r_1 + r_2)^2 \rangle, \quad (11.36a)$$

$$S(0) = 2, \quad (11.36b)$$

$$S(1) = -\frac{4}{3}(\varepsilon_0 - \varepsilon_1), \quad (11.36c)$$

$$S(2) = \frac{2\pi Z}{3} \langle \delta(r_1) + \delta(r_2) \rangle, \quad (11.36d)$$

where $S(k) = \sum_n [\varepsilon_0(n^1P) - \varepsilon_0(1^1S)]^k f_{0n}$, with energies in a.u., and f_{0n} is the $1^1S - n^1P$ oscillator strength (see Sect. 11.6.1).

11.5 TOTAL ENERGIES

As discussed in Chaps. 21 and 27, relativistic and QED corrections must be added to the nonrelativistic eigenvalues of Sect. 11.4 before a meaningful comparison with measured transition frequencies can be made. The corrections are discussed in detail in Refs. [21, 30].

The terms in order of decreasing size are:

1. Relativistic Corrections of $O(\alpha^2)$.

²For high precision work, the helium electronic binding energy of 8.48×10^{-8} amu should be added to M_A .

Table 11.5. Nonrelativistic eigenvalues $E = \varepsilon_0 + (\mu/M)\varepsilon_1 + (\mu/M)^2\varepsilon_2$ for helium-like ions (in units of e^2/a_μ).

Atom	$\varepsilon_0(1^1S)$	$\varepsilon_1(1^1S)$	$\varepsilon_2(1^1S)$
H ⁻	-0.527 751 016 544 377	0.032 879 781 852 30	-0.059 779 492 64(1)
He	-2.903 724 377 034 119 5	0.159 069 475 085 84	-0.470 391 870(1)
Li ⁺	-7.279 913 412 669 305 9	0.288 975 786 393 99	-1.277 369 377 6(2)
Be ⁺⁺	-13.155 566 238 423 586 7	0.420 520 303 439 44	-2.491 572 858 1(1)

Table 11.6. Expectation values of various operators for He-like ions for the case $M = \infty$ (in a.u.).

Quantity	H ⁻	He	Li ⁺	Be ⁺⁺
$\langle r_1^2 \rangle$	11.913 699 678 05(6)	1.193 482 995 019	0.446 279 011 201	0.232 067 315 531
$\langle r_{12}^2 \rangle$	25.202 025 291 2(1)	2.516 439 312 833	0.927 064 803 063	0.477 946 525 143
$\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle$	-0.687 312 967 569	-0.064 736 661 398	-0.017 253 390 330	-0.006 905 947 040
$\langle r_1 \rangle$	2.710 178 278 444(1)	0.929 472 294 874	0.572 774 149 971	0.414 283 328 006
$\langle r_{12} \rangle$	4.412 694 497 992(2)	1.422 070 255 566	0.862 315 375 456	0.618 756 314 066
$\langle 1/r_1 \rangle$	0.683 261 767 652	1.688 316 800 717	2.687 924 397 413	3.687 750 406 344
$\langle 1/r_{12} \rangle$	0.311 021 502 214	0.945 818 448 800	1.567 719 559 137	2.190 870 773 906
$\langle 1/r_1^2 \rangle$	1.116 662 824 6(1)	6.017 408 867 0(1)	14.927 623 721 4(2)	27.840 105 671 33(2)
$\langle 1/r_{12}^2 \rangle$	0.155 104 152 58(3)	1.464 770 923 350(1)	4.082 232 787 55(2)	8.028 801 781 824(1)
$\langle 1/r_1 r_2 \rangle$	0.382 627 890 340	2.708 655 474 480	7.011 874 111 824(1)	13.313 954 940 144(1)
$\langle 1/r_1 r_{12} \rangle$	0.253 077 567 065	1.920 943 921 900	5.069 790 932 379	9.717 071 116 528
$\langle \delta(r_1) \rangle$	0.164 552 872 86(3)	1.810 429 318 49(3)	6.852 009 434 4(1)	17.198 172 544 74(3)
$\langle \delta(r_{12}) \rangle$	0.002 737 992 3(3)	0.106 345 371 2(2)	0.533 722 537 1(9)	1.522 895 354 1(2)
$\langle p^4 \rangle$	2.462 558 614(3)	54.088 067 230(2)	310.547 150 179(6)	1047.278 491 476(2)
$\langle H_{00} \rangle / \alpha^2$	-0.008 875 022 10(1)	-0.139 094 690 556(1)	-0.427 991 611 178(9)	-0.878 768 694 709(1)

$$H_{\text{rel}} = H_{\text{NFS}} + H_{\text{FS}},$$

$$H_{\text{NFS}} = H_{\text{mass}} + H_{\text{D}} + H_{\text{SSC}} + H_{\text{OO}},$$

$$H_{\text{FS}} = H_{\text{SO}} + H_{\text{SOO}} + H_{\text{SS}}.$$

The various nonfine-structure (NFS) and fine-structure (FS) terms are defined in Sect. 21.1. The off-diagonal matrix elements of H_{FS} mix states of different spin and cause a break-down of LS -coupling.

2. Anomalous Magnetic Moment Corrections of $O(\alpha^3)$. The general FS matrix elements between states with spins S and S' due to the anomalous magnetic moment a_e are (see Sect. 27.5)

$$\langle \gamma S | H_{\text{FS}}^{\text{anom}} | \gamma' S' \rangle = 2a_e \langle \gamma S | H_{\text{SO}} + \frac{2}{3} \delta_{S,S'} H_{\text{SOO}} + (1 + \frac{1}{2} a_e) H_{\text{SS}} | \gamma' S' \rangle, \quad (11.37)$$

where $a_e = (g_e - 2)/2 = \alpha/(2\pi) - 0.328 479 \alpha^2 + \dots$

3. QED Corrections of $O(\alpha^3)$. The lowest order QED corrections (including NFS anomalous magnetic moment terms) can be written in the form $\Delta_{L,1} + \Delta_{L,2}$, where

$$\Delta_{E_{L,1}} = \frac{4}{3} Z \alpha^3 [\ln(Z\alpha)^{-2} + \frac{19}{30} - \ln k_0] \langle \delta(r_1) + \delta(r_2) \rangle \quad (11.38)$$

$$\Delta_{E_{L,2}} = \alpha^3 \left[\frac{89}{15} + \frac{14}{3} \ln \alpha - \frac{20}{3} \mathbf{s}_1 \cdot \mathbf{s}_2 \right] \langle \delta(r_{12}) \rangle - \frac{14}{3} \alpha^3 Q, \quad (11.39)$$

$\ln k_0$ is the two-electron Bethe logarithm defined by Eq. (27.86) and Q is the matrix element defined by Eq.

(27.83). For a highly excited $1snl$ state, $\Delta_{E_{L,2}} \rightarrow 0$, $\langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle \rightarrow Z^3/\pi$, $\ln k_0 \rightarrow \ln k_0(1s) = 2.984 128 555$, and $\Delta_{E_{L,1}}$ reduces to the Lamb shift of the $1s$ core state (see Sects. 28.3.4 and 28.3.5). Thus $\Delta_{E_{L,1}}$ represents the essentially one-electron part of the QED shift with the factor of Z^3/π replaced by the correct electron density at the nucleus. Values of $\ln k_0$ for two-electron atoms are in general difficult to calculate. For a $1snl$ state with large l , the asymptotic expansion [31]

$$\ln k_0(1snl) \sim \ln k_0(1s) + \frac{1}{n^3} \left(\frac{Z-1}{Z} \right)^4 \ln k_0(nl) + 0.316 26 Z^{-6} \langle r^{-4} \rangle_{nl} \quad (11.40)$$

becomes essentially exact. Here $\ln k_0(nl)$ is the one-electron Bethe logarithm [32] and

$$\langle r^{-4} \rangle_{nl} = \frac{16(Z-1)^4 [3n^2 - l(l+1)]}{(2l-1)2l(2l+1)(2l+2)(2l+3)}. \quad (11.41)$$

For the low-lying S -states of helium [33],

$$\ln k_0(1^1S) = 2.983 856(2), \quad (11.42a)$$

$$\ln k_0(2^1S) = 2.980 058(2), \quad (11.42b)$$

$$\ln k_0(2^3S) = 2.977 720(1). \quad (11.42c)$$

For higher Z , the $1/Z$ expansions [34]

Table 11.7. Total ionization energies for ^4He , calculated with $R_M = 3 289 391 007.44$ MHz.

State	$E(n^1L_L)$	$E(n^3L_{L-1})$	$E(n^3L_L)$	$E(n^3L_{L+1})$
1 S	5 945 204 258(180)			
2 S	960 332 042.6(8.0)			1 152 842 738.0(8.0)
2 P	814 709 153.5(8.0)	876 078 647.4(8.0)	876 108 270.6(8.0)	876 110 563.6(8.0)
3 S	403 096 136.5(34.0)			451 903 467.1(41.0)
3 P	362 787 969.7(2.4)	382 109 904.0(2.4)	382 118 019.2(2.4)	382 118 678.5(2.4)
3 D	365 917 749.11(2)	366 018 892.94(2)	366 020 218.06(2)	366 020 293.39(2)
4 S	220 948 853.8(13.0)			240 193 898.6(16.0)
4 P	204 397 211.4(1.2)	212 658 041.6(1.2)	212 661 349.1(1.2)	212 661 618.8(1.2)
4 D	205 783 935.87(1)	205 842 547.90(1)	205 843 103.14(1)	205 843 139.16(1)
4 F	205 620 797.192 1(7)	205 621 029.649 2(7)	205 621 502.065 8(7)	205 621 288.021 5(7)
5 S	139 318 271.7(6.0)			148 807 319.8(8.0)
5 P	130 955 542.2(4)	135 203 443.6(4)	135 205 105.9(4)	135 205 241.4(4)
5 D	131 680 211.973(6)	131 714 043.935(6)	131 714 327.495(6)	131 714 346.715(6)
5 F	131 595 041.530 6(5)	131 595 195.264 3(6)	131 595 419.770 5(6)	131 595 327.483 4(6)
5 G	131 580 320.162 1(2)	131 580 370.975 8(2)	131 580 529.548 1(2)	131 580 446.489 9(2)
6 S	95 807 694.1(4.0)			101 166 450.4(4.0)
6 P	91 009 810.75(24)	93 472 041.87(24)	93 472 992.88(24)	93 473 070.37(24)
6 D	91 433 655.865(3)	91 454 440.606(3)	91 454 604.487(3)	91 454 615.833(3)
6 F	91 383 852.051 7(3)	91 383 954.321 5(3)	91 384 078.920 4(3)	91 384 030.814 4(3)
6 G	91 374 997.981 5(2)	91 375 027.438 1(2)	91 375 119.156 5(2)	91 375 071.134 2(2)
6 H	91 372 940.632 7(2)	91 372 961.833 9(1)	91 373 021.550 7(1)	91 372 990.247 1(1)
7 S	69 904 830.2(2.0)			73 222 276.7(2.0)
7 P	66 901 127.65(20)	68 452 586.84(20)	68 453 181.14(20)	68 453 229.54(20)
7 D	67 169 717.174(2)	67 183 264.592(2)	67 183 367.712(2)	67 183 374.936(2)
7 F	67 138 158.572 2(3)	67 138 228.573 5(2)	67 138 305.080 6(2)	67 138 276.734 8(2)
7 G	67 132 455.962 6(2)	67 132 474.536 7(3)	67 132 532.272 2(3)	67 132 502.051 9(3)
7 H	67 131 109.030 24(4)	67 131 122.381 75(4)	67 131 159.987 28(4)	67 131 140.274 18(4)
7 I	67 130 692.494 97(2)	67 130 702.504 47(2)	67 130 728.929 98(2)	67 130 715.103 36(2)
8 S	53 246 292.0(1.0)			55 440 840.7(2.0)
8 P	51 242 587.47(12)	52 282 092.17(12)	52 282 488.12(12)	52 282 520.36(12)
8 D	51 423 248.154(2)	51 432 523.250(2)	51 432 592.295(2)	51 432 597.169(2)
8 F	51 402 021.640 5(2)	51 402 071.121 6(2)	51 402 121.545 8(2)	51 402 103.381 7(2)
8 G	51 398 146.249 44(8)	51 398 158.704 3(1)	51 398 197.371 4(1)	51 398 177.136 6(1)
8 H	51 397 221.590 77(5)	51 397 230.535 37(6)	51 397 255.727 95(6)	51 397 242.521 70(6)
8 I	51 396 931.954 56(2)	51 396 938.660 18(2)	51 396 956.363 16(2)	51 396 947.100 39(2)
8 K	51 396 822.746 08(1)	51 396 827.941 01(1)	51 396 841.064 37(1)	51 396 834.214 80(1)
9 S	41 903 986.9(8)			43 430 388.7(1.0)
9 P	40 501 246.45(8)	41 231 283.33(8)	41 231 560.29(8)	41 231 582.83(8)
9 D	40 628 480.277(1)	40 635 090.450(1)	40 635 138.924(1)	40 635 142.364(1)
9 F	40 613 531.518 0(1)	40 613 567.564 1(1)	40 613 602.586 8(1)	40 613 590.219 4(1)
9 G	40 610 783.207 7(1)	40 610 791.961 35(7)	40 610 819.112 53(7)	40 610 804.906 48(7)
9 H	40 610 123.045 0(2)	40 610 129.327 1(1)	40 610 147.020 6(1)	40 610 137.745 4(1)
9 I	40 609 914.525 83(3)	40 609 919.235 42(2)	40 609 931.668 77(2)	40 609 925.163 22(2)
9 K	40 609 835.106 61(1)	40 609 838.755 19(1)	40 609 847.972 14(1)	40 609 843.161 46(1)
10 S	33 834 686.3(6)			34 938 889.0(7)
10 P	32 814 665.36(6)	33 346 784.43(6)	33 346 985.68(6)	33 347 002.06(6)
10 D	32 907 601.923(2)	32 912 470.759(1)	32 912 506.087(1)	32 912 508.602(1)
10 F	32 896 683.103 7(4)	32 896 710.074 1(4)	32 896 735.404 2(4)	32 896 726.588 7(4)
10 G	32 894 665.778 26(4)	32 894 672.163 03(4)	32 894 691.953 01(4)	32 894 681.599 81(4)
10 H	32 894 178.916 98(5)	32 894 183.496 72(5)	32 894 196.395 17(5)	32 894 189.633 59(5)
10 I	32 894 024.248 39(1)	32 894 027.681 69(1)	32 894 036.745 59(1)	32 894 032.003 04(1)
10 K	32 893 964.934 34(1)	32 893 967.594 16(1)	32 893 974.313 31(1)	32 893 970.806 33(1)

Table 11.8. QED corrections included in Table 11.7 for the S - and P -states of helium (in MHz).

State	$\Delta E_{L,1}$		$\Delta E_{L,2}$	
	Singlet	Triplet	Singlet	Triplet
1 S	-45410.2		4208.06	
2 S	-3135.7	-4099.2	330.359	36.883
3 S	-854.1	-1035.6	91.960	8.468
4 S	-336.8	-397.3	37.590	3.203
5 S	-161.7	-188.8	18.880	1.544
6 S	-87.8	-102.4	10.785	0.861
7 S	-51.8	-60.6	6.729	0.528
8 S	-32.4	-38.3	4.476	0.347
9 S	-21.19	-25.3	3.126	0.240
10 S	-14.32	-17.37	2.269	0.173
2 P	-100.1	1214.0	62.819	45.502
3 P	-33.8	347.3	19.632	12.376
4 P	-14.5	143.4	8.445	5.036
5 P	-7.49	72.50	4.364	2.529
6 P	-4.35	41.60	2.539	1.446
7 P	-2.74	26.05	1.604	0.904
8 P	-1.84	17.37	1.077	0.602
9 P	-1.29	12.16	0.758	0.421
10 P	-0.942	8.842	0.553	0.306

$$\ln k_0(1^1S) = \ln[19.769\,2669(1 - 0.00615/Z)^2] \quad (11.43a)$$

$$\ln k_0(2^1S) = \ln[19.394\,2687(1 + 0.02040/Z)^2] \quad (11.43b)$$

$$\ln k_0(2^3S) = \ln[19.394\,2687(1 + 0.01388/Z)^2] \quad (11.43c)$$

are useful.

4. Relativistic Finite Mass Corrections of $O(\alpha^2\mu/M)$. Relativistic finite mass corrections come from two sources. First, a transformation to relative coordinates as in Eq. (11.3) is applied to the pairwise Breit interactions among the three particles, generating the new terms [35]

$$\Delta = \Delta_{oo} + \Delta_{so} + 2\frac{m_e}{M}H_{so}$$

where

$$\Delta_{oo} = \frac{-Z\alpha^2 m_e}{2M} \sum_{i,j} \frac{1}{r_i} [\mathbf{p}_j \cdot \mathbf{p}_i + \hat{\mathbf{r}}_i \cdot (\hat{\mathbf{r}}_i \cdot \mathbf{p}_j) \mathbf{p}_i], \quad (11.44)$$

$$\Delta_{so} = \frac{Z\alpha^2 m_e}{M} \sum_{i \neq j} \frac{1}{r_i^3} \mathbf{r}_i \times \mathbf{p}_j \cdot \mathbf{s}_i. \quad (11.45)$$

Second, the mass polarization term H_{mp} in Eq. (11.3) generates second-order cross-terms between H_{mp} and H_{rel} . If the wave functions are calculated by solving Eq. (11.4) in scaled atomic units, the H_{mp} correction is then automatically included to all orders and the mass-corrected relativistic energy shift is (in units of e^2/a_0)

$$\Delta E_{rel} = \left(\frac{\mu}{m_e}\right)^3 \left\langle \left(\frac{\mu}{m_e}\right) H_{mass} + H_D + H_{ssc} + H_{oo} + \Delta_{oo} + \left(1 + \frac{2m_e}{M}\right) H_{so} + H_{soo} + H_{ss} + \Delta_{so} \right\rangle \quad (11.46)$$

with $\mu/m_e = 1 - \mu/M$. The difference $\Delta E_{rel} - \langle H_{rel} \rangle_{\infty}$ calculated for infinite nuclear mass is the relativistic finite mass correction.

5. Higher-order Corrections. Spin-dependent terms of $O(\alpha^4)$ are known in their entirety, and have recently been calculated to high precision [36]. Nonrelativistic operators for the spin-independent part are not known in their entirety, but the one-electron part is known from the one-electron Lamb shift to be

$$\Delta E'_{L,1} = Z\alpha^3 \left[\pi Z\alpha \left(\frac{427}{96} - 2 \ln 2 \right) + 0.538\,931 \frac{\alpha}{\pi} \right] \times \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle. \quad (11.47)$$

As an example, $\Delta E'_{L,1}$ contributes -50.336 MHz and -88.267 MHz to the $2^1P - 2^1S$ and $2^3P_J - 2^3S_1$ transition frequencies respectively, while the differences between theory and experiment are ~ 1 MHz and ~ -7 MHz for the two cases (see Ref. [30]). Thus, two-electron corrections (for example, relativistic corrections of relative order $Z\alpha$ to $\Delta E_{L,2}$) are evidently small.

Table 11.7 lists the calculated ionization energies for all states of helium up to $n = 10$ and $L = 7$. For the D -states and beyond, the uncertainties are sufficiently small that these states can be taken as known points of reference in the interpretation of experimental transition frequencies. However, long-range Casimir-Polder corrections [37] are not included since they still lack experimental confirmation [38]. For the S - and P -states, the QED uncertainties are much larger. The contributions from $\Delta E_{L,1} + \Delta E'_{L,1}$ and $\Delta E_{L,2}$ for these states are listed separately in Table 11.8 so that the entries in Table 11.7 can be adjusted as better calculations become available. Applications to isotope shifts and measurements of the nuclear radius are discussed in Sects. 16.3 and 86.2.

11.5.1 Quantum Defect Extrapolations

As discussed in Sect. 14.2, the ionization energies of an isolated Rydberg series of states can be expressed in the form

$$W_n = R_M(Z-1)^2/n^{*2}, \quad (11.48)$$

where $Z-1$ is the screened nuclear charge and n^* is the effective principal quantum number defined by an iterative solution to the equation

$$n^* = n - \delta(n^*), \quad (11.49)$$

Table 11.9. Quantum defects for the total energies of helium with the ΔW_n term subtracted [see Eq. (11.52)].

δ_i	Value			
	$1S_0$			$3S_1$
δ_0	0.139 737 6(34)			0.296 676 7(31)
δ_2	0.025 05(39)			0.035 47(34)
δ_4	0.139(12)			0.126(10)
δ_6	-1.60(11)			-1.478(86)
	$1P_1$	$3P_0$	$3P_1$	$3P_2$
δ_0	-0.012 141 803 603(64)	0.068 328 002 51(27)	0.068 357 857 65(27)	0.068 360 283 79(23)
δ_2	0.007 519 080 4(59)	-0.018 641 975(24)	-0.018 630 462(24)	-0.018 629 228(21)
δ_4	0.013 977 80(15)	-0.012 331 65(57)	-0.012 330 40(57)	-0.012 332 75(51)
δ_6	0.004 837 3(12)	-0.007 951 5(45)	-0.007 951 2(45)	-0.007 952 7(41)
δ_8	0.001 228 3(29)	-0.005 448(10)	-0.005 450(10)	-0.005 451(9)
	$1D_2$	$3D_1$	$3D_2$	$3D_3$
δ_0	0.002 113 378 464(49)	0.002 885 580 281(22)	0.002 890 941 493(25)	0.002 891 328 825(26)
δ_2	-0.003 090 051 0(58)	-0.006 357 601 2(27)	-0.006 357 183 6(30)	-0.006 357 704 0(33)
δ_4	0.000 008 27(22)	0.000 336 67(11)	0.000 337 77(11)	0.000 336 70(13)
δ_6	-0.000 309 4(31)	0.000 839 4(16)	0.000 839 2(16)	0.000 839 5(18)
δ_8	-0.000 401(14)	0.000 379 8(72)	0.000 432 3(75)	0.000 381 1(83)
	$1F_3$	$3F_2$	$3F_3$	$3F_4$
δ_0	0.000 440 294 26(62)	0.000 444 869 89(22)	0.000 448 594 83(28)	0.000 447 379 27(21)
δ_2	-0.001 689 446(65)	-0.001 739 275(24)	-0.001 727 232(30)	-0.001 739 217(23)
δ_4	-0.000 118 3(20)	0.000 104 76(76)	0.000 152 4(9)	0.000 104 78(71)
δ_6	0.000 326(18)	0.000 033 7(69)	-0.000 248 6(83)	0.000 033 1(64)
	$1G_4$	$3G_3$	$3G_4$	$3G_5$
δ_0	0.000 124 734 490(79)	0.000 125 707 43(12)	0.000 128 713 16(10)	0.000 127 141 67(11)
δ_2	-0.000 796 230(12)	-0.000 796 498(19)	-0.000 796 246(15)	-0.000 796 484(17)
δ_4	-0.000 012 05(53)	-0.000 009 80(81)	-0.000 011 89(66)	-0.000 009 85(75)
δ_6	-0.000 013 6(69)	-0.000 019(11)	-0.000 014 1(85)	-0.000 019(10)
	$1H_5$	$3H_4$	$3H_5$	$3H_6$
δ_0	0.000 047 100 899(61)	0.000 047 797 067(43)	0.000 049 757 614(51)	0.000 048 729 846(45)
δ_2	-0.000 433 227 7(84)	-0.000 433 232 2(55)	-0.000 433 227 4(65)	-0.000 433 228 1(57)
δ_4	-0.000 008 14(26)	-0.000 008 07(16)	-0.000 008 13(19)	-0.000 008 10(16)
	$1I_6$	$3I_5$	$3I_6$	$3I_7$
δ_0	0.000 021 868 881(17)	0.000 022 390 759(20)	0.000 023 768 483(14)	0.000 023 047 609(26)
δ_2	-0.000 261 067 3(22)	-0.000 261 068 0(28)	-0.000 261 066 2(18)	-0.000 261 067 2(35)
δ_4	-0.000 004 048(67)	-0.000 004 042(87)	-0.000 004 076(58)	-0.000 004 04(11)

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

$$\delta(n^*) = \delta_0 + \frac{\delta_2}{(n-\delta)^2} + \frac{\delta_4}{(n-\delta)^4} + \dots \quad (11.50)$$

with constant coefficients δ_i . The absence of *odd* terms in this series is a special property of the eigenvalues of Hamiltonians of the form $H_C + V$, where H_C is a pure one-electron Coulomb Hamiltonian, and V is a local, short-range, spherically symmetric potential of arbitrary strength (see Ref. [39] for further discussion). For the Rydberg states of helium, odd terms must be included in the Ritz expansion (11.50) due to relativistic and mass

polarization corrections, but they can be removed again by first adjusting the energies according to

$$W'_n = W_n - \Delta W_n \quad (11.51)$$

where, to sufficient accuracy [39] [see discussion following Eq. (11.64)]

$$\Delta W_n = R_M \left\{ \frac{-3\alpha^2(Z-1)^4}{4n^4} + \left(\frac{\mu}{M}\right)^2 \frac{(Z-1)^2}{n^2} \times \left[1 + \frac{5}{6}(\alpha Z)^2 \right] \right\}, \quad (11.52)$$

with $Z = 2$ for helium. The quantum defect parameters listed in Table 11.9 provide accurate extrapolations to

higher-lying Rydberg states, with

$$W_n = R_M/n^{*2} + \Delta W_n. \quad (11.53)$$

11.5.2 Asymptotic Expansions

The asymptotic expansion method [30, 40] rapidly increases in accuracy with increasing angular momentum L of the Rydberg electron, and can be used to high precision for $L \geq 7$. The method is based on a model in which:

1. the Rydberg electron, treated as a distinguishable particle, moves in the field of the core consisting of the He nucleus and a tightly bound $1s$ electron.
2. the core, as characterized by its various multipole moments, is perturbed by the electric field of the Rydberg electron.

A systematic perturbation expansion yields an asymptotic series of the form

$$\varepsilon_0^{nL} = -2 - \frac{(Z-1)^2}{2n^2} + a_0 \sum_{j=4}^N A_j \langle r^{-j} \rangle_{nL} \frac{e^2}{a_0}, \quad (11.54)$$

where the expectation value $\langle r^{-j} \rangle_{nL}$ is calculated with respect to the hydrogenic nL -electron wave function [41] and the series is truncated at the upper limit N where the series begins diverging. The leading coefficients A_j are

$$A_4 = -\frac{1}{2}\alpha_1, \quad A_5 = 0, \quad A_6 = -\frac{1}{2}(\alpha_2 - 6\beta_1),$$

where α_k is the 2^k -pole polarizability of the hydrogenic core and β_k is a nonadiabatic correction. The exact hydrogenic values are

$$\alpha_1 = \frac{9a_0^3}{2Z^4}, \quad \alpha_2 = \frac{15a_0^5}{Z^6}, \quad \beta_1 = \frac{43a_0^5}{8Z^6}.$$

All terms are known up to A_{10} (see Refs. [30, 40] for detailed results). The expansions for the terms ε_0 , ε_1 , and ε_2 in Eq. (11.6) for helium are

$$\begin{aligned} \varepsilon_0^{nL} = & -2 - \frac{1}{2n^2} - \frac{9}{64} \langle r^{-4} \rangle + \frac{69}{512} \langle r^{-6} \rangle + \frac{3833}{15360} \langle r^{-7} \rangle \\ & - \left[\frac{55923}{65536} + \frac{957L(L+1)}{10240} \right] \langle r^{-8} \rangle - \frac{908185}{688128} \langle r^{-9} \rangle \\ & + \left[\frac{3824925}{1048576} + \frac{33275L(L+1)}{28672} \right] \langle r^{-10} \rangle \\ & + e^{(1,1)} - \frac{23}{20} e^{(1,2)}, \end{aligned} \quad (11.55)$$

$$\begin{aligned} \varepsilon_1^{nL} = & -\frac{9}{32} \langle r^{-4} \rangle + \frac{249}{256} \langle r^{-6} \rangle + \frac{319}{3840} \langle r^{-7} \rangle \\ & - \left[\frac{34659}{16384} + \frac{957L(L+1)}{5120} \right] \langle r^{-8} \rangle - \frac{14419}{3072} \langle r^{-9} \rangle \\ & + \left[\frac{6413781}{262144} + \frac{24155L(L+1)}{8192} \right] \langle r^{-10} \rangle \\ & + 4e^{(1,1)} - \frac{53}{5} e^{(1,2)}, \end{aligned} \quad (11.56)$$

$$\begin{aligned} \varepsilon_2^{nL} = & -\frac{1}{2n^2} - \frac{45}{64} \langle r^{-4} \rangle + \frac{165}{512} \langle r^{-6} \rangle + \frac{2555}{3072} \langle r^{-7} \rangle \\ & - \left[\frac{268485}{32768} + \frac{957L(L+1)}{2048} \right] \langle r^{-8} \rangle + \frac{598909}{172032} \langle r^{-9} \rangle \\ & + \left[\frac{3907923}{524288} + \frac{629515L(L+1)}{114688} \right] \langle r^{-10} \rangle \\ & + 14e^{(1,1)} - \frac{251}{10} e^{(1,2)}. \end{aligned} \quad (11.57)$$

The terms $e^{(1,1)}$ and $e^{(1,2)}$ are second-order dipole-dipole and dipole-quadrupole perturbation corrections. Defining $f_p^L = (L+p)!/(L-p)!$, they are given by

$$\begin{aligned} e^{(i,j)} = & -\frac{(2-\delta_{j,k})2^{2i+2j+1}(2L-2i)!(2L-2j)!}{n^3(2L+2i+1)!(2L+2j+1)!} \\ & \times \left[\frac{2^{2i+2j}(2L-2i-2j)!A^{(i,j)}}{n^{2i+2j+2}(2L+2i+2j+1)!} + \frac{B^{(i,j)}}{n^{2i+2j+1}} \right] \end{aligned} \quad (11.58)$$

with

$$\begin{aligned} A^{(1,1)} = & 3n^2(3n^2 - 2f_1)(f_1 - 2)(45 + 623f_1^L + 3640f_2^L \\ & + 560f_3^L), \\ B^{(1,1)} = & (9n^2 - 7f_1^L)(3n^2 - f_1^L), \\ A^{(1,2)} = & -21n^6(94500 + 122850f_1^L - 1126125f_2^L \\ & - 18931770f_3^L - 11171160f_4^L \\ & - 1029600f_5^L - 18304f_6^L) \\ & - 15n^4(94500 - 444150f_1^L + 7747425f_2^L \\ & + 337931880f_3^L + 375290190f_4^L \\ & + 66518760f_5^L + 2880416f_6^L + 29568f_7^L) \\ & + 9n^2f_1^L(90300 - 177450f_1^L + 1738450f_2^L \\ & + 133125575f_3^L + 160040870f_4^L \\ & + 29322216f_5^L + 1293600f_6^L + 13440f_7^L) \\ & + 2f_1^L f_2^L f_3^L (45 + 252f_1^L - 1680f_2^L - 2240f_3^L), \\ B^{(1,2)} = & 315n^6 + 125n^4(3 - 5f_1^L) - 7n^2f_1^L(43 - 39f_1^L) \\ & - 27f_1^L f_2^L. \end{aligned}$$

The accuracy of the expansion for the ε_0 , ε_1 , and ε_2 can be reliably estimated to be one-half of the last $\langle r^{-j} \rangle$ term included in the sum. Formulas for the $\langle r^{-j} \rangle$ are given in Table 11.10.

The asymptotic formulas for the NFS relativistic corrections are [30, 42]

$$\begin{aligned} \langle H_{\text{mass}} + H_D \rangle \rightarrow & -\frac{\alpha^2 Z^4}{8} + h_1(nL) + \chi_1(nL) \\ & + \frac{(Z\alpha)^2}{2} \left[\frac{14}{3Z^4} \langle r^{-4} \rangle - \frac{5041}{240Z^6} \langle r^{-6} \rangle \right] \end{aligned} \quad (11.59)$$

$$\begin{aligned} \langle H_{\text{oo}} \rangle \rightarrow & \frac{\alpha^2}{Z^2} \left[\langle r^{-4} \rangle + \frac{3(Z-1)}{Z^2} \langle r^{-5} \rangle \right. \\ & \left. - \frac{3(f_1^L + 8)}{4Z^2} \langle r^{-6} \rangle \right], \end{aligned} \quad (11.60)$$

Table 11.10. Formulas for the hydrogenic expectation value $\langle r^{-j} \rangle \equiv \langle nl|r^{-j}|nl \rangle$ in terms of

$$G_p^{nl} = \frac{2^p Z^p (2l-p+2)!}{n^{p+1} (2l+p-1)!}, \quad f_p^l = \frac{(l+p)!}{(l-p)!}.$$

j	$\langle r^{-j} \rangle (a_0)$
2	$\frac{1}{2} G_2^{nl}$
3	$n G_3^{nl}$
4	$G_4^{nl} (3n^2 - f_1^l)$
5	$2G_5^{nl} [5n^3 - n(3f_1^l - 1)]$
6	$G_6^{nl} [35n^4 - 5n^2(6f_1^l - 5) + 3f_2^l]$
7	$2G_7^{nl} [63n^5 - 35n^3(2f_1^l - 3) + n(15f_2^l - 20f_1^l + 12)]$
8	$G_8^{nl} [462n^6 - 210n^4(3f_1^l - 7) + 42n^2(5f_2^l - 15f_1^l + 14) - 10f_3^l]$
9	$2G_9^{nl} [858n^7 - 462n^5(3f_1^l - 10) + 42n^3(15f_2^l - 75f_1^l + 101) - 2n(35f_3^l - 105f_2^l + 252f_1^l - 180)]$
10	$G_{10}^{nl} [6435n^8 - 6006n^6(2f_1^l - 9) + 1155n^4(6f_2^l - 44f_1^l + 81) - 6n^2(210f_3^l - 1365f_2^l + 4648f_1^l - 4566) + 35f_4^l]$

where

$$h_1(nL) = \frac{\alpha^2 (Z-1)^4}{2n^3} \left[\frac{3}{4n} - \frac{1}{L + \frac{1}{2}} \right] \quad (11.61)$$

is the leading one-electron Dirac energy and

$$\begin{aligned} \chi_1(nL) = & \frac{\alpha^2 \alpha_1}{2} \left\{ 3 \left(\frac{Z-1}{n} \right)^2 \langle r^{-4} \rangle - (Z-1) \langle r^{-5} \rangle \right. \\ & - \frac{4(2L-2)!}{(2L+3)!} \left[4 \left(\frac{Z-1}{n} \right)^6 \left(n + \frac{9n^2 - 5f_1^L}{2L+1} \right) \right. \\ & \left. \left. + (Z-1)^2 \left(\frac{40f_2^L + 70f_1^L - 3}{2L+1} \right) \langle r^{-4} \rangle \right] \right\} \end{aligned} \quad (11.62)$$

is the correction due to the dipole perturbation of the Rydberg electron. The relativistic recoil terms due to mass polarization are

$$\begin{aligned} \langle H_{\text{mass}} + H_D \rangle_{\text{RR}} \rightarrow & \frac{\mu}{M} \left[\frac{22(Z\alpha)^2(Z-1)}{9Z^4} \langle r^{-4} \rangle + 2(Z-1)\chi_1(nL) \right] \\ & + \left(\frac{\mu}{M} \right)^2 \left[-\frac{5}{12} \left(\frac{\alpha Z(Z-1)}{n} \right)^2 + 4h_1(nL) \right], \end{aligned} \quad (11.63)$$

$$\begin{aligned} \langle H_{\text{oo}} \rangle_{\text{RR}} + \langle \Delta_{\text{oo}} \rangle \rightarrow & -\frac{\alpha^2 \mu}{M} \left[Z^4 + \frac{(Z-1)^4}{n^3} \left(\frac{1}{n} - \frac{3}{2L+1} \right) \right. \\ & \left. - \frac{25[1 + 13f(Z)]}{16Z^2} \langle r^{-4} \rangle \right], \end{aligned} \quad (11.64)$$

with $f(Z) \simeq 1 + (Z-2)/6$. The $-(5/12)[\alpha Z(Z-1)/n]^2$ term in (11.63) is the dominant contribution in helium for $L \geq 4$. It is included in Eq. (11.52) for ΔW_n , along with the leading $1/n^2$ term from (11.57), and the $1/n^4$ term from (11.61). The complete relativistic finite mass correction includes also the mass-scaling terms $-(\mu/M)\langle 4H_{\text{mass}} + 3H_D + 3H_{\text{oo}} \rangle$ obtained by expanding μ/m_e in Eq. (11.46). The $\langle \delta(\mathbf{r}_1) \rangle$ term is [43]

$$\begin{aligned} \pi \langle \delta(\mathbf{r}_1) \rangle \rightarrow & \frac{Z^3}{2} - \frac{31}{4Z^3} \langle r^{-4} \rangle + \frac{1447}{32Z^5} \langle r^{-7} \rangle \\ & - \frac{-31(Z-1)}{2Z^3} \left(\frac{\mu}{M} \right) \langle r^{-4} \rangle + \dots \end{aligned} \quad (11.65)$$

$\langle \delta(\mathbf{r}_{12}) \rangle$ vanishes exponentially as $1/n^{2L+4}$ with increasing L . The complete asymptotic expressions for the FS matrix elements are summarized by the formulas

$$\begin{aligned} \langle nL^3 L_J | H_{\text{FS}} | nL^3 L_J \rangle \rightarrow & T_{nL}(J) \{ Z - 3 + 2S_L(J) + 2a_e [Z - 2 \\ & + (2 + a_e)S_L(J)] + (\mu/M)[2 - 4S_L(J)] \}, \end{aligned} \quad (11.66)$$

$$\langle nL^3 L_J | H_{\text{FS}} | nL^1 L_J \rangle \rightarrow T_{nL}(L) (Z + 1 + 2a_e Z - 2\mu/M) \sqrt{L(L+1)}, \quad (11.67)$$

where

$$T_{nL}(J) = \begin{cases} -\alpha^2(L+1)\langle r^{-3} \rangle/4 & J = L-1, \\ -\alpha^2 \langle r^{-3} \rangle/4 & J = L, \\ \alpha^2 L \langle r^{-3} \rangle/4 & J = L+1, \end{cases}$$

$$S_L(J) = \begin{cases} 1 & J = L, \\ \pm 1/(2J+1) & J = L \pm 1. \end{cases}$$

The asymptotic form for the QED term $\Delta E_{L,1}$ follows from Eq. (11.38) with the use of (11.65) for $\langle \delta(\mathbf{r}_1) \rangle$ and (11.40) for $\ln k_0$. The two-electron part is

$$\Delta E_{L,2} \rightarrow -\frac{7\alpha^3}{6\pi} \left(\langle r^{-3} \rangle + \frac{3}{Z^2} \langle r^{-5} \rangle \right). \quad (11.68)$$

With the use of the formulas in this section, the variationally calculated ionization energies for the K -states ($L=7$) in Table 11.7 can be reproduced to within ± 20 Hz. For $L > 7$, the uncertainty becomes less than 1 Hz, up to the Casimir-Polder retardation effects which have not been included.

11.6 RADIATIVE TRANSITIONS

11.6.1 Basic Formulation

In a semiclassical picture, the interaction Hamiltonian with the radiation field is obtained by making the minimal coupling replacements

$$\begin{aligned} \mathbf{P}_N & \rightarrow \mathbf{P}_N - \frac{Ze}{c} \mathbf{A}(\mathbf{R}_N) \\ \mathbf{P}_i & \rightarrow \mathbf{P}_i + \frac{e}{c} \mathbf{A}_i(\mathbf{R}_i) \end{aligned} \quad (11.69)$$

in Eq. (11.1), where

$$\mathbf{A}(\mathbf{R}) = c \left(\frac{2\pi\hbar}{\omega\mathcal{V}} \right)^{1/2} \hat{\mathbf{e}} e^{i\mathbf{k}\cdot\mathbf{R}} \quad (11.70)$$

is the time-independent part of the vector potential $\mathbf{A}(\mathbf{r}, t) = \mathbf{A}(\mathbf{r})e^{-i\omega t} + \text{c.c.}$ for a photon of frequency ω , wave vector \mathbf{k} , and polarization $\hat{\mathbf{e}} \perp \mathbf{k}$ normalized to unit photon energy $\hbar\omega$ in volume \mathcal{V} . The linear coupling terms then yield

$$H_{\text{int}} = -\frac{Zc}{Mc} \mathbf{P}_N \cdot \mathbf{A}(\mathbf{R}_N) + \frac{e}{m_e c} \sum_{i=1}^2 \mathbf{P}_i \cdot \mathbf{A}(\mathbf{R}_i), \quad (11.71)$$

and from Fermi's Golden Rule, the decay rate for spontaneous emission from state γ to γ' is

$$w_{\gamma, \gamma'} d\Omega = \frac{2\pi}{\hbar} |\langle \gamma | H_{\text{int}} | \gamma' \rangle|^2 \rho_f, \quad (11.72)$$

where $\rho_f = \mathcal{V}\omega^2 d\omega / (2\pi c)^3 \hbar$ is the number of photon states with polarization $\hat{\mathbf{e}}$ per unit energy and solid angle in the normalization volume \mathcal{V} . In the long wavelength and electric dipole approximations, the factor $e^{i\mathbf{k}\cdot\mathbf{R}}$ in Eq. (11.70) is replaced by unity. After integrating over angles $d\Omega$ and summing over polarizations $\hat{\mathbf{e}}$, the decay rate reduces to

$$w_{\gamma, \gamma'} = \frac{4}{3} \alpha \omega_{\gamma, \gamma'} |\langle \gamma | \mathbf{Q}_p | \gamma' \rangle|^2, \quad (11.73)$$

where $\omega_{\gamma, \gamma'}$ is the transition frequency and \mathbf{Q}_p is the velocity form of the transition operator

$$\mathbf{Q}_p = \frac{Z}{Mc} \mathbf{P}_N + \frac{1}{m_e c} \sum_{i=1}^N \mathbf{P}_i \quad (11.74)$$

for the general case of N electrons. From the commutator $[H_0, \mathbf{Q}_p / \hbar \omega_{\gamma, \gamma'}] = \mathbf{Q}_p$, where H_0 is the field-free Hamiltonian in Eq. (11.1), the equivalent length form is

$$\mathbf{Q}_r = -\frac{i}{c} \omega_{\gamma, \gamma'} \left(Z \mathbf{R}_N - \sum_{i=1}^N \mathbf{R}_i \right). \quad (11.75)$$

After transforming to c.m. plus relative coordinates in parallel with Eq. (11.3), the dipole transition operators become

$$\mathbf{Q}_p = \frac{Z_p}{m_c} \sum_{i=1}^N \mathbf{p}_i, \quad \mathbf{Q}_r = \frac{i\omega_{\gamma, \gamma'}}{c} Z_r \sum_{i=1}^N \mathbf{r}_i, \quad (11.76)$$

with

$$Z_p = \frac{Zm_e + M}{M}, \quad Z_r = \frac{Zm_e + M}{Nm_e + M},$$

and H_0 now contains the H_{mp} term. If Eq. (11.3) is solved exactly for the states $|\gamma\rangle$ and $|\gamma'\rangle$, then the identity

$$\langle \gamma | \mathbf{Q}_p | \gamma' \rangle = \langle \gamma | \mathbf{Q}_r | \gamma' \rangle \quad (11.77)$$

is satisfied to all orders in m_e/M . For a neutral atom, $N = Z$ and $Z_r = 1$. If the oscillator strength is defined by

$$f_{\gamma, \gamma'} = \frac{2m_e \omega_{\gamma, \gamma'}}{3\hbar} \left(\frac{Z_r}{Z_p} \right) |\langle \gamma' | \sum_{i=1}^N \mathbf{r}_i | \gamma \rangle|^2 \\ = \frac{2}{3m_e \hbar \omega_{\gamma, \gamma'}} \left(\frac{Z_p}{Z_r} \right) |\langle \gamma' | \sum_{i=1}^N \mathbf{p}_i | \gamma \rangle|^2 \quad (11.78)$$

then the sum rule $\sum_{\gamma'} f_{\gamma, \gamma'} = N$ remains valid, independent of m_e/M . The decay rate, summed over final states and averaged over initial states, is

$$\bar{w}_{\gamma, \gamma'} = -\frac{2\alpha \hbar \omega_{\gamma, \gamma'}}{m_e c^2} Z_p Z_r \bar{f}_{\gamma, \gamma'} \quad (11.79)$$

where $\bar{f}_{\gamma, \gamma'} = -(g_\gamma/g_{\gamma'}) \bar{f}_{\gamma, \gamma'}$ is the (negative) oscillator strength for photon emission, and $g_\gamma, g_{\gamma'}$ are the statistical weights of the states.

11.6.2 Oscillator Strength Table

Table 11.11 provides arrays of nonrelativistic oscillator strengths among various states of helium, including the effects of finite nuclear mass as a separate factor. In the absence of mass polarization, the correction factor would be $(1 + \mu/M)^{-1} \simeq 1 - \mu/M$. Mass polarization effects are particularly strong for P -states, and for transitions with $\Delta n = 0$.

The largest relativistic correction comes from singlet-triplet mixing between states with the same n, L , and J (e.g. 3^1D_2 and 3^3D_2) due to H_{FS} . The wave functions obtained by diagonalizing the 2×2 matrices $\mathbf{H}_0 + \mathbf{H}_{\text{NFS}} + \mathbf{H}_{\text{FS}}$ are then

$$\Psi(n^1L_L) = \Psi_0(n^1L_L) \cos \theta + \Psi_0(n^3L_L) \sin \theta \\ \Psi(n^3L_L) = -\Psi_0(n^1L_L) \sin \theta + \Psi_0(n^3L_L) \cos \theta.$$

Values of $\sin \theta$ are listed in Table 11.12. The corrected oscillator strengths $\tilde{f}_{\gamma, \gamma'}$ for the singlet (s) and triplet (t) components of a $\gamma \rightarrow \gamma'$ transition can then be calculated from the values in Table 11.11 according to

$$\tilde{f}_{\gamma, \gamma'}^{\text{ss}} = \omega_{\gamma, \gamma'}^{\text{ss}} (X_{\gamma, \gamma'}^{\text{ss}} \cos \theta_\gamma \cos \theta_{\gamma'} + X_{\gamma, \gamma'}^{\text{tt}} \sin \theta_\gamma \sin \theta_{\gamma'})^2, \\ \tilde{f}_{\gamma, \gamma'}^{\text{tt}} = \omega_{\gamma, \gamma'}^{\text{tt}} (X_{\gamma, \gamma'}^{\text{ss}} \sin \theta_\gamma \sin \theta_{\gamma'} + X_{\gamma, \gamma'}^{\text{tt}} \cos \theta_\gamma \cos \theta_{\gamma'})^2, \\ \tilde{f}_{\gamma, \gamma'}^{\text{st}} = \omega_{\gamma, \gamma'}^{\text{st}} (X_{\gamma, \gamma'}^{\text{ss}} \cos \theta_\gamma \sin \theta_{\gamma'} - X_{\gamma, \gamma'}^{\text{tt}} \sin \theta_\gamma \cos \theta_{\gamma'})^2, \\ \tilde{f}_{\gamma, \gamma'}^{\text{ts}} = \omega_{\gamma, \gamma'}^{\text{ts}} (X_{\gamma, \gamma'}^{\text{ss}} \sin \theta_\gamma \cos \theta_{\gamma'} - X_{\gamma, \gamma'}^{\text{tt}} \cos \theta_\gamma \sin \theta_{\gamma'})^2,$$

where $X_{\gamma, \gamma'}^{\text{ss}} = (f_{\gamma, \gamma'}^{\text{ss}}/\omega_{\gamma, \gamma'}^{\text{ss}})^{1/2}$, and similarly for $X_{\gamma, \gamma'}^{\text{tt}}$. From Eq. (11.78), $X_{\gamma, \gamma'}$ is proportional to the dipole length form of the transition operator, for which there

Table 11.11. Oscillator strengths for helium. The factor in brackets gives the finite mass correction, with $y = \mu/M$.

	1 ¹ S	2 ¹ S	3 ¹ S	4 ¹ S
2 ¹ P	0.276 1647(1 - 2.282y)	0.376 4403(1 + 1.255y)	-0.145 4703(1 + 1.351y)	-0.025 8703(1 + 0.885y)
3 ¹ P	0.073 4349(1 - 1.789y)	0.151 3417(1 - 3.971y)	0.626 1931(1 + 1.234y)	-0.307 5074(1 + 1.097y)
4 ¹ P	0.029 8629(1 - 1.583y)	0.049 1549(1 - 3.235y)	0.143 8889(1 - 4.650y)	0.858 0214(1 + 1.205y)
5 ¹ P	0.015 0393(1 - 1.474y)	0.022 3377(1 - 2.967y)	0.050 4714(1 - 3.764y)	0.146 2869(1 - 5.080y)
6 ¹ P	0.008 6277(1 - 1.407y)	0.012 1340(1 - 2.829y)	0.024 1835(1 - 3.444y)	0.052 7562(1 - 4.105y)
7 ¹ P	0.005 4054(1 - 1.362y)	0.007 3596(1 - 2.75y)	0.013 6794(1 - 3.279y)	0.025 8918(1 - 3.75y)
	2 ³ S	3 ³ S	4 ³ S	5 ³ S
2 ³ P	0.539 0861(1 - 3.185y)	-0.208 5359(1 - 3.773y)	-0.031 7208(1 - 2.819y)	-0.011 3409(1 - 2.609y)
3 ³ P	0.064 4612(1 + 5.552y)	0.890 8513(1 - 2.967y)	-0.435 6711(1 - 3.362y)	-0.067 6073(1 - 2.359y)
4 ³ P	0.025 7689(1 + 3.886y)	0.050 0833(1 + 7.505y)	1.215 2630(1 - 2.878y)	-0.668 3003(1 - 3.185y)
5 ³ P	0.012 4906(1 + 3.332y)	0.022 9141(1 + 5.209y)	0.044 2305(1 + 9.009y)	1.530 6287(1 - 2.827y)
6 ³ P	0.006 9822(1 + 3.063y)	0.011 9933(1 + 4.460y)	0.021 6301(1 + 6.198y)	0.041 5177(1 + 10.215y)
7 ³ P	0.004 2990(1 + 2.908y)	0.007 0772(1 + 4.092y)	0.011 7754(1 + 5.292y)	0.021 1003(1 + 6.981y)
	2 ¹ P	3 ¹ P	4 ¹ P	5 ¹ P
3 ¹ D	0.710 1641(1 - 0.281y)	-0.021 1401(1 + 29.947y)	-0.015 3034(1 - 6.680y)	-0.003 1128(1 - 6.27y)
4 ¹ D	0.120 2704(1 - 1.307y)	0.648 1049(1 + 0.435y)	-0.040 0610(1 + 29.183y)	-0.039 2932(1 - 6.163y)
5 ¹ D	0.043 2576(1 - 1.681y)	0.141 3027(1 - 0.566y)	0.647 6679(1 + 0.817y)	-0.057 3258(1 + 28.903y)
6 ¹ D	0.020 9485(1 - 1.866y)	0.056 2766(1 - 0.936y)	0.152 8104(1 - 0.170y)	0.669 8361(1 + 1.056y)
7 ¹ D	0.011 8970(1 - 1.975y)	0.028 8961(1 - 1.127y)	0.063 5953(1 - 0.538y)	0.163 0272(1 + 0.082y)
8 ¹ D	0.007 4645(1 - 2.046y)	0.017 0777(1 - 1.241y)	0.033 6403(1 - 0.731y)	0.069 3063(1 - 0.26y)
	2 ³ P	3 ³ P	4 ³ P	5 ³ P
3 ³ D	0.610 2252(1 - 2.029y)	0.112 1004(1 + 6.653y)	-0.036 9592(1 + 3.292y)	-0.006 9009(1 + 2.678y)
4 ³ D	0.122 8469(1 - 1.001y)	0.477 5938(1 - 3.059y)	0.200 9498(1 + 6.368y)	-0.088 3017(1 + 2.939y)
5 ³ D	0.047 0071(1 - 0.631y)	0.124 5532(1 - 2.019y)	0.438 3888(1 - 3.607y)	0.280 0558(1 + 6.225y)
6 ³ D	0.023 4692(1 - 0.449y)	0.053 0093(1 - 1.631y)	0.123 9414(1 - 2.555y)	0.429 4411(1 - 3.961y)
7 ³ D	0.013 5638(1 - 0.346y)	0.028 1587(1 - 1.432y)	0.055 2332(1 - 2.153y)	0.125 2389(1 - 2.904y)
8 ³ D	0.008 6047(1 - 0.280y)	0.016 9809(1 - 1.315y)	0.030 2853(1 - 1.94y)	0.057 0589(1 - 2.498y)
	3 ¹ D	4 ¹ D	5 ¹ D	6 ¹ D
4 ¹ F	1.015 0829(1 - 1.010y)	0.002 4920(1 + 3.833y)	-0.012 6968(1 - 0.888y)	-0.002 2631(1 - 0.890y)
5 ¹ F	0.156 8808(1 - 0.993y)	0.886 1343(1 - 1.023y)	0.004 6467(1 + 4.139y)	-0.033 2539(1 - 0.893y)
6 ¹ F	0.054 0508(1 - 0.984y)	0.186 0576(1 - 1.001y)	0.839 1374(1 - 1.031y)	0.006 6028(1 + 4.302y)
7 ¹ F	0.025 6799(1 - 0.978y)	0.072 3229(1 - 0.994y)	0.196 3692(1 - 1.014y)	0.826 9464(1 - 1.039y)
8 ¹ F	0.014 4782(1 - 0.978y)	0.036 6627(1 - 0.987y)	0.080 7847(1 - 1.003y)	0.203 1182(1 - 1.019y)
9 ¹ F	0.009 0730(1 - 0.977y)	0.021 5401(1 - 0.975y)	0.042 4256(1 - 1.000y)	0.086 0955(1 - 1.01y)
	3 ³ D	4 ³ D	5 ³ D	6 ³ D
4 ³ F	1.014 3389(1 - 0.997y)	0.003 3992(1 - 2.166y)	-0.012 8084(1 - 1.042y)	-0.002 2830(1 - 1.044y)
5 ³ F	0.156 9831(1 - 1.004y)	0.884 5767(1 - 0.991y)	0.006 5121(1 - 2.387y)	-0.033 5369(1 - 1.043y)
6 ³ F	0.054 1179(1 - 1.006y)	0.186 0264(1 - 1.003y)	0.837 0221(1 - 0.988y)	0.009 3836(1 - 2.499y)
7 ³ F	0.025 7201(1 - 1.008y)	0.072 3579(1 - 1.003y)	0.196 2031(1 - 0.996y)	0.824 4031(1 - 0.984y)
8 ³ F	0.014 5037(1 - 1.009y)	0.036 6936(1 - 1.004y)	0.080 7712(1 - 1.00y)	0.202 8407(1 - 0.993y)
9 ³ F	0.009 0903(1 - 1.008y)	0.021 5632(1 - 1.011y)	0.042 4344(1 - 0.99y)	0.086 0373(1 - 0.99y)

Table 11.12. Singlet-triplet mixing angles for helium.

State	$\sin\theta$	State	$\sin\theta$	State	$\sin\theta$
2 P	0.0002783				
3 P	0.0002558	3 D	0.0156095		
4 P	0.0002498	4 D	0.0113960	4 F	0.6041024
5 P	0.0002473	5 D	0.0101143	5 F	0.5499291
6 P	0.0002460	6 D	0.0095289	6 F	0.5180737
7 P	0.0002452	7 D	0.0092067	7 F	0.4984184
8 P	0.0002447	8 D	0.0090087	8 F	0.4855768
9 P	0.0002444	9 D	0.0088777	9 F	0.4767620
10 P	0.0002442	10 D	0.0087862	10 F	0.4704595
5 G	0.6934752				
6 G	0.6931996	6 H	0.6962385		
7 G	0.6929889	7 H	0.6962377	7 I	0.6979315
8 G	0.6928356	8 H	0.6962372	8 I	0.6979315
9 G	0.6927195	9 H	0.6962374	9 I	0.6979316
10 G	0.6926329	10 H	0.6962353	10 I	0.6979316
8 K	0.6991671				
9 K	0.6991671	9 L	0.7001089		
10 K	0.6991671	10 L	0.7001089	10 M	0.7008507

are no spin-dependent relativistic corrections [44]. The mixing corrections are particularly significant for $D-F$ and $F-G$ transitions, where intermediate coupling prevails. The two-state approximation becomes increasingly accurate with increasing L , but for P -states, where $\sin\theta$ is small, states with $n' \neq n$ must also be included [45].

11.7 FUTURE PERSPECTIVES

The variational calculations, together with quantum defect extrapolations for high n and asymptotic expansions for high L , provide essentially exact results for the entire singly-excited spectrum of helium. In this sense, helium joins hydrogen as a fundamental atomic system. The dominant uncertainties arise from two-electron QED effects beyond the current realm of standard atomic physics. Transition frequencies from the $1s2s^1S_0$ state are now known to better than ± 0.5 MHz (± 1.8 parts in 10^9) [46], and the fine structure intervals in the $1s2p^3P$ state have been measured to an accuracy approaching 1 kHz [47]. Transition frequencies among the $n = 10$ states are known even more accurately [38]. A complete analysis of relativistic and QED corrections of order α^4 , $\alpha^5 \ln\alpha$, and α^5 a.u. will be required to match these levels of accuracy. Some progress has been made [48, 49], but this remains an important challenge in fundamental atomic physics for the future.

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