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Energies and relativistic corrections for the Rydberg states of helium: Variational results and asymptotic analysis

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The results of an extended series of high-precision variational calculations for all states of helium up to $n=10$ and $L=7$ (excluding S states above $n=2$) are presented. Convergence of the nonrelativistic eigenvalues ranges from five parts in 10^{15} for the $2P$ states to four parts in 10^{19} for the $10K$ states. Relativistic and quantum electrodynamic corrections of order α^2, α^3, $\alpha^2\mu/M$, $\alpha^2(\mu/M)^2$, and $\alpha^3\mu/M$ are included and the required matrix elements listed for each state. For the $1s2p\,^3P_J$ states, the lowest-order spin-dependent matrix elements of the Breit interaction are determined to an accuracy of three parts in 10^9, which, together with higher-order corrections, would be sufficient to allow an improved measurement of the fine-structure constant. Methods of asymptotic analysis are extended to provide improved precision for the relativistic and relativistic-recoil corrections. A comparison with the variational results for the high-angular-momentum states shows that the "standard-atomic-theory" and "long-range-interaction" pictures discussed by Hessels *et al.* [Phys. Rev. Lett. **65**, 2765 (1990)] come into agreement, thereby resolving what appeared to be a discrepancy. The comparison shows that the asymptotic expansions for the total energies are accurate to better than ± 100 Hz for $L>7$, and results are presented for the $9L$, $10L$, and $10M$ states (i.e., angular momentum $L=8$ and 9). Significant discrepancies with experiment persist for transitions among the $n=10$ states, which cannot be easily accommodated by supposed higher-order corrections or additional terms. Finally, the asymptotic analysis indicates that a revision to the quantum-defect method is required for the analysis of high-precision data.

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I. INTRODUCTION

Transition frequencies among the $n=10$ manifold of states of helium have recently attracted much attention because of the high precision that has been achieved, both experimentally [1,2] and theoretically [3–6]. A comparison between the two appears to show well-defined systematic discrepancies that are much larger than the estimated uncertainties in either. A unique feature of the comparison is that the precision is sufficient to be sensitive to quantum electrodynamic (QED) effects of both the Lamb shift [3–6] and long-range Casimir-Polder-retardation types [7–12]. The latter arises (in lowest order) from corrections to short-range approximations made in the usual form of the retarded Breit electron-electron interaction [13]. The result is a form appropriate for low-lying states in the following sense. For a Rydberg electron with radial coordinate x in the range $a_0 \ll x < a_0/\alpha$, the retardation terms are proportional to $e^2\alpha^2 a_0^3/x^4$; but for $x \gg a_0/\alpha$, the power-law dependence changes to $e^2\alpha a_0^4/x^5$. The change in power-law dependence is a unique signature of Casimir effects in their many forms [12], but no precise confirmation yet exists. Since the effect can now, in principle, be detected as a residual energy shift in the Rydberg states of helium, it is essential to verify that all other aspects of the theory are correct and under good numerical control.

The experiment of Hessels *et al.* [1,2] referred to above consists of measuring the frequencies for the sequence of transitions $10F$-$10G$, $10G$-$10H$, ..., $10K$-$10L$. For these transitions, there are two very different theoretical approaches with overlapping ranges of validity, which can be checked against each other. A demonstrated agreement between the two would provide a strong confirmation of both, assuming of course that the underlying formulation of quantum electrodynamics is correct. In historical order, the asymptotic-expansion (AE) method [14–21], valid for high angular momentum L, regards the Rydberg electron as moving in the field of a polarizable core consisting of the inner $1s$ electron and the nucleus with charge Z. This gives rise to an asymptotic expansion for the effective nonrelativistic potential experienced by the Rydberg electron of the form

$$V(x) = -\frac{Z-1}{x} - \frac{\alpha_1}{2x^4} - \frac{\alpha_2 - 6\beta_1}{2x^6} - \cdots \qquad (1)$$

together with corresponding asymptotic expansions for the relativistic and other higher-order corrections. Here, x is the radial coordinate for the Rydberg electron, $Z-1$ is the screened nuclear charge, α_1 is the dipole polarizability of the core, α_2 is the quadrupole polarizability, and β_1 is a nonadiabatic correction to the dipole term. This method has been developed to a high degree of refinement by Drachman [18–21], with the terms in (1) now being known in their entirety up to x^{-10} [21]. The major limitation of (1) is that the series is an asymptotic one which eventually diverges and so must be terminated after a finite number of terms, depending on the value of L. Its great virtue is that the results are entirely analytic and cover all high-L states.

The second method, valid for both low- and high-L states, consists of finding high-precision variational solutions to the complete nonrelativistic Schrödinger equation, using correlated basis sets [22–24,6]. The relativistic corrections are then determined directly from matrix elements of the Breit interaction, including finite nuclear mass, anomalous magnetic moment, and Lamb-shift corrections. In their presentation of experimental data, Hessels *et al.* [1] and Lundeen [2] refer to this approach as "standard atomic theory" (SAT). They also introduce a hybrid "long-range-interaction" (LRI) picture in which the nonrelativistic variational eigenvalues are used, together with the AE results for the relativistic corrections and an approximate version of the Lamb shift. A slight additional complication is that the LRI results also contain the retardation terms and their modifications due to the Casimir-Polder effect [9–11]. However, the short-range form of the retardation terms is already included in SAT. If the small residual Casimir-Polder modifications, denoted by Au and Mesa [11] as $\Delta V''_{\rm ret}$, are added to SAT, then one would expect it to come into agreement with LRI, at least in the asymptotic limit of high L. The results presented by Hessels *et al.* [1] indicate that they do not agree, with differences of the same order of magnitude as $\Delta V''_{\rm ret}$ itself. Since the primary purpose of their experiment is to observe the effects of $\Delta V''_{\rm ret}$, it is essential to resolve this theoretical discrepancy.

An important result of this paper is to show that if higher-order terms in the asymptotic expansion for the relativistic corrections are included in LRI, and the same expression for the Lamb-shift terms is used, then SAT and LRI come into close agreement for high L. What is left is a much larger discrepancy between both theories and experiment for the transition frequencies. However, the main purpose of this paper is to present a detailed listing and asymptotic analysis of high-precision variational calculations to supplement the results already given in Ref. [5]. Except for details of the variational calculations described there and in previous work [22–24], the present paper is reasonably self-contained. In Sec. II, the basic theory of asymptotic expansions is reviewed, and contributions to the nonrelativistic energy discussed. Section III first discusses the relativistic terms of relative order α^2Z^2, and their finite-nuclear-mass (relativistic-recoil) corrections of order $\alpha^2Z^2\mu/M$; and then extends the asymptotic expansion for these terms to higher order in $1/x$. Section IV compares the AE results with the variationally determined matrix elements. This section presents a complete tabulation of the necessary matrix elements for all states up to $n=10$ and $1\le L\le 7$, together with the $1s2s\,{}^1S$ and ${}^3S$ states. A comparison with the AE results for the total energies clearly shows that there is no fundamental difference between SAT and LRI. For low L, the differences are due entirely to the lack of convergence in the asymptotic expansions. Section V presents a brief update of the comparison with experiment, especially for transitions among the $n=10$ states. Section VI describes an important modification that should be made to the quantum-defect method due to terms quadratic in the reduced mass ratio $y=\mu/M$. Finally, Sec. VII summarizes the results and presents conclusions.

II. ASYMPTOTIC EXPANSION THEORY

The aim of this section is to review asymptotic-expansion theory and the contributions to the nonrelativistic energy, including new terms recently derived by Drachman [21]. Since the effects of mass polarization on both the nonrelativistic energy and the relativistic corrections can be obtained in parallel with little extra effort, these will also be included in both this section and the next.

The basic starting point is the three-particle nonrelativistic Schrödinger equation

$$\left[-\frac{\hbar^2}{2M}\nabla^2_{R_0}-\frac{\hbar^2}{2m}\nabla^2_{R_1}-\frac{\hbar^2}{2m}\nabla^2_{R_2}-\frac{Ze^2}{|\mathbf{R}_0-\mathbf{R}_1|}-\frac{Ze^2}{|\mathbf{R}_0-\mathbf{R}_2|}+\frac{e^2}{|\mathbf{R}_1-\mathbf{R}_2|}\right]\Psi=E_{\rm NR}\Psi\ , \quad (2)$$

where $\mathbf{R}_0$ is the position vector of the nucleus of mass M, and $\mathbf{R}_1$ and $\mathbf{R}_2$ are the position vectors of the two electrons of mass m. The standard transformation to center-of-mass and relative coordinates [25] generates a mass-polarization term of the form $-(\mu/M)\nabla_1\cdot\nabla_2$, where $\mu=mM/(m+M)$ is the reduced mass. This could be treated by perturbation theory; but as pointed out by Drachman [20,21], it is simpler to use instead Jacobi coordinates defined by

$$\mathbf{r}=(\mathbf{R}_1-\mathbf{R}_0)/a_\mu\ , \quad (3)$$

$$\mathbf{x}=\Lambda[\mathbf{R}_2-\mathbf{R}_0-y(\mathbf{R}_1-\mathbf{R}_0)]/a_\mu\ , \quad (4)$$

$$\mathbf{X}=\Lambda[\mathbf{R}_0+y(\mathbf{R}_1+\mathbf{R}_2-\mathbf{R}_0)]/a_\mu\ , \quad (5)$$

where

$$y=\mu/M,\quad \Lambda=1/(1-y^2)\ , \quad (6)$$

and $a_\mu=(m/\mu)a_0$ is the reduced Bohr radius. The derivatives in (2) transform according to

$$\nabla_{R_1}=a_\mu^{-1}(\nabla_r-\Lambda y\nabla_x+\Lambda y\nabla_X)\ ,$$

$$\nabla_{R_2}=a_\mu^{-1}(\Lambda\nabla_x+\Lambda y\nabla_X)\ ,$$

$$\nabla_{R_0}=-a_\mu^{-1}[\nabla_r+\Lambda(1-y)(\nabla_x-\nabla_X)]\ .$$

Since X is an ignorable coordinate, the Hamiltonian becomes

$$H=\left[-\tfrac{1}{2}\nabla_r^2-\frac{Z}{r}\right]+\Lambda\left[-\tfrac{1}{2}\nabla_x^2-\frac{Z-1}{x}\right]+V(\mathbf{r},\mathbf{x})$$

$$\equiv h_r+\Lambda h_x+V(\mathbf{r},\mathbf{x}) \quad (7)$$

with

$$V(\mathbf{r},\mathbf{x})=\Lambda\left[\frac{Z-1}{x}-\frac{Z}{|\mathbf{x}+\Lambda y\mathbf{r}|}+\frac{1}{|\mathbf{x}-\Lambda(1-y)\mathbf{r}|}\right] \quad (8)$$

in units of e^2/a_μ throughout. In the above, adding and subtracting the term $-\Lambda(Z-1)/x$ gives the screened hydrogenic form for $h_r+\Lambda h_x$, leaving a perturbation $V(\mathbf{r},\mathbf{x})$ which becomes asymptotically small. Equation (7) immediately implies that the screened hydrogenic energies for a $1snL$ configuration are [20]

$$E_0=-Z^2/2-\Lambda(Z-1)^2/(2n^2)\ . \tag{9}$$

This differs from the $y=0$ case by

$$\begin{aligned}\Delta E_M^{(2)}&=-(\Lambda-1)(Z-1)^2/(2n^2)\\&\simeq-(y^2+y^4)(Z-1)^2/(2n^2)\ ,\end{aligned} \tag{10}$$

which gives in a trivial way the leading term in the second-order mass-polarization correction.

Equation (7) has the important advantage that there is no "mass-polarization" term in the kinetic-energy part, but at the expense of making the potential more complicated. This is not a disadvantage for the polarization model because the multipole expansion of $V(\mathbf{r},\mathbf{x})$ still has the simple form [20]

$$V(\mathbf{r},\mathbf{x})=\frac{1}{x}\sum_{l=1}^{\infty}C_l\left[\frac{r}{x}\right]^l P_l(\hat{\mathbf{r}}\cdot\hat{\mathbf{x}}) \tag{11}$$

with

$$C_l=\frac{(1-y)^l-Z(-y)^l}{(1-y^2)^{l+1}}\ . \tag{12}$$

It is then a simple matter to incorporate the effects of finite mass as follows. Each coefficient in the asymptotic potential (1) is multiplied by combinations of C_l factors according to the combinations of multipolarities that contribute. For example, the 2^l-pole polarizability α_l is quadratic in C_l, and so is replaced by $C_l^2\alpha_l$. The same is true of β_l. Provided that μ/M is small, the C_l factors can be expanded according to

$$\begin{aligned}C_1&=1+(Z-1)y+2y^2+\cdots\ ,\\C_2&=1-2y+(4-Z)y^2+\cdots\ ,\\C_3&=1-3y+7y^2+\cdots\ ,\\C_4&=1-4y+11y^2+\cdots\ .\end{aligned} \tag{13}$$

Thus, for example, the leading term $-\alpha_1\langle x^{-4}\rangle_{nL}/2$ in the asymptotic potential (1) becomes $-\alpha_1C_1^2\langle x^{-4}\rangle_{nL}/2$ because α_1 involves two dipole interactions. The difference $-\alpha_1(C_1^2-1)\langle x^{-4}\rangle_{nL}/2$, together with Eq. (10), are the leading terms in the mass-polarization correction to the energy. The expansions in (13) allow the first- and second-order contributions to the corresponding mass-polarization energy coefficients $\varepsilon_M^{(1)}$ and $\varepsilon_M^{(2)}$ to be separated. Terms of order $\langle x^{-9}\rangle_{nL}$ and $\langle x^{-10}\rangle_{nL}$ have recently been evaluated by Drachman [21], and additional nonadiabatic corrections by Drake [26]. Combining these and separating the mass dependence, the result is

$$\begin{aligned}\varepsilon_M^{(1)}=&-(Z-1)\alpha_1\langle x^{-4}\rangle_{nL}+[2\alpha_2+6(Z-1)\beta_1]\langle x^{-6}\rangle_{nL}+[(Z-2)\delta+\tfrac{16}{5}(Z-1)^2\gamma]\langle x^{-7}\rangle_{nL}\\&+\{3\alpha_3-30\beta_2+2(Z-1)(\alpha_1\beta_1-\epsilon)-72(Z-1)\gamma[1+L(L+1)/10]\}\langle x^{-8}\rangle_{nL}+\tfrac{1}{2}c_9^{(1)}\langle x^{-9}\rangle_{nL}\\&+\tfrac{1}{2}c_{10}^{(1)}\langle x^{-10}\rangle_{nL}+4(Z-1)e_{2,0}^{(1,1)}+2[(Z-3)-12(Z-1)\beta_1/\alpha_2]e_{2,0}^{(1,2)}\ ,\end{aligned} \tag{14}$$

$$\begin{aligned}\varepsilon_M^{(2)}=&-\tfrac{1}{2}(Z-1)^2n^{-2}-\tfrac{1}{2}[5+Z(Z-2)]\alpha_1\langle x^{-4}\rangle_{nL}-\{(6-Z)\alpha_2-3[5+Z(Z-2)]\beta_1\}\langle x^{-6}\rangle_{nL}\\&+\{\tfrac{1}{2}[3+(Z-2)(Z-5)]\delta+\tfrac{8}{5}(Z-1)[5+Z(Z-2)]\}\langle x^{-7}\rangle_{nL}\\&+\{-\tfrac{23}{2}\alpha_3+15(6-Z)\beta_2+[7+3Z(Z-2)](\alpha_1\beta_1-\epsilon)\\&\quad-36[5+Z(Z-2)]\gamma[1+L(L+1)/10]\}\langle x^{-8}\rangle_{nL}+2[7+3(Z-2)]e_{2,0}^{(1,1)}\ ,\end{aligned} \tag{15}$$

where

$$e_{2,0}^{(j,k)}=-\tfrac{1}{2}\alpha_j\alpha_k(2-\delta_{j,k})\langle\phi_1^{(2j+2)}|x^{-2k-2}|\phi_0\rangle_{nL} \tag{16}$$

is a second-order adiabatic polarization energy in which $\phi_1^{(i)}$ satisfies a first-order hydrogenic perturbation equation for the Rydberg electron with $-1/(2x^i)$ as the perturbation. Closed-form analytic expressions are known for $e_{2,0}^{(1,1)}$ and $e_{2,0}^{(1,2)}$ [27,28], and numerical values are tabulated by Drachman [19,21]. Numerical values for the quantities $\alpha_i,\beta_i,\gamma,\delta$, and ϵ in Eqs. (14) and (15) are listed by Drachman [18], and by Drake and Swainson [27]. The $c_j^{(1)}$ in Eq. (14) represent collections of several coefficients [21,26] multiplied by the terms linear in y in Eq. (13). The final result is

$$c_9^{(1)}=-Z^{-10}[\tfrac{7581}{4}+\tfrac{80\,637}{14}(Z-1)+\tfrac{493\,323}{252}(Z-1)^2]\ , \tag{17}$$

$$\begin{aligned}c_{10}^{(1)}=&Z^{-12}[31\,422+\tfrac{26\,677}{32}(Z-1)\\&+\tfrac{71\,445}{4}Z^2+\tfrac{48\,365}{2}(Z-1)Z^2]\\&+Z^{-10}L(L+1)[\tfrac{35\,985}{42}+\tfrac{145\,095}{28}(Z-1)]\ .\end{aligned} \tag{18}$$

Similar results can be obtained for $c_9^{(2)}$ and $c_{10}^{(2)}$ [26] and a contribution $\tfrac{1}{2}c_9^{(2)}\langle x^{-9}\rangle_{nL}+\tfrac{1}{2}c_{10}^{(2)}\langle x^{-10}\rangle_{nL}$ added to Eq. (15) for $\varepsilon_M^{(2)}$, but the change is too small to be important. The asymptotic mass-polarization correction to the energy is then

$$\Delta E_{\rm mp}=y\varepsilon_M^{(1)}+y^2\varepsilon_M^{(2)}+\cdots \ . \tag{19}$$

Detailed numerical comparisons with variational calculations for the Rydberg states of helium will be discussed in Sec. IV A. Note that $y^2\varepsilon_M^{(2)}$ eventually becomes larger than $y\varepsilon_M^{(1)}$ because of the n^{-2} term in (15). However, this does not indicate poor convergence, it merely indicates an even-odd alternation in the magnitudes of the terms.

III. RELATIVISTIC CORRECTIONS

A. Standard formulation

This section reviews the standard formulation for the Breit interaction operators and their finite-mass corrections, expressed in terms of conventional coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ for the positions of the two electrons relative to the nucleus. Starting from the Dirac Hamiltonian summed over particles, and the Breit interaction summed over all pairwise interactions, the terms in the center-of-mass frame are [25,29] (in units of e^2/a_μ)

$$H_1=-\frac{\alpha^2}{8}\left[\frac{\mu}{m}\right]^3(\nabla_1^4+\nabla_2^4)\ , \tag{20}$$

$$H_3=\frac{\alpha^2}{2}\left[\frac{\mu}{m}\right]^2[(\nabla_1 V\times\mathbf{p}_1)\cdot\mathbf{s}_1+(\nabla_2 V\times\mathbf{p}_2)\cdot\mathbf{s}_2]\ , \tag{21}$$

$$H_4=\frac{\alpha^2}{4}\left[\frac{\mu}{m}\right]^2(\nabla_1^2V+\nabla_1V\cdot\nabla_1+\nabla_2^2V+\nabla_2V\cdot\nabla_2)\ , \tag{22}$$

$$\begin{aligned}M_2=\frac{\alpha^2}{2}\left[\frac{\mu}{m}\right]^2\left[\frac{1}{r_{12}}\nabla_1\cdot\nabla_2+\frac{1}{r_{12}^3}\mathbf{r}_{12}\cdot(\mathbf{r}_{12}\cdot\nabla_1)\nabla_2\right]&+\frac{Z\alpha^2}{2}\left[\frac{\mu}{M}\right]\left[\frac{\mu}{m}\right]^2\left[\frac{1}{r_1}(\nabla_1+\nabla_2)\cdot\nabla_1+\frac{1}{r_1^3}\mathbf{r}_1\cdot[\mathbf{r}_1\cdot(\nabla_1+\nabla_2)]\nabla_1\right]\\&+\frac{Z\alpha^2}{2}\left[\frac{\mu}{M}\right]\left[\frac{\mu}{m}\right]^2\left[\frac{1}{r_2}(\nabla_1+\nabla_2)\cdot\nabla_2+\frac{1}{r_2^3}\mathbf{r}_2\cdot[\mathbf{r}_2\cdot(\nabla_1+\nabla_2)]\nabla_2\right]\ ,\end{aligned} \tag{23}$$

$$\begin{aligned}M_3=&-\tfrac{1}{2}g_e\alpha^2\left[\frac{\mu}{m}\right]^2\{[(\nabla_1 r_{12}^{-1})\times\mathbf{p}_2]\cdot\mathbf{s}_1+[(\nabla_2 r_{12}^{-1})\times\mathbf{p}_1]\cdot\mathbf{s}_2\}\\&-\tfrac{1}{2}g_eZ\alpha^2\left[\frac{\mu}{M}\right]\left[\frac{\mu}{m}\right]^2\{[(\nabla_1 r_1^{-1})\times(\mathbf{p}_1+\mathbf{p}_2)]\cdot\mathbf{s}_1+[(\nabla_2 r_2^{-1})\times(\mathbf{p}_1+\mathbf{p}_2)]\cdot\mathbf{s}_2\}\ ,\end{aligned} \tag{24}$$

$$M_3'=-\gamma_eZ\alpha^2\left[\frac{\mu}{m}\right]^2\{[(\nabla_1 r_1^{-1})\times\mathbf{p}_1]\cdot\mathbf{s}_1+[(\nabla_2 r_2^{-1})\times\mathbf{p}_2]\cdot\mathbf{s}_2\}+\gamma_e\alpha^2\left[\frac{\mu}{m}\right]^2\{[(\nabla_1 r_{12}^{-1})\times\mathbf{p}_1]\cdot\mathbf{s}_1+[(\nabla_2 r_{12}^{-1})\times\mathbf{p}_2]\cdot\mathbf{s}_2\}\ , \tag{25}$$

$$M_5=\tfrac{1}{4}g_e^2\alpha^2\left[\frac{\mu}{m}\right]^2\nabla_1\cdot[(\nabla_2 r_{12}^{-1})\cdot\mathbf{s}_1]\mathbf{s}_2\ , \tag{26}$$

$$M_6=-\tfrac{8}{3}\pi\alpha^2\left[\frac{\mu}{m}\right]^2\delta(\mathbf{r}_{12})\mathbf{s}_1\cdot\mathbf{s}_2\ , \tag{27}$$

where

$$V=-Z/r_1-Z/r_2+1/r_{12}\ .$$

$\gamma_e\simeq\alpha/2\pi$ is the electron anomalous magnetic moment, $g_e=2(1+\gamma_e)$, and $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$. The H_i are the Dirac terms and the M_i are the Breit interaction terms, numbered in accordance with the convention of the Bethe and Salpeter [25]. The terms are written out in detail because the origin of all the finite-mass corrections is not evident from the derivation of Bethe and Salpeter.

For purposes of numerical calculation, it is usual to transform together the two terms H_1+H_4 to a form in which the singular matrix elements $(\Psi,\nabla_1^4\Psi)+(\Psi,\nabla_2^4\Psi)$ are replaced by the less singular form $(\nabla_2^2\Psi,\nabla_1^2\Psi)$ [25,30]. With the use of arguments similar to those of Bethe and Salpeter [25], the result for the finite-nuclear-mass case is [5,24]

$$\begin{aligned}\langle H_1+H_4\rangle=&-\frac{\alpha^2}{4}\left[\frac{\mu}{m}\right]^3\langle 2f^2-4yf\mathbf{p}_1\cdot\mathbf{p}_2\\&+2(y\mathbf{p}_1\cdot\mathbf{p}_2)^2-p_1^2p_2^2\rangle\\&+\alpha^2\pi\left[\frac{\mu}{m}\right]^2[Z\langle\delta(\mathbf{r}_1)\rangle-\langle\delta(\mathbf{r}_{12})\rangle]\ ,\end{aligned} \tag{28}$$

where

$$f=E-V$$
$$=E+Z/r_1+Z/r_2-1/r_{12} \;. \tag{29}$$

The $-4yf\mathbf{p}_1\cdot\mathbf{p}_2+2(y\mathbf{p}_1\cdot\mathbf{p}_2)^2$ terms are additional contributions which do not appear in standard treatments. Only the first part linear in y is included in the variational results presented previously [3–5,22–24]. The very small correction of order α^2y^2 from the second part is further discussed in Sec. IV B in terms of its asymptotic expansion.

To facilitate a systematic presentation of the results, the terms H_1 to H_4 and M_2 to M_6 are now separated into terms of lowest order α^2, relativistic reduced-mass corrections of order α^2y, and anomalous magnetic-moment corrections of order α^3. Collecting terms of similar type, the lowest-order Pauli form of the Breit interaction is

$$B_1=-\frac{\alpha^2}{8}(\nabla_1^4+\nabla_2^4) \;, \tag{30}$$

$$B_2=\frac{\alpha^2}{2}\left[\frac{1}{r_{12}}\nabla_1\cdot\nabla_2+\frac{1}{r_{12}^3}\mathbf{r}_{12}\cdot(\mathbf{r}_{12}\cdot\nabla_1)\nabla_2\right] , \tag{31}$$

$$B_4=\alpha^2\pi\left[\frac{Z}{2}\delta(\mathbf{r}_1)+\frac{Z}{2}\delta(\mathbf{r}_2)-\delta(\mathbf{r}_{12})\right] . \tag{32}$$

The spin-dependent terms are

$$B_3=B_{3,Z}+B_{3,e} \tag{33}$$

with

$$B_{3,Z}=\frac{Z\alpha^2}{2}\left[\frac{1}{r_1^3}(\mathbf{r}_1\times\mathbf{p}_1)\cdot\mathbf{s}_1+\frac{1}{r_2^3}(\mathbf{r}_2\times\mathbf{p}_2)\cdot\mathbf{s}_2\right] , \tag{34}$$

$$B_{3,e}=\frac{\alpha^2}{2r_{12}^3}\{[(\mathbf{r}_2-\mathbf{r}_1)\times\mathbf{p}_1]\cdot(\mathbf{s}_1+2\mathbf{s}_2)$$
$$+[(\mathbf{r}_1-\mathbf{r}_2)\times\mathbf{p}_2]\cdot(\mathbf{s}_2+2\mathbf{s}_1)\} \;, \tag{35}$$

and

$$B_5=\alpha^2\nabla_1\cdot[(\nabla_2 r_{12}^{-1})\cdot\mathbf{s}_1]\mathbf{s}_2$$
$$=\alpha^2\left[\frac{1}{r_{12}^3}\mathbf{s}_1\cdot\mathbf{s}_2-\frac{3}{r_{12}^5}(\mathbf{s}_1\cdot\mathbf{r}_{12})(\mathbf{s}_2\cdot\mathbf{r}_{12})\right] , \tag{36}$$

$$B_6=-\tfrac{8}{3}\pi\alpha^2\delta(\mathbf{r}_{12})\mathbf{s}_1\cdot\mathbf{s}_2 \;, \tag{37}$$

all in units of e^2/a_μ, and expectation values are assumed with respect to Ψ_∞ satisfying the nonrelativistic Schrödinger equation for infinite nuclear mass. B_5 vanishes for singlet states because the operator can be written as the tensor product of orbital and spin parts of rank two. Because of the $\delta(\mathbf{r}_{12})$ factor, B_6 only contributes for singlet states, where

$$\langle\mathbf{s}_1\cdot\mathbf{s}_2\rangle=\tfrac{1}{2}\langle S^2-s_1^2-s_2^2\rangle=-\tfrac{3}{4} \;. \tag{38}$$

In summary, the lowest-order relativistic correction is

$$\Delta E_{\rm rel}=\langle B_1\rangle+\langle B_2\rangle+\langle B_3\rangle+\langle B_5\rangle$$
$$+\pi\alpha^2\langle Z\delta(r_1)+\delta(r_{12})\rangle \;, \tag{39}$$

where the contributions involving δ functions in B_4 and B_6 have been combined to give the last term.

The finite-mass corrections can now be simply expressed in terms of the above. With the use of

$$\left[\frac{\mu}{m}\right]^n\simeq 1-ny \tag{40}$$

in Eqs. (20)–(27), the results are

$$B_1^M=-3yB_1 \;, \tag{41}$$

$$B_2^M=-2yB_2+\Delta_2 \;, \tag{42}$$

$$B_3^M=-2yB_{3,e}+\Delta_3 \;, \tag{43}$$

$$B_4^M=-2yB_4 \;, \tag{44}$$

$$B_5^M=-2yB_5 \;, \tag{45}$$

$$B_6^M=-2yB_6 \;, \tag{46}$$

where, from (23) and (24),

$$\Delta_2=\tfrac{1}{2}Z\alpha^2y\left[\frac{1}{r_1}(\nabla_1+\nabla_2)\cdot\nabla_1+\frac{1}{r_1^3}\mathbf{r}_1\cdot[\mathbf{r}_1\cdot(\nabla_1+\nabla_2)]\nabla_1\right]$$
$$+\tfrac{1}{2}Z\alpha^2y\left[\frac{1}{r_2}(\nabla_1+\nabla_2)\cdot\nabla_2\right.$$
$$\left.+\frac{1}{r_2^3}\mathbf{r}_2\cdot[\mathbf{r}_2\cdot(\nabla_1+\nabla_2)]\nabla_2\right] , \tag{47}$$

$$\Delta_3=Z\alpha^2y\left[\frac{1}{r_1^3}(\mathbf{r}_1\times\mathbf{p}_2)\cdot\mathbf{s}_1+\frac{1}{r_2^3}(\mathbf{r}_2\times\mathbf{p}_1)\cdot\mathbf{s}_2\right] . \tag{48}$$

Notice that the term $-2yB_{3,Z}$ that would otherwise appear in Eq. (43) cancels with similar terms that would otherwise appear in the definition of Δ_3; i.e., $(\mathbf{r}_1\times\mathbf{p}_1)\cdot\mathbf{s}_1$ and $(\mathbf{r}_2\times\mathbf{p}_2)\cdot\mathbf{s}_2$ terms. (Δ_3 corresponds to Δ_1 of Stone [29] and our previous work. The notation has been changed to emphasize the connection with B_3.) The total relativistic-recoil correction due to the explicit reduced-mass dependence of the Breit interaction is

$$(\Delta E_{\rm RR})_M=\sum_{i=1}^{6}\langle B_i^M\rangle \;. \tag{49}$$

The above correction reduces to a well-known result in the one-electron case. In this limit, Δ_3 does not contribute and Δ_2 reduces to

$$\Delta_2=\frac{Z\alpha^2}{2r}y(\nabla^2+\nabla_r^2) \;, \tag{50}$$

where $\nabla_r^2=r^{-2}\mathbf{r}\cdot(\mathbf{r}\cdot\nabla)\nabla$. This term, when combined with the others in Eq. (49), gives the operator

$$H_b=\alpha^2y\left[\frac{3}{8}\nabla^4+\frac{Z}{2r}(\nabla^2+\nabla_r^2)+\tfrac{1}{2}Z\nabla^2(r^{-1})\right] . \tag{51}$$

As shown by Bethe and Salpeter [25] (see Eq. 42.7, p. 195), the expectation value of H_b reduces to the one-electron relativistic reduced-mass shift

$$E_b=-\left[\frac{Z\alpha}{2n}\right]^2 y|E_{\rm NR}| \ , \quad (52)$$

where $E_{\rm NR}=-1/(2n^2)$. This is *in addition* to the mass shift already contained implicitly in Eq. (39) due to the use of the reduced-mass Rydberg. A corresponding limit can be expected for Rydberg states of two-electron atoms (see Sec. III B 2).

Second-order cross terms with the mass-polarization operator produce further corrections of order $\alpha^2 y$ in the two-electron case. Denoting these relativistic recoil terms by $B_i^{\rm X}$ ($i=1,\ldots,6$), they can each be expressed in the form

$$\begin{aligned}B_i^{\rm X}&=2\langle\delta\Psi_\infty|B_i|\Psi_\infty\rangle\\ &=2y\sum_{k\neq 0}\frac{\langle\Psi_\infty|\mathbf{p}_1\cdot\mathbf{p}_2|k\rangle\langle k|B_i|\Psi_\infty\rangle}{E_\infty(0)-E_\infty(k)} \ , \quad (53)\end{aligned}$$

where $k=0$ denotes the unperturbed state Ψ_∞, and $\delta\Psi_\infty$ is the perturbation due to mass polarization. The perturbation sum can be calculated explicitly by solving a first-order perturbation equation, as done by Lewis and Serafino [31], or implicitly by recalculating the matrix elements of the B_i with respect to the Ψ_M solutions of the finite-mass Schrödinger equation (i.e., with mass polarization included) and writing

$$\begin{aligned}B_i^{\rm X}\simeq&\langle\Psi_M|B_i|\Psi_M\rangle-\langle\Psi_\infty|B_i|\Psi_\infty\rangle\\ &+\alpha^2 y\langle\Psi_M|f\mathbf{p}_1\cdot\mathbf{p}_2|\Psi_M\rangle\delta_{i,1} \ . \quad (54)\end{aligned}$$

The last term is the $y=\mu/M$ correction in (28) for $i=1$. This procedure automatically includes higher-order terms in the $(\mu/M)\mathbf{p}_1\cdot\mathbf{p}_2$ perturbation series, but since μ/M is small, it gives the coefficient of the $\alpha^2\mu/M$ cross term to sufficient accuracy that isotope shifts can be calculated without redoing the calculations for each nuclear mass. However, higher-order terms quadratic in μ/M affect the comparison with asymptotic expansions, as further discussed in Sec. IV B. The total correction due to second-order cross terms is

$$(\Delta E_{\rm RR})_{\rm X}=\sum_{i=1}^{6}\langle B_i^{\rm X}\rangle \ . \quad (55)$$

The spin-dependent anomalous magnetic moment corrections only affect B_3 and B_5. The terms are

$$B_{3,Z}^A=2\gamma_e B_{3,Z} \ , \quad (56)$$

$$\begin{aligned}B_{3,e}^A=2\gamma_e\frac{\alpha^2}{2r_{12}^3}\{&[(\mathbf{r}_2-\mathbf{r}_1)\times\mathbf{p}_1]\cdot(\mathbf{s}_1+\mathbf{s}_2)\\ &+[(\mathbf{r}_1-\mathbf{r}_2)\times\mathbf{p}_2]\cdot(\mathbf{s}_2+\mathbf{s}_1)\} \ , \quad (57)\end{aligned}$$

$$B_5^A=2\gamma_e B_5 \ . \quad (58)$$

Comparing with Eq. (35) and using

$$\mathbf{s}_1+\mathbf{s}_2=\tfrac{2}{3}(\mathbf{s}_1+2\mathbf{s}_2)+\tfrac{1}{3}(\mathbf{s}_1-\mathbf{s}_2) \ , \quad (59)$$

it can be seen that the matrix elements of $B_{3,e}^A$ between states with different total spin $\mathbf{S}=\mathbf{s}_1+\mathbf{s}_2$ are

$$\langle a'S'|B_{3,e}^A|aS\rangle=\tfrac{4}{3}\gamma_e\delta_{S,S'}\langle a'S'|B_{3,e}|aS\rangle \ , \quad (60)$$

and the right-hand side is zero if $S=0$. Thus, only the diagonal matrix elements are nonvanishing in LS coupling, and only then for triplet states. The total anomalous magnetic-moment matrix elements in LS coupling are thus

$$\begin{aligned}&\langle a'S'|\Delta H_{\rm anom}|aS\rangle\\ &\quad=2\gamma_e\langle a'S'|B_{3,Z}+\tfrac{2}{3}\delta_{S,S'}B_{3,e}+B_5|aS\rangle \quad (61)\end{aligned}$$

excluding δ-function terms. For consistency, these will be included along with other QED corrections of the same order [see Eqs. (118) and (134) to follow]. The corresponding energy change is $\Delta E_{\rm anom}$.

B. Asymptotic expansions

This section applies the asymptotic expansion methods introduced in Sec. II to the calculation of the relativistic terms contained in the Breit interaction and their finite-mass corrections. The results substantially extend the known terms due to the one-electron Dirac energy and relativistic polarizability discussed previously by Drachman [19].

1. Spin-independent terms

Consider first the spin-independent parts of the Breit interaction. As discussed, for example, by Drachman [19] and Drake [5], the asymptotic limit for $\langle B_1+B_4\rangle$ is (in units of e^2/a_μ throughout)

$$\langle B_1+B_4\rangle\to-\alpha^2Z^4/8+h_1(nL)+\Delta B_1(\alpha_{\rm rel})+\Delta B_1(\phi_1) \ , \quad (62)$$

where

$$h_1(nL)=\frac{\alpha^2(Z-1)^4}{2n^3}\left[\frac{3}{4n}-\frac{1}{L+\frac{1}{2}}\right] , \quad (63)$$

$$\begin{aligned}\Delta B_1(\alpha_{\rm rel})=\tfrac{1}{2}(Z\alpha)^2[&\alpha_{1,\rm rel}\langle x^{-4}\rangle\\ &+(\alpha_{2,\rm rel}-6\beta_{1,\rm rel})\langle x^{-6}\rangle+\cdots\ ] \ , \quad (64)\end{aligned}$$

$$\Delta B_1(\phi_1)=-\tfrac{1}{4}\alpha^2\langle\phi_1|p^4|\phi_0\rangle_{nL} \ , \quad (65)$$

and expectation values are with respect to the Rydberg electron. Equation (63) is just the Pauli approximation for the one-electron relativistic correction (in LS coupling), and $\Delta B_1(\alpha_{\rm rel})$ is the energy shift due to the relativistic correction $(Z\alpha)^2\alpha_{\rm rel}$ to the multipole polarizabilities [19], with $\alpha_1=9/(2Z^4)$, $\alpha_{1,\rm rel}=14/(3Z^4)$, $\alpha_{2,\rm rel}=879/(40Z^6)$, and $\beta_{1,\rm rel}=2063/(288Z^6)$. The last is the nonadiabatic correction to $\alpha_{1,\rm rel}$ recently obtained by Hessels [32]. The term $\Delta B_1(\phi_1)$ defined by (65) represents the correction to the lowest-order matrix element $-\alpha^2\langle p^4\rangle_{nL}/8$ due to the perturbing effect of the $-\alpha_1/(2x^4)$ polarization potential on the Rydberg electron [5]. Thus ϕ_1 satisfies the perturbation equation

$$(\tfrac{1}{2}p^2+V_0-E_0)|\phi_1\rangle+(V_1-E_1)|\phi_0\rangle=0\ , \tag{66}$$

with

$$V_0=-(Z-1)/x,\quad E_0=-(Z-1)^2/(2n^2)\ ,$$
$$V_1=-\alpha_1/(2x^4),\quad E_1=-\alpha_1\langle x^{-4}\rangle/2\ .$$

This equation can be solved analytically as a finite power-series expansion for an arbitrary nL state, as discussed by Drake and Swainson [27]. Then, integrating by parts and using

$$p^2\phi_0=2(E_0-V_0)\phi_0 \tag{67}$$

and

$$p^2\phi_1=2(E_0-V_0)\phi_1+2(E_1-V_1)\phi_0 \tag{68}$$

it follows that, for $Z=2$,

$$\Delta B_1(\phi_1)=\alpha^2[\langle\phi_1|x^{-1}(n^{-2}-x^{-1})|\phi_0\rangle_{nL}+\tfrac{1}{2}\alpha_1\langle\phi_0|x^{-4}(n^{-2}-x^{-1})|\phi_0\rangle_{nL}]\ . \tag{69}$$

For arbitrary Z and α_1, $\Delta B_1(\phi_1)$ scales in proportion to $\alpha_1(Z-1)^6$.

A general formula for the integrals involving ϕ_1 in the first term of (69) can be derived by applications of the Dalgarno interchange theorem as follows. The integral involving x^{-1} can be obtained by considering an equation parallel to (66) with the perturbation being a change in the nuclear charge. If $Z\rightarrow Z+\epsilon$, then, up to first order in ϵ,

$$\phi_0(Z+\epsilon)=\phi_0(Z)+\epsilon\phi_1'(Z)\ , \tag{70}$$

where $\phi_1'(Z)$ satisfies

$$(\tfrac{1}{2}p^2+V_0-E_0)|\phi_1'\rangle-(x^{-1}-\langle x^{-1}\rangle)|\phi_0\rangle=0\ . \tag{71}$$

It is clear from Eq. (70) that

$$\phi_1'(Z)=\frac{d\phi_0(Z)}{dZ}\ . \tag{72}$$

Multiply (71) by $\langle\phi_1|$, (66) by $\langle\phi_1'|$, and subtract to obtain

$$\langle\phi_1|x^{-1}|\phi_0\rangle_{nL}=\tfrac{1}{2}\alpha_1\langle\phi_1'|x^{-4}|\phi_0\rangle_{nL}\ . \tag{73}$$

Using Eq. (72) for ϕ_1' and taking the d/dZ operation outside the integral gives the final result

$$\langle\phi_1|x^{-1}|\phi_0\rangle_{nL}=\tfrac{1}{4}\alpha_1\frac{d}{dZ}\langle\phi_0|x^{-4}|\phi_0\rangle_{nL}=\frac{\alpha_1}{Z-1}\langle x^{-4}\rangle_{nL}\ , \tag{74}$$

where

$$\langle x^{-4}\rangle_{nL}=\frac{16(Z-1)^4[3n^2-L(L+1)]}{n^5(2L-1)(2L)(2L+1)(2L+2)(2L+3)}\ .$$

The integral containing x^{-2} can be obtained in a completely analogous way by considering the perturbation resulting from the change $L\rightarrow L+\epsilon$ to the centrifugal barrier term $L(L+1)/2x^2$ in the effective radial potential. The result is

$$\langle\phi_1|x^{-2}|\phi_0\rangle_{nL}=-\frac{\alpha_1}{2(2L+1)}\frac{d}{dL}\langle x^{-4}\rangle_{nL}=\langle x^{-4}\rangle_{nL}\frac{\alpha_1}{2(2L+1)}\left[\sum_{j=2L-1}^{2L+3}\frac{2}{j}+\frac{9n-5L(L+1)/n+2L+1}{3n^2-L(L+1)}\right]\ . \tag{75}$$

The one additional subtlety in evaluating the above derivative with respect to L arises from the fact that n and L are connected by the equation $n=N+L+1$, where N is the fixed number of nodes, in order to preserve the boundary condition at infinity for ϕ_0. Thus n must change in step with L such that $dn/dL=1$. Otherwise, the integral is no longer defined. The above integrals have been checked numerically. Collecting results and using

$$\sum_{j=2L-1}^{2L+3}\frac{2}{j}=\frac{4(2L-2)!}{(2L+3)!}(40f_2+70f_1-3)\ ,$$

where $f_1=L(L+1)$ and $f_2=(L-1)L(L+1)(L+2)$, the final result is

$$\Delta B_1(\phi_1)=\tfrac{1}{2}\alpha^2\alpha_1\left\{3\left[\frac{Z-1}{n}\right]^2\langle x^{-4}\rangle-(Z-1)\langle x^{-5}\rangle-4\frac{(2L-2)!}{(2L+3)!}\left[4\left[\frac{Z-1}{n}\right]^6\left[n+\frac{9n^2-5f_1}{2L+1}\right]+(Z-1)^2\langle x^{-4}\rangle\left[\frac{40f_2+70f_1-3}{2L+1}\right]\right]\right\}\ . \tag{76}$$

Except for the additional $\Delta B_1(\phi_1)$ and $\beta_{1,\mathrm{rel}}$ contributions, Eq. (62) corresponds to the spin-independent relativistic corrections discussed by Drachman [19]. A comparison with variational calculations is given in the following section.

Drachman [21] has obtained the leading term in the asymptotic expansion of $\langle B_2\rangle$ by a direct perturbation calculation, in agreement with the limit deduced from variational calculations [3,4]. Higher-order extensions have recently been obtained by Hessels [32] with the result

$$\langle B_2\rangle \to \frac{\alpha^2}{Z^2}\left\{\langle x^{-4}\rangle+\frac{3(Z-1)}{Z^2}\langle x^{-5}\rangle - \frac{1}{Z^2}\left[\frac{51}{4}-\frac{27(Z-1)}{2Z}+\frac{3L(L+1)}{4}\right]\langle x^{-6}\rangle\right\} . \quad (77)$$

The operator B_2 scales nominally as Z^3 with nuclear charge [see Eq. (31)], but the leading term in a Z^{-1} expansion of $\langle B_2\rangle$ vanishes exactly, resulting in the overall $(Z-1)^4/Z^2 \simeq Z^2$ scaling of (77) due to correlation effects. Aside from the nonrelativistic energy, the differences between the left- and right-hand sides of (62) and (77) are the dominant sources of error in the asymptotic-expansion method. The differences are not fundamental, they merely represent the degree of convergence of the asymptotic expansion.

2. *Relativistic-recoil corrections*

The asymptotic expansion corresponding to the relativistic-recoil terms represented by Eq. (55) can be obtained in a fairly simple way by transforming to Jacobi coordinates. Starting from Eqs. (20) and (22), and keeping terms up to order $(\alpha y)^2$, the operators H_1 and H_4 in Jacobi coordinates are

$$H_1 = -\tfrac{1}{8}(1-y)^3\alpha^2[\nabla_r^4 - 4\Lambda y \nabla_r\cdot\nabla_x\nabla_r^2 + 2\Lambda^2 y^2\nabla_r^2\nabla_x^2 + 4\Lambda^2 y^2(\nabla_r\cdot\nabla_x)^2 + \Lambda^4\nabla_x^4] , \quad (78)$$

$$H_4 = \pi Z\alpha^2(1-y)^2[\delta(\mathbf{r})+\delta(\mathbf{x}+\Lambda y\mathbf{r})] . \quad (79)$$

The second δ function in (79) gives a negligibly small contribution for high-L states and can be neglected. The factors of $(1-y)^3$ and $(1-y)^2$ produce the reduced-mass corrections B_1^M and B_4^M [see Eqs. (41) and (44)], which are counted separately. What remains are the recoil terms

$$H_1' + H_4' = T_1 + T_2 + T_3 + T_4 \quad (80)$$

with

$$\begin{aligned} T_1 &= \alpha^2[-\tfrac{1}{8}\nabla_r^4 + \pi Z\delta(\mathbf{r})] ,\\ T_2 &= -\tfrac{1}{8}\alpha^2\Lambda^4\nabla_x^4 ,\\ T_3 &= \tfrac{1}{2}\alpha^2\Lambda y \nabla_r\cdot\nabla_x\nabla_r^2 ,\\ T_4 &= -\tfrac{1}{4}\alpha^2 y^2\Lambda^2[\nabla_r^2\nabla_x^2 + 2(\nabla_r\cdot\nabla_x)^2] . \end{aligned} \quad (81)$$

For a $1snL$ configuration, T_1 gives the asymptotic contributions

$$\langle T_1\rangle_{1snL} = \alpha^2 Z^2\left[-\frac{Z^2}{8}+\tfrac{1}{2}\alpha_{1,\mathrm{rel}}\langle x^{-4}\rangle_{nL} + O(\langle x^{-6}\rangle_{nL})\right] , \quad (82)$$

where the first term is the relativistic energy for the $1s$ electron, the second term is the relativistic polarizability discussed by Drachman [19], and the third term contains the relativistic quadrupole polarizability and nonadiabatic corrections. Since the transformation to Jacobi coordinates changes $\alpha_{1,\mathrm{rel}}$ in the same way as α_1 (i.e., by a factor of C_1^2), the mass-polarization correction is

$$\langle T_1^X\rangle_{1snL} = \alpha^2 Z^2 y(Z-1)\alpha_{1,\mathrm{rel}}\langle x^{-4}\rangle_{nL} . \quad (83)$$

T_2 gives the corresponding terms in Eq. (62) for the Rydberg electron

$$\langle T_2\rangle_{1snL} = \Lambda^4[h_1(nL)+\Delta B_1(\phi_1)] . \quad (84)$$

Expanding $\Lambda^4 \simeq 1+4y^2$, and remembering that ϕ_1 changes in proportion to α_1, the only significant mass-polarization terms are

$$\langle T_2^X\rangle_{1snL} = 2y(Z-1)\Delta B_1(\phi_1) + 4y^2 h_1(nL) . \quad (85)$$

T_4 can also be simply evaluated, using the virial theorem to obtain

$$\langle \nabla_r^2\nabla_x^2\rangle_{1snL} = Z^2(Z-1)^2/n^2$$

and

$$\langle (\nabla_r\cdot\nabla_x)^2\rangle_{1snL} = \tfrac{1}{3}Z^2(Z-1)^2/n^2 ,$$

with the result

$$\langle T_4^X\rangle_{1snL} = -\tfrac{5}{12}\alpha^2 y^2\left[\frac{Z(Z-1)}{n}\right]^2 . \quad (86)$$

T_3 is more difficult to calculate because the matrix element vanishes in a one-electron approximation, as does the adiabatic perturbation correction due to the leading dipole polarization term in Eq. (11). However, the nonadiabatic correction does not vanish. Introducing sums over intermediate states, the leading contribution is

$$\langle T_3^X\rangle_{1snL} = 2\sum_{n',n''}\frac{\langle 1snL|V_1|n'pn''L\pm 1\rangle\langle n'pn''L\pm 1|(h_x-e_n)T_3|1snL\rangle}{(E_{1s}-E_{n'})^2} , \quad (87)$$

where $V_1 = r\cos(\hat{\mathbf{r}}\cdot\hat{\mathbf{x}})/x^2$ is the dipole term in Eq. (11), $E_{n'} = -Z^2/(2n'^2)$, and $e_n = -(Z-1)^2/(2n^2)$. The sums over intermediate states can be efficiently evaluated using the method of Dalgarno and Lewis [33] (see also Drachman [18,19,21]). To this end, we define an operator $G_1^{(2)}$ by

$$V_1|1s\rangle = [h_r,[h_r,G_1^{(2)}]]|1s\rangle . \quad (88)$$

Substituting (88) into (87) gives a factor of $(E_{1s}-E_{n'})^2 G_1^{(2)}$ in the numerator which cancels the corresponding factor in the denominator, and the sums can be completed by closure. Commuting $(h_x - e_n)$ to the right then yields

$$\langle T_3^{\rm X}\rangle_{1snL} = 2\langle 1snL|G_1^{(2)}[h_x, T_3]|1snL\rangle\ . \qquad (89)$$

The solution to (88) is

$$G_1^{(2)} = \frac{\mathbf{r}\cdot\hat{\mathbf{x}}}{Z^4x^2}\left[\frac{11}{6}+\frac{11}{12}Zr+\frac{1}{6}(Zr)^2\right], \qquad (90)$$

and the commutator in (89) is

$$[h_x, T_3]|1snL\rangle = \tfrac{1}{2}y\alpha^2Z^3(Z-1)\frac{\hat{\mathbf{r}}\cdot\hat{\mathbf{x}}}{x^2}\left[1-\frac{2}{Zr}-\frac{2}{Z^2r^2}\right]|1snL\rangle\ . \qquad (91)$$

Substituting (90) and (91) into (89) and performing the integrations gives the final result

$$\langle T_3^{\rm X}\rangle_{1snL} = -y\alpha^2(Z-1)\tfrac{20}{9}\langle x^{-4}\rangle_{nL}\ . \qquad (92)$$

The sum of $\langle T_1^{\rm X}\rangle$ to $\langle T_4^{\rm X}\rangle$ from Eqs. (83), (85), (86), and (92) yields the asymptotic matrix element

$$\begin{aligned}\langle B_1^{\rm X}+B_4^{\rm X}\rangle \to y(Z\alpha)^2(Z-1)&\left[\alpha_{1,\rm rel}-\frac{20}{9Z^4}\right]\langle x^{-4}\rangle_{nL}\\ &+2y(Z-1)\Delta B_1(\phi_1)\\ &+y^2\left[-\frac{5}{12}\left[\frac{\alpha Z(Z-1)}{n}\right]^2+4h_1(nL)\right.\\ &\left.+O(\alpha^2\langle x^{-4}\rangle_{nL})\right]\ . \end{aligned} \qquad (93)$$

It is necessary to include the terms of order $(\alpha y)^2$ because the leading $1/n^2$ term is in fact the dominant contribution for Rydberg states down as far as 4F. All other terms decrease as $1/n^3$.

The asymptotic limits for the spin-independent recoil terms are

$$\langle B_2^{\rm X}\rangle \to -yh_2(nL)\ , \qquad (94)$$

$$\langle \Delta_2\rangle \to y[-\alpha^2Z^4+Zh_2(nL)]\ , \qquad (95)$$

where

$$h_2(nL) = \frac{\alpha^2(Z-1)^3}{n^3}\left[\frac{1}{n}-\frac{3}{2(L+\frac{1}{2})}\right] \qquad (96)$$

is the expectation value of

$$\frac{1}{2}\frac{\alpha^2}{r}(\nabla^2+\nabla_r^2)$$

[see Eq. (50)]. The two terms combine to give

$$\langle B_2^{\rm X}+\Delta_2\rangle \to -y[\alpha^2Z^4+(Z-1)h_2(nL)] \qquad (97)$$

in agreement with the recent discussion of these terms from quite a different point of view by Au, Feinberg, and Sucher [34]. Note that $\langle B_2^{\rm X}\rangle$ asymptotically becomes much larger than $\langle B_2\rangle$ [see Eq. (94)], even though the former contains an extra factor of y. This is because $\langle B_2^{\rm X}\rangle$ does not vanish in a one-electron approximation, while $\langle B_2\rangle$ does.

The asymptotic expansion for the matrix element of the δ function is known to be [35]

$$\begin{aligned}\pi\langle\delta(\mathbf{r}_1)\rangle = Z^3/2 &- \frac{31}{4Z^3}\langle x^{-4}\rangle_{nL}+\frac{1447}{32Z^5}\langle x^{-6}\rangle_{nL}+O(\langle x^{-7}\rangle_{nL})\\ &+y\left[-\frac{31}{2Z^3}(Z-1)\langle x^{-4}\rangle_{nL}+\frac{1}{16Z^5}[4789+2561(Z-2)]\langle x^{-6}\rangle_{nL}\right]a_\mu^{-3}\ .\end{aligned} \qquad (98)$$

This is useful in calculating QED corrections, as well as matrix elements of the Breit interaction. The polarization corrections to $\langle B_2^{\rm X}\rangle$ and $\langle\Delta_2\rangle$ of order $\langle x^{-4}\rangle_{nL}$ have not been derived, but the variational results for helium are well represented by

$$\langle B_2^{\rm X}\rangle \to -y\left[h_2(nL)-\frac{25}{16Z^2}\langle x^{-4}\rangle_{nL}\right], \qquad (99)$$

$$\langle\Delta_2\rangle \to y\left[-\alpha^2Z^4+Zh_2(nL)+\frac{325}{16Z^2}\alpha^2 f(Z)\langle x^{-4}\rangle_{nL}\right]. \qquad (100)$$

The Z scaling of the coefficient $\frac{325}{16}$ in (100) has the form

$$f(Z) = 1+b(Z-2) \qquad (101)$$

because of the multiplicity of terms which contribute to Δ_2 [see Eq. (47)]. From the variational calculations, $b\simeq\frac{1}{6}$.

Adding the B_1^M, B_2^M, and B_4^M reduced-mass terms from Eqs. (41)–(44) to the above $B_2^{\rm X}$ and Δ_2 term gives

$$\langle -y(3B_1+2B_2+2B_4)+B_2^X+\Delta_2\rangle \to -\tfrac{1}{8}y\alpha^2Z^4-\tfrac{1}{8}y\left[\frac{(Z-1)^2\alpha}{n^2}\right]^2+\alpha^2yZ^{-2}\langle x^{-4}\rangle_{nL}[-7-\tfrac{31}{4}-2+\tfrac{25}{16}+\tfrac{325}{16}f(Z)] \; . \tag{102}$$

The first two terms are the one-electron relativistic reduced-mass shifts expected from Eq. (52), with the second term coming from the combination $y[-3h_1(nL)+(Z-1)h_2(nL)]$. The remaining terms proportional to $\langle x^{-4}\rangle_{nL}$ come from $\alpha_{1,\mathrm{rel}}$, $\langle\delta(\mathbf{r}_1)\rangle$, B_2, B_2^X, and Δ_2, respectively. This, together with (93), gives the total spin-independent part of the relativistic-recoil shift. For $L\geq 4$, the asymptotic expansions are at least as accurate as the variational calculations.

3. Spin-dependent terms

Turning now to the spin-dependent terms, the matrix elements $\langle B_3\rangle$, $\langle\Delta_3\rangle$, and $\langle B_5\rangle$ can all be simply expressed to high accuracy in terms of the single matrix element $\langle x^{-3}\rangle_{nL}$ [36] given by

$$\langle x^{-3}\rangle_{nL}=\frac{(Z-1)^3}{n^3L(L+1/2)(L+1)} \; . \tag{103}$$

Defining $T_{nL}(J)$ by

$$\begin{aligned} T_{nL}(L-1)&=-\alpha^2(L+1)\langle x^{-3}\rangle_{nL}/4 \; ,\\ T_{nL}(L)&=-\alpha^2\langle x^{-3}\rangle_{nL}/4 \; ,\\ T_{nL}(L+1)&=\alpha^2L\langle x^{-3}\rangle_{nL}/4 \; , \end{aligned} \tag{104}$$

together with

$$S_L(J)=\begin{cases}1 & \text{for } J=L,\\ \pm1/(2J+1) & \text{for } J=L\pm1 \; ,\end{cases} \tag{105}$$

the results for the diagonal matrix elements are

$$\begin{aligned} \langle nL\,{}^3L_J|B_{3,Z}|nL\,{}^3L_J\rangle &\to ZT_{nL}(J) \; ,\\ \langle nL\,{}^3L_J|B_{3,e}|nL\,{}^3L_J\rangle &\to -3T_{nL}(J) \; ,\\ \langle nL\,{}^3L_J|B_5|nL\,{}^3L_J\rangle &\to 2S_L(J)T_{nL}(J) \; ,\\ \langle nL\,{}^3L_J|B_{3,Z}^X|nL\,{}^3L_J\rangle &\to yT_{nL}(J) \; ,\\ \langle nL\,{}^3L_J|B_{3,e}^X|nL\,{}^3L_J\rangle &\to -3yT_{nL}(J) \; ,\\ \langle nL\,{}^3L_J|\Delta_3|nL\,{}^3L_J\rangle &\to -2yT_{nL}(J) \; ,\\ \langle nL\,{}^3L_J|B_5^X|nL\,{}^3L_J\rangle &\to 0+O[(\alpha y)^2] \; . \end{aligned} \tag{106}$$

The off-diagonal matrix elements are

$$\begin{aligned} \langle nL\,{}^3L_L|B_{3,Z}|nL\,{}^1L_L\rangle &\to ZT_{nL}(L)[L(L+1)]^{1/2} \; ,\\ \langle nL\,{}^3L_L|B_{3,e}|nL\,{}^1L_L\rangle &\to T_{nL}(L)[L(L+1)]^{1/2} \; ,\\ \langle nL\,{}^3L_L|B_{3,Z}^X|nL\,{}^1L_L\rangle &\to -yT_{nL}(L)[L(L+1)]^{1/2} \; ,\\ \langle nL\,{}^3L_L|B_{3,e}^X|nL\,{}^1L_L\rangle &\to -yT_{nL}(L)[L(L+1)]^{1/2} \; ,\\ \langle nL\,{}^3L_L|\Delta_3|nL\,{}^1L_L\rangle &\to 2yT_{nL}(L)[L(L+1)]^{1/2} \; . \end{aligned} \tag{107}$$

The complete matrix elements, including the reduced-mass and anomalous-magnetic-moment corrections from Eqs. (49) and (61), are thus

$$\begin{aligned} &\langle nL\,{}^3L_J|B_3+B_5+B_3^X+B_5^X+B_3^M+B_5^M+\Delta_3+B_3^A+B_5^A|nL\,{}^3L_J\rangle\\ &\qquad\to T_{nL}(J)\left[Z-3+2S_L(J)+\frac{\mu}{M}[2-4S_L(J)]+2\gamma_e[Z-2+(2+\gamma_e)S_L(J)]\right] \end{aligned} \tag{108}$$

and

$$\begin{aligned} &\langle nL\,{}^3L_L|B_3+B_3^X+B_3^M+\Delta_3+B_3^A|nL\,{}^1L_L\rangle\\ &\qquad\to T_{nL}(L)\left[Z+1-2\frac{\mu}{M}+2\gamma_eZ\right][L(L+1)]^{1/2} \end{aligned} \tag{109}$$

in units of e^2/a_μ, with $\gamma_e\simeq\alpha/2\pi-0.328\,48(\alpha/\pi)^2$. It is interesting that the Z dependence of the relativistic-recoil plus reduced-mass terms cancels in the asymptotic limit.

The above matrix elements of $B_{3,Z}$, $B_{3,e}$, and B_5 follow in a simple way from the asymptotic forms of the operators themselves. Concerning Δ_3, its matrix elements seem surprising at first sight because the expectation values of $\mathbf{r}_1\times\mathbf{p}_2$ and $\mathbf{r}_2\times\mathbf{p}_1$ [see Eq. (48)] vanish in any one-electron approximation. However, nonvanishing contributions proportional to $T_{nL}(J)$ come from first-order polarization corrections to the wave functions, as can be shown by a direct perturbation calculation (see the Appendix). Since the matrix elements vanish in lowest order, the Z scaling of $\langle\Delta_3\rangle$ is one power of Z lower than the nominal Z^4 scaling indicated by Eq. (48). Furthermore, a transformation to Jacobi coordinates shows that in the asymptotic limit, $\Delta_3\to-2B_{3,Z}^X$ (see the Appendix). This establishes the correct Z scaling of $B_{3,Z}^X$ and ties together the relative signs of the off-diagonal matrix elements. A comparison with the derivation of Au, Feinberg, and Sucher [34] is not meaningful for this case because their effective two-body formalism does not contain a complete representation of the spin-dependent interactions. The derivation of Hessels *et al.* [36] corresponds to replacing Δ_3 and B_3^M by $\tilde{\Delta}_3=\Delta_3+2yB_{3,Z}$ and

$\tilde{B}_3^M = B_3^M - 2yB_{3,Z}$, which restores the terms that were canceled in deriving Δ_3 [see the discussion following Eq. (48)], and then neglecting the contributions from $\tilde{\Delta}_3$, $B_{3,Z}^X$, and $B_{3,e}^X$. The neglected terms sum to zero (asymptotically) for the off-diagonal matrix element.

For completeness, the finite-mass corrections to the anomalous-magnetic-moment terms can be extracted directly from Eqs. (25)–(27). They are

$$-2\gamma_e y \langle B_{3,Z} + \tfrac{4}{3}\delta_{S,S'} B_{3,e} + 2B_5 \rangle + \gamma_e \langle 2B_{3,Z}^X + \tfrac{4}{3}\delta_{S,S'} B_{3,e}^X + \Delta_3 + 2B_5^X \rangle \rightarrow \begin{cases} -2\gamma_e y [Z - 2 + 4S_L(J)] T_{nL}(J) & \text{for } S = S' = 1, \\ -2\gamma_e y Z T_{nL}(L)[L(L+1)]^{1/2} & \text{for } S = 1,\ S' = 0 . \end{cases} \quad (110)$$

The only term not included so far in the asymptotic expansions is the term proportional to $\pi\langle \delta(\mathbf{r}_{12}) \rangle$ in Eq. (39). In a simple screening approximation, with $R_{nL}(r,Z)$ the hydrogenic radial wave function for nuclear charge Z, the matrix element is given by

$$\begin{aligned} \pi\langle \delta(\mathbf{r}_{12}) \rangle &= \tfrac{1}{2}\int_0^\infty |R_{1s}(r,Z)|^2 |R_{nL}(r,Z-1)|^2 r^2 dr \\ &= \frac{2Z^3(n+L)!}{(2L+1)!(n-L-1)!} \left[\frac{Z-1}{nZ} \right]^{2L+4} \left[\frac{ZL+1}{Z-1} \right] e^{-2(Z-1)/Z} \end{aligned} \quad (111)$$

and so decreases exponentially with L. However, the above is asymptotically larger than the actual variational matrix elements (see Sec. IV) by approximately a factor of 4 for helium. As a function of Z, the required asymptotic correction factor is approximately

$$g(Z) = \left[\frac{Z-1}{Z} \right]^2 . \quad (112)$$

With $g(Z)$ included, the above reproduces the variational calculations to within 18% for $L \geq 4$. For the low-L states of helium, the correction factors are $2.07g(Z)$, $1.58g(Z)$, $1.32g(Z)$, $1.18g(Z)$, and $1.08g(Z)$, respectively, for $L = 1$, 2, 3, 4, and 5, with little dependence on n. That $g(Z)$ is substantially smaller than unity indicates that correlation effects and the "Coulomb hole" [37] about the point $\mathbf{r}_{12} = 0$ continue to play an important role, even in the asymptotic limit.

IV. COMPARISON WITH VARIATIONAL CALCULATIONS

A comparison of the asymptotic expansions with matrix elements obtained from high-precision variational wave functions serves two purposes. First, for low to moderate L, it allows a precise assessment of the accuracy of the truncated asymptotic expansions. Second, for high L, the comparison should be regarded instead as a test of the variational results. Since the rate of convergence of the asymptotic expansions rapidly improves with increasing L, the expansions eventually exceed the accuracy of the variational matrix elements.

A. Nonrelativistic energies

Tables I and II summarize the nonrelativistic energies for infinite nuclear mass, together with the first- and second-order mass-polarization corrections. This and the subsequent tables include the $2S$ states and all higher-L states up to $n = 10$ and $L = 7$. As an example of the spectroscopic notation, $2P$ means $1s2p\ ^1P$ or ^3P. A full discussion of the double basis-set variational methods and convergence studies for each state can be found in Ref. [5], together with comparisons with previous work. Detailed comparisons with the asymptotic expansions for the nonrelativistic energies have been presented previously [4,21] and will not be repeated here. However, comparisons with the asymptotic expansions for the first- and second-order mass-polarization corrections (in units of e^2/a_μ)

$$\varepsilon_M^{(1)} = \langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle \quad (113)$$

and

$$\varepsilon_M^{(2)} \simeq [E_M - E_\infty - y\varepsilon_M^{(1)}]/y^2 \quad (114)$$

to the nonrelativistic energies provide important tests of the variational results. In Eq. (114), E_∞ is the energy for infinite nuclear mass, and E_M is the energy corresponding to ^{4}He obtained by explicitly including the $y\mathbf{p}_1 \cdot \mathbf{p}_2$ mass-polarization term in the Hamiltonian ($y = 1.370\,745\,620 \times 10^{-4}$). The $\varepsilon_M^{(2)}$ comparison is particularly interesting because it provides a profound test of the variational calculations to the full extent of their estimated convergence. The extreme sensitivity follows from the fact that the terms $E_\infty + y\varepsilon_M^{(1)}$ in Eq. (114) account for the first nine significant figures of E_M, and so the first significant figure of $\varepsilon_M^{(2)}$ is determined by the tenth significant figure of E_M. A failure of the variational basis sets to converge to the correct answer (relative to E_∞) is immediately revealed by a comparison with the asymptotic $\varepsilon_M^{(2)}$ from Eq. (18). The one slight complication is that the variational estimate of $\varepsilon_M^{(2)}$ from Eq. (114) is contaminated by terms of higher order in y. For the present levels of accuracy, the only significant such term is the contribution $-y^4(Z-1)^2/(2n^2)$ in Eq. (10) to $y^2\varepsilon_M^{(2)}$. The asymptotic $\varepsilon_M^{(2)}$ is therefore modified to be

$$\tilde{\varepsilon}_M^{(2)}(y) = \varepsilon_M^{(2)} - y^2(Z-1)^2/(2n^2) \quad (115)$$

in order to compare with the variational values from Eq.

(114) for ^{4}He. The small-y dependence of $\varepsilon_M^{(2)}$ should be taken into account for very-high-precision applications to isotope shifts, etc.

Table III shows the comparison for $\varepsilon_M^{(1)}$. The asymptotic expansion for the H, I, and K states includes the new Drachman [21] terms of order $\langle x^{-9}\rangle_{nL}$ and $\langle x^{-10}\rangle_{nL}$ shown in Eq. (14). As recommended by him, the quantity added is $\frac{1}{4}(c_9^{(1)}\langle x^{-9}\rangle_{nL}+c_{10}^{(1)}\langle x^{-10}\rangle_{nL})$ with $\pm\frac{1}{4}(c_9^{(1)}\langle x^{-9}\rangle_{nL}+c_{10}^{(1)}\langle x^{-10}\rangle_{nL})$ regarded as the uncertainty. These terms improve the agreement with the variational results by about one significant figure. In every case, the actual differences are close to the uncertainty estimate for the asymptotic expansion.

As discussed above, the comparison for $\tilde{\varepsilon}_M^{(2)}(y)$ in Table IV provides instead a test of the variational results. For $L>3$, the asymptotic expansion (15) [including Eq. (115)] becomes the more accurate of the two. The differences are in reasonably good accord with the accuracies estimated from the apparent convergence of the variational calculations [5]. At present levels of accuracy, terms beyond $\langle x^{-8}\rangle_{nL}$ in the asymptotic expansion are not necessary, although they are known [26] and are included

TABLE I. Nonrelativistic variational energies $E_\infty=-2-1/(2n^2)+\Delta E_\infty$ for infinite nuclear mass, and first- and second-order mass-polarization coefficients $\varepsilon_M^{(1)}$ and $\varepsilon_M^{(2)}$ for the singlet states of helium (in units of 10^{-3} a.u.).

State	$\Delta E_\infty(n\,^1L)$	$\varepsilon_M^{(1)}(n\,^1L)$	$\varepsilon_M^{(2)}(n\,^1L)$
2*S*	−20.974 046 054 43(5)	9.503 864 419 0(2)	−135.276 89(2)
2*P*	1.156 913 501 908(8)	46.044 524 94(1)	−168.271 40(5)
3*P*	0.409 193 463 61(3)	14.548 047 097(1)	−66.047 859(3)
4*P*	0.180 349 549 76(3)	6.254 923 554 3(1)	−35.159 71(6)
5*P*	0.094 010 099 17(2)	3.230 021 84(2)	−21.847 6(3)
6*P*	0.054 909 217 15(2)	1.878 058 536(1)	−14.902 86(9)
7*P*	0.034 767 103 30(2)	1.186 152 30(1)	−10.818 6(2)
8*P*	0.023 372 866 78(2)	0.796 195 83(5)	−8.211 7(5)
9*P*	0.016 454 853 31(5)	0.559 978 028(2)	−6.445 7(2)
10*P*	0.012 016 197 78(4)	0.408 649 426(2)	−5.197 (1)
3*D*	−0.065 177 296 690(6)	−0.249 399 992 1(1)	−57.201 299(9)
4*D*	−0.029 846 178 687(7)	−0.129 175 188 7(8)	−32.150 91(2)
5*D*	−0.015 836 159 984(4)	−0.071 883 131(6)	−20.510 1(2)
6*D*	−0.009 338 535 397(5)	−0.043 412 268 9(9)	−14.199 4(2)
7*D*	−0.005 946 825 32(1)	−0.028 027 840(2)	−10.405 09(3)
8*D*	−0.004 012 563 811(7)	−0.019 076 181(1)	−7.950 7(4)
9*D*	−0.002 831 931 468(6)	−0.013 542 185(3)	−6.270 99(7)
10*D*	−0.002 071 654 250(6)	−0.009 947 506 0(6)	−5.072 4(4)
4*F*	−0.005 144 381 749(1)	−0.010 024 269 4(2)	−31.274 336(4)
5*F*	−0.002 937 158 7427(5)	−0.005 704 294 6(4)	−20.013 498(6)
6*F*	−0.001 794 926 6608(3)	−0.003 482 257(7)	−13.896 984(2)
7*F*	−0.001 166 441 3586(3)	−0.002 262 00(4)	−10.209 2(3)
8*F*	−0.000 797 115 0141(6)	−0.001 545 48(1)	−7.815 9(3)
9*F*	−0.000 567 391 1518(8)	−0.001 099 967 1(3)	−6.175 20(1)
10*F*	−0.000 417 564 669(2)	−0.000 809 442(9)	−5.001 76(2)
5*G*	−0.000 710 898 584 714(7)	−0.001 404 413 64(4)	−20.003 560 85(5)
6*G*	−0.000 456 498 424 34(3)	−0.000 898 579 9(7)	−13.891 179(6)
7*G*	−0.000 304 592 119 49(7)	−0.000 598 396 3(3)	−10.205 61(5)
8*G*	−0.000 211 494 024 1(1)	−0.000 415 004 03(5)	−7.813 563(1)
9*G*	−0.000 152 121 413 5(1)	−0.000 298 267 2(1)	−6.173 579 6(1)
10*G*	−0.000 112 764 318 2(4)	−0.000 220 982(2)	−5.000 55(2)
6*H*	−0.000 145 865 390 8318(7)	−0.000 290 347 0899(3)	−13.889 619 06(3)
7*H*	−0.000 101 173 828 98(2)	−0.000 201 097 79(3)	−10.204 590(2)
8*H*	−0.000 071 828 655 81(1)	−0.000 142 649 2(3)	−7.812 855(4)
9*H*	−0.000 052 397 446 30(2)	−0.000 104 002 216(2)	−6.173 104(2)
10*H*	−0.000 039 214 394 52(2)	−0.000 077 806 68(4)	−5.000 193 5(2)
7*I*	−0.000 038 973 538 2601(1)	−0.000 077 775 526(3)	−10.204 276 73(2)
8*I*	−0.000 028 549 584 5853(4)	−0.000 056 935 91(1)	−7.812 642 88(1)
9*I*	−0.000 021 226 209 733(1)	−0.000 042 313 59(3)	−6.172 945 9(1)
10*I*	−0.000 016 086 516 194(2)	−0.000 032 059 0(1)	−5.000 080 3(4)
8*K*	−0.000 012 570 229 3050(0)	−0.000 025 111 3316(0)	−7.812 563 02(1)
9*K*	−0.000 009 590 156 9404(1)	−0.000 019 151 6195(1)	−6.172 887 59(1)
10*K*	−0.000 007 388 375 8771(7)	−0.000 014 751 409(2)	−5.000 036 93(5)

in the tabulated values. Even for the P states, where only the leading two terms of Eq. (15) are nondivergent, deviations from a systematic trend in the differences can indicate errors in the variational eigenvalues as small as 10^{-13} a.u. For example, for the $10P$ state in Table IV, a change of 0.01×10^{-3} in the "difference" of $0.078(1)\times10^{-3}$ would correspond to an energy change of $0.01\times10^{-3}y^2=1.88\times10^{-13}$ a.u. The eventual dominance of $y^2\varepsilon_M^{(2)}$ over $y\varepsilon_M^{(1)}$ for sufficiently high L is evident from the table.

B. Relativistic corrections

Aside from the nonrelativistic energy, the largest source of error in the asymptotic-expansion method is the lowest-order relativistic correction. Beginning with the spin-independent part given by Eq. (62), the variational matrix elements $-\frac{1}{8}\langle p_1^4+p_2^4\rangle$ are listed for the singlet and triplet states in Table V. The matrix elements $\pi\langle\delta(\mathbf{r}_1)\rangle$ are given separately in Table VI for L up to 2. This completes the tabulation of these matrix elements given previously for $3\le L\le 7$ [35]. The left-hand side of Eq. (62) also contains the term $\alpha^2\langle\pi\delta(\mathbf{r}_{12})\rangle$, but as shown in Eq. (111) (see also Table VII), this decreases exponentially with L, and is negligible for $L>3$.

The comparison in Table VIII with the asymptotic expansion shows that the $\Delta B_1(\phi_1)$ term removes what would otherwise be a significant discrepancy with the

TABLE II. Same as Table I for the triplet states of helium (in units of 10^{-3} a.u.).

State	$\Delta E_\infty(n\,^3L)$	$\varepsilon_M^{(1)}(n\,^3L)$	$\varepsilon_M^{(2)}(n\,^3L)$
2S	−50.229 378 236 7912(1)	7.442 130 705(1)	−57.495 840(8)
2P	−8.164 190 779 27(1)	−64.572 425 024(3)	−204.959 93(2)
3P	−2.525 528 718 72(4)	−18.369 001 636(2)	−70.292 710(2)
4P	−1.074 354 296 62(2)	−7.555 178 98(1)	−36.129 973(2)
5P	−0.551 187 256 25(1)	−3.810 911 035(1)	−22.166 61(9)
6P	−0.319 069 884 85(1)	−2.184 346 463(1)	−15.033 58(5)
7P	−0.200 878 375 28(2)	−1.366 500 8(3)	−10.879 (2)
8P	−0.134 513 771 12(1)	−0.911 053 5(3)	−8.248 7(6)
9P	−0.094 427 860 24(4)	−0.637 531 359(5)	−6.464 937(1)
10P	−0.068 805 497 8(1)	−0.463 433 718(8)	−5.206 7(1)
3D	−0.080 753 897 706(4)	0.025 322 839(1)	−54.737 73(1)
4D	−0.038 847 501 795(3)	0.029 442 651(2)	−30.747 891(7)
5D	−0.021 027 446 911(5)	0.019 568 85(1)	−19.706 2(2)
6D	−0.012 526 564 903(7)	0.012 742 22(3)	−13.707 27(1)
7D	−0.008 024 322 942(2)	0.008 563 121(3)	−10.085 212(1)
8D	−0.005 434 711 706(3)	0.005 971 123 4(3)	−7.731 59(2)
9D	−0.003 845 378 524(2)	0.004 306 538(6)	−6.115 2(1)
10D	−0.002 818 080 232(8)	0.003 198 298(8)	−4.958 0(8)
4F	−0.005 168 403 2456(6)	−0.009 669 639 550(9)	−31.277 992 1(3)
5F	−0.002 957 377 3694(4)	−0.005 406 490 0(5)	−20.016 561(4)
6F	−0.001 809 459 6431(2)	−0.003 268 458 6(8)	−13.899 22(3)
7F	−0.001 176 742 2112(2)	−0.002 110 58(3)	−10.210 7(3)
8F	−0.000 804 535 0908(5)	−0.001 436 452(2)	−7.817 0(2)
9F	−0.000 572 858 8702(7)	−0.001 019 651(2)	−6.176 0254(7)
10F	−0.000 421 686 604(1)	−0.000 748 926 4(2)	−5.002 386(2)
5G	−0.000 710 925 343 925(4)	−0.001 404 001 25(2)	−20.003 564 58(5)
6G	−0.000 456 528 064 07(3)	−0.000 898 123 7(7)	−13.891 184(8)
7G	−0.000 304 617 564 87(6)	−0.000 598 005 (1)	−10.205 61(5)
8G	−0.000 211 514 424 82(9)	−0.000 414 690 37(1)	−7.813 568(2)
9G	−0.000 152 137 492 2(3)	−0.000 298 019 82(6)	−6.173 592(4)
10G	−0.000 112 777 003 3(6)	−0.000 220 785(3)	−5.000 55(2)
6H	−0.000 145 865 412 6648(6)	−0.000 290 346 7263(1)	−13.889 618 97(3)
7H	−0.000 101 173 858 985(8)	−0.000 201 097 257(7)	−10.204 587(2)
8H	−0.000 071 828 685 73(1)	−0.000 142 648 7(2)	−7.812 859(5)
9H	−0.000 052 397 473 04(2)	−0.000 104 001 89(2)	−6.173 101(2)
10H	−0.000 039 214 417 41(2)	−0.000 077 806 22(1)	−5.000 193 46(7)
7I	−0.000 038 973 538 2737(1)	−0.000 077 775 520(3)	−10.204 276 78(1)
8I	−0.000 028 549 584 608(1)	−0.000 056 935 91(2)	−7.812 642 94(4)
9I	−0.000 021 226 209 7577(6)	−0.000 042 313 62(5)	−6.172 946 0(2)
10I	−0.000 016 086 516 219(2)	−0.000 032 058 9(2)	−5.000 081(1)
8K	−0.000 012 570 229 3050(0)	−0.000 025 111 3317(0)	−7.812 563 02(1)
9K	−0.000 009 590 156 9404(1)	−0.000 019 151 6197(3)	−6.172 887 59(1)
10K	−0.000 007 388 375 8771(7)	−0.000 014 751 413(6)	−5.000 036 83(2)

variational matrix elements. The residual differences decrease more rapidly with L than $\langle x^{-6}\rangle_{nL}$ since the relativistic quadrupole polarizability [19] and nonadiabatic correction terms [32] are included. The close agreement leaves little room for doubt that the variational results are correct.

The above does not include the contribution from $\langle B_2\rangle$ because this corresponds asymptotically to the largest part of what is called the retardation term in the asymptotic expansion and LRI pictures [see Eq. (120) below]. Table IX lists the variational matrix elements, and Table X shows the good agreement that is obtained with the asymptotic expansion (77) for high L, provided that the higher-order corrections in (77) are included.

Turning now to the relativistic-recoil terms, the asymptotic expansion Eq. (93) does not quite correspond to the variational matrix elements because of terms of order α^2y^2. Although the mass-polarization operator is included to all orders in the variational matrix elements, the term $-y^2(\mathbf{p}_1\cdot\mathbf{p}_2)^2/2$, which was dropped from Eq. (28), contributes to the $1/n^2$ term. Its expectation value is asymptotically

$$-(\alpha y)^2(\mathbf{p}_1\cdot\mathbf{p}_2)^2/2\rightarrow-(\alpha y)^2[Z(Z-1)/n]^2/6\ , \qquad (116)$$

and this is precisely the difference between Eq. (93) and the high-L limit of the variational results. If this term is of importance ($-4.39/n^2$ kHz for ^{4}He), then it should be added to $(\Delta E_{\mathrm{RR}})_{\mathrm{X}}$ [see Eqs. (54) and (55)] and the total energy obtained from the variational matrix elements. Table XI compares the two methods of calculation, with the missing term in Eq. (116) subtracted from the asymptotic expansion. The variational results correspond to the quantity (in a.u.)

$$\langle B_1^X+B_4^X\rangle=\alpha^2(\mu/M)(p_4^X+Zd_1^X)$$

with p_4^X from Table V and d_1^X from Table VI (or Table IV of Ref. [35] for $L>2$). For consistency with the asymptotic expansions, the small $-d_{12}^X$ term [see Eq. (32)] listed in Table VII is not included. For $L\geq4$, the asymptotic expansion becomes comparable in accuracy to the variational results owing to loss of precision in the latter due to the differencing of nearly equal numbers [see Eq. (114)]. In addition, there is severe cancellation between the singlet and triplet D states on taking the spin average.

TABLE III. Comparison of spin-averaged variational matrix elements with the asymptotic values [see Eq. (14)] for the first-order mass-polarization coefficient $\varepsilon_M^{(1)}$ (in units of 10^{-3} a.u.).

State	Variational	Asymptotic	Difference
$3D$	−0.112 038 577(1)	−0.10(6)	−0.01(6)
$4D$	−0.049 866 269(2)	−0.04(3)	−0.01(3)
$5D$	−0.026 157 14(2)	−0.02(2)	−0.00(2)
$6D$	−0.015 335 02(3)	−0.01(1)	−0.00(1)
$7D$	−0.009 732 359(4)	−0.008(8)	−0.002(8)
$8D$	−0.006 552 529(1)	−0.005(5)	−0.001(5)
$9D$	−0.004 617 823(6)	−0.004(4)	−0.001(4)
$10D$	−0.003 374 604(8)	−0.003(3)	−0.001(3)
$4F$	−0.009 846 954 5(2)	−0.010 1(4)	0.000 3(4)
$5F$	−0.005 555 392 3(6)	−0.005 7(3)	0.000 2(3)
$6F$	−0.003 375 358(7)	−0.003 5(2)	0.000 1(2)
$7F$	−0.002 186 29(5)	−0.002 3(1)	0.000 1(1)
$8F$	−0.001 490 97(1)	−0.001 55(9)	0.000 06(9)
$9F$	−0.001 059 809(2)	−0.001 10(7)	0.000 04(7)
$10F$	−0.000 779 184(9)	−0.000 81(5)	0.000 03(5)
$5G$	−0.001 404 207 44(5)	−0.001 403 7(9)	−0.000 000 5(9)
$6G$	−0.000 898 352(1)	−0.000 898(1)	−0.000 000(1)
$7G$	−0.000 598 201(1)	−0.000 597 8(8)	−0.000 000 4(8)
$8G$	−0.000 414 847 20(5)	−0.000 414 6(6)	−0.000 000 2(6)
$9G$	−0.000 298 143 5(1)	−0.000 297 9(5)	−0.000 000 2(5)
$10G$	−0.000 220 883(3)	−0.000 220 7(4)	−0.000 000 2(4)
$6H$	−0.000 290 346 908 1(3)	−0.000 290 348(3)	0.000 000 001(2)
$7H$	−0.000 201 097 52(3)	−0.000 201 098(3)	0.000 000 001(3)
$8H$	−0.000 142 648 9(4)	−0.000 142 650(3)	0.000 000 001(3)
$9H$	−0.000 104 002 05(2)	−0.000 104 003(3)	0.000 000 001(3)
$10H$	−0.000 077 806 45(4)	−0.000 077 807(2)	0.000 000 001(2)
$7I$	−0.000 077 775 523(4)	−0.000 077 775 54(3)	0.000 000 000 02(3)
$8I$	−0.000 056 935 91(2)	−0.000 056 935 94(5)	0.000 000 000 03(5)
$9I$	−0.000 042 313 60(6)	−0.000 042 313 67(5)	0.000 000 000 06(8)
$10I$	−0.000 032 058 9(3)	−0.000 032 059 00(5)	0.000 000 000 0(3)
$8K$	−0.000 025 111 331 651(1)	−0.000 025 111 332(1)	0.000 000 000 001(1)
$9K$	−0.000 019 151 619 6(3)	−0.000 019 151 621(2)	0.000 000 000 002(2)
$10K$	−0.000 014 751 411(7)	−0.000 014 751 390(2)	−0.000 000 000 021(7)

For the F states, there is severe cancellation between the positive terms of order $\alpha^2 y$ and the negative terms of order $\alpha^2 y^2$ in Eq. (93). For higher L, the latter terms become dominant, which explains the changes in sign evident in Table XI and p_4^X in Table V. The residual differences in the last column are approximately $-4\alpha^2 y\langle x^{-6}\rangle_{nL}$ a.u., which is taken to be the uncertainty in the asymptotic values. Matrix elements of the remaining recoil term Δ_2 are listed in Table XII. The asymptotic form is given by Eq. (100).

For completeness, Table XIII lists the variational values for the Q matrix elements defined by

$$Q=\frac{1}{4\pi}\lim_{a\to 0}\langle r_{12}^{-3}(a)+4\pi(\gamma+\ln a)\delta(\mathbf{r}_{12})\rangle \ , \qquad (117)$$

where γ is Euler's constant and a is the radius of a sphere centered at $r_{12}=0$ which is excluded from the integration over r_{12}. This is required in the calculation of the Araki-Sucher electron-electron QED contribution to the energy given by [38,39]

$$\Delta E_{L,2}(nLS)=\alpha^3\left(\tfrac{14}{3}\ln\alpha+\tfrac{164}{15}\right)\langle\delta(\mathbf{r}_{12})\rangle-\tfrac{14}{3}\alpha^3 Q \ . \qquad (118)$$

The above contains contributions from one- and two-photon exchange, vertex terms, vacuum-polarization terms, anomalous-magnetic-moment terms, and Coulomb corrections. For Rydberg states $\langle\delta(\mathbf{r}_{12})\rangle$ decreases exponentially with L and can be neglected (see Table VII). The Q term is well approximated by its asymptotic expansion

TABLE IV. Comparison of spin-averaged variational matrix elements with the asymptotic values [see Eq. (15)] for the second-order mass-polarization coefficient $\varepsilon_M^{(2)}$ (in units of 10^{-3} a.u.).

State	Variational	Asymptotic	Difference
$2P$	−86.615 66(6)	−54.296 9	32.318 8
$3P$	−68.170 284(4)	−65.200 6	−2.969 7
$4P$	−35.644 84(6)	−35.461 4	−0.183 4
$5P$	−22.007 1(3)	−22.190 0	0.182 9(3)
$6P$	−14.968 2(1)	−15.166 9	0.198 6(1)
$7P$	−10.849(2)	−11.012 9	0.164(2)
$8P$	−8.230 2(8)	−8.356 1	0.125 8(8)
$9P$	−6.455 3(2)	−6.555 5	0.100 1(2)
$10P$	−5.202(1)	−5.279 4	0.078(1)
$3D$	−55.969 51(2)	−55.94(2)	−0.03(2)
$4D$	−31.449 40(2)	−31.43(1)	−0.02(1)
$5D$	−20.108 1(2)	−20.098(7)	−0.011(7)
$6D$	−13.953 3(3)	−13.947(4)	−0.006(4)
$7D$	−10.245 15(3)	−10.241(3)	−0.004(3)
$8D$	−7.841 2(4)	−7.838(2)	−0.004(2)
$9D$	−6.193 1(1)	−6.191(1)	−0.003(1)
$10D$	−5.015 2(9)	−5.013(1)	−0.002(1)
$4F$	−31.276 164(4)	−31.276 1(1)	−0.000 0(1)
$5F$	−20.015 030(7)	−20.014 96(9)	−0.000 07(9)
$6F$	−13.898 10(3)	−13.898 05(6)	−0.000 05(7)
$7F$	−10.209 9(4)	10.210 04(4)	0.000 1(4)
$8F$	−7.816 5(3)	−7.816 57(3)	0.000 1(3)
$9F$	−6.175 61(1)	−6.175 74(2)	0.000 13(3)
$10F$	−5.002 07(2)	−5.002 14(2)	0.000 06(2)
$5G$	−20.003 562 72(7)	−20.003 568(3)	0.000 005(3)
$6G$	−13.891 18(1)	−13.891 183(3)	0.000 00(1)
$7G$	−10.205 61(7)	−10.205 613(2)	0.000 00(7)
$8G$	−7.813 566(3)	−7.813 564(2)	−0.000 002(3)
$9G$	−6.173 586(4)	−6.173 605(1)	0.000 019(5)
$10G$	−5.000 55(3)	−5.000 568(1)	0.000 02(3)
$6H$	−13.889 619 02(4)	−13.889 619 36(7)	0.000 000 34(8)
$7H$	−10.204 589(2)	−10.204 588 49(8)	−0.000 000(2)
$8H$	−7.812 857(6)	−7.812 859 93(7)	0.000 003(6)
$9H$	−6.173 103(3)	−6.173 102 12(6)	−0.000 000(3)
$10H$	−5.000 193 5(2)	−5.000 196 56(5)	0.000 003 1(2)
$7I$	−10.204 276 76(2)	−10.204 276 794(4)	0.000 000 04(2)
$8I$	−7.812 642 91(4)	−7.812 642 992(5)	0.000 000 08(4)
$9I$	−6.172 945 9(2)	−6.172 945 836(5)	−0.000 000 1(2)
$10I$	−5.000 081(1)	−5.000 080 594(4)	−0.000 000(1)
$8K$	−7.812 563 02(1)	−7.812 563 0145(4)	−0.000 000 01(1)
$9K$	−6.172 887 59(1)	−6.172 887 5893(5)	−0.000 000 00(1)
$10K$	−5.000 036 88(5)	−5.000 037 0503(5)	0.000 000 17(5)

$$Q=\frac{1}{4\pi}(\langle x^{-3}\rangle_{nL}+3Z^{-2}\langle x^{-5}\rangle_{nL}) , \tag{119}$$

where the second term follows simply from a multipole expansion of $1/|\mathbf{r}-\mathbf{x}|^3$. In the LRI picture, substituting the leading term of (119) in (118) gives the second term in

$$\Delta V_{\rm ret}=\frac{\alpha^2}{Z^2}\langle x^{-4}\rangle_{nL}-\frac{7\alpha^3}{6\pi}\langle x^{-3}\rangle_{nL} , \tag{120}$$

which is the short-range form of the asymptotic expansion for the retardation terms [9–11] (see Ref. [5] for a full discussion). The leading term is related to $\langle B_2\rangle$ through Eq. (77).

The spin-dependent matrix elements are listed in Tables XIV–XVII. In each case, the matrix element refers to the $J=L$ component of the triplet. The $J=L\pm1$ components are obtained from the tabulated quantities according to

$$\langle n\,^3L_J|B_3|n\,^3L_J\rangle=t_L(J)\langle n\,^3L_L|B_3|n\,^3L_L\rangle , \tag{121}$$

$$\langle n\,^3L_J|\Delta_3|n\,^3L_J\rangle=t_L(J)\langle n\,^3L_L|\Delta_3|n\,^3L_L\rangle , \tag{122}$$

$$\langle n\,^3L_J|B_5|n\,^3L_J\rangle=S_L(J)t_L(J)\langle n\,^3L_L|B_5|n\,^3L_L\rangle , \tag{123}$$

where $t_L(L)=1$,

$$t_L(J)=\tfrac{1}{2}\mp(L+\tfrac{1}{2}) \tag{124}$$

TABLE V. Variational matrix elements $-\langle nL|p_1^4+p_2^4|nL\rangle/8+10=p_4+(\mu/M)p_4^X$ (in units of 10^{-3} a.u.).

State	$p_4(n\,^1L)$	$p_4^X(n\,^1L)$	$p_4(n\,^3L)$	$p_4^X(n\,^3L)$
2S	−279.668 907(5)	40.057 (3)	−458.885 204 60(2)	1.118 52(6)
2P	−29.251 357(5)	−262.585 0(7)	87.906 284 33(5)	472.640 5(2)
3P	−11.372 887(6)	−71.319 7(3)	21.921 78(2)	85.562 9(5)
4P	−5.316 142(5)	−29.255 6(3)	8.420 154(3)	28.446(2)
5P	−2.877 712 9(6)	−14.827(7)	4.071 218(4)	12.783(6)
6P	−1.725 117 5(3)	−8.555(1)	2.267 379(2)	6.824(2)
7P	−1.113 216(2)	−5.37(2)	1.389 223(3)	4.06(2)
8P	−0.759 251(2)	−3.61(1)	0.911 721 9(7)	2.65(2)
9P	−0.540 617(1)	−2.542(1)	0.630 175 3(4)	1.798(3)
10P	−0.398 414(1)	−1.86(1)	0.453 562 9(4)	1.284(2)
3D	−1.682 462(2)	4.207 2(3)	−1.413 358(2)	−1.035 5(7)
4D	−1.164 716 9(3)	2.18(1)	−1.012 563 12(2)	−0.804(5)
5D	−0.738 292 78(4)	1.222(3)	−0.651 406(1)	−0.494 3(1)
6D	−0.482 554 5(4)	0.716 1(1)	−0.429 472(1)	−0.331(8)
7D	−0.328 925 1(2)	0.472 (1)	−0.294 438 673(7)	−0.206(1)
8D	−0.232 997 11(4)	0.315 5(6)	−0.209 433 9(5)	−0.148(8)
9D	−0.170 574 3(5)	0.237(6)	−0.153 803 6(4)	−0.096(4)
10D	−0.128 397(5)	0.11(4)	−0.116 059(2)	−0.10(1)
4F	−0.677 002 7(3)	0.148(7)	−0.676 447 81(7)	0.153(7)
5F	−0.491 578 2(6)	0.082(5)	−0.491 112 3(9)	0.087(5)
6F	−0.340 764 3(2)	0.049(4)	−0.340 432 21(4)	0.052(4)
7F	−0.240 021 7(5)	0.032(2)	−0.239 786 61(5)	0.034(2)
8F	−0.173 612 82(8)	0.021(2)	−0.173 443 7(2)	0.023(2)
9F	−0.128 951 4(2)	0.015(1)	−0.128 827 14(3)	0.016(1)
10F	−0.098 107 2(7)	0.011(1)	−0.098 013 0(4)	0.012(1)
5G	−0.276 268 92(3)	0.016 36(2)	−0.276 268 027(2)	0.016 37(2)
6G	−0.216 969 3(2)	0.010 07(2)	−0.216 968 7(3)	0.010 08(2)
7G	−0.162 368 1(5)	0.006 41(2)	−0.162 368 6(8)	0.006 41(2)
8G	−0.121 724 8(1)	0.004 23(2)	−0.121 723 9(2)	0.004 23(2)
9G	−0.092 573 5620(9)	0.002 88(1)	−0.092 573 040(3)	0.002 88(1)
10G	−0.071 620 616(4)	0.001 86(1)	−0.071 620 320(6)	0.001 98(2)
6H	−0.128 923 6(4)	0.000 709 7(6)	−0.128 923 5(3)	0.000 709 7(6)
7H	−0.107 055 52(3)	0.000 313(1)	−0.107 055 48(3)	0.000 313 0(7)
8H	−0.084 726 80(3)	0.000 061(4)	−0.084 726 83(3)	0.000 062(5)
9H	−0.066 617 4(5)	−0.000 096 4(6)	−0.066 617 0(3)	−0.000 094(1)
10H	−0.052 712 5(1)	−0.000 172(2)	−0.052 712 7(1)	−0.000 175 3(5)
7I	−0.067 384 60(2)	−0.001 602(1)	−0.067 384 60(2)	−0.001 601 7(6)
8I	−0.058 178 27(2)	−0.001 274(2)	−0.058 178 27(5)	−0.001 272 08(5)
9I	−0.047 984 27(8)	−0.001 049 0(2)	−0.047 984 27(6)	−0.001 049 26(5)
10I	−0.039 136 33(2)	−0.000 885 54(5)	−0.039 136 32(2)	−0.000 884 6(3)
8K	−0.038 430 866(6)	−0.001 763 99(3)	−0.038 430 866(5)	−0.001 763 98(2)
9K	−0.034 122 1966(7)	−0.001 407 02(2)	−0.034 122 194(1)	−0.001 407 04(2)
10K	−0.029 034 706(6)	−0.001 167(4)	−0.029 034 709(6)	−0.001 15(2)

TABLE VI. Variational matrix elements $\pi\langle\delta(\mathbf{r}_1)\rangle-4=d_1+(\mu/M)d_1^{\mathrm{X}}$ (in units of 10^{-3} a.u.).

State	$d_1(n\,^1L)$	$d_1^{\mathrm{X}}(n\,^1L)$	$d_1(n\,^3L)$	$d_1^{\mathrm{X}}(n\,^3L)$
2S	113.792 370(1)	−1.262 31(5)	148.017 828 713(3)	6.838 86(4)
2P	3.623 328(3)	123.774 8(3)	−45.172 772 175(1)	−225.207 82(8)
3P	1.218 155(3)	35.431 8(1)	−12.936 273(9)	−45.908 0(2)
4P	0.522 308(2)	14.740 1(1)	−5.344 949(2)	−16.242 3(6)
5P	0.268 418 8(3)	7.500(3)	−2.702 571(2)	−7.554 (2)
6P	0.155 519 4(1)	4.327 7(1)	−1.551 215 0(9)	−4.118 8(8)
7P	0.097 985(1)	2.72(1)	−0.971 255(1)	−2.49(1)
8P	0.065 659(1)	1.822(6)	−0.647 908 00(5)	−1.628(4)
9P	0.046 122 8(6)	1.280 5(5)	−0.453 566 5(2)	−1.117(1)
10P	0.033 628 8(6)	0.934(6)	−0.329 798 99(2)	−0.801 2(9)
3D	−0.437 798(1)	−1.816 1(1)	−0.539 766 1(8)	0.334 7(2)
4D	−0.200 015 7(2)	−0.944(7)	−0.257 910 150(7)	0.287(3)
5D	−0.106 073 39(1)	−0.528(2)	−0.139 181 5(6)	0.180 5(1)
6D	−0.062 541 7(2)	−0.313 6(1)	−0.082 779 1(5)	0.120(4)
7D	−0.039 824 4(1)	−0.205 0(5)	−0.052 974 123(3)	0.076 3(5)
8D	−0.026 870 38(1)	−0.138 1(3)	−0.035 855 1(3)	0.054(4)
9D	−0.018 963 6(2)	−0.101(3)	−0.025 357 9(2)	0.036(2)
10D	−0.013 874(2)	−0.06(2)	−0.018 578 2(9)	0.034(6)

for $J=L\pm1$, and $S_L(J)$ is given by Eq. (105). The off-diagonal matrix elements $n\,^3L_L-n\,^1L_L$ are also tabulated. It is evident from the tables that the asymptotic limits contained in Eqs. (106) and (107) are satisfied.

For all the above terms, the corrections to the leading asymptotic values given in Eqs. (106) and (107) arise from short-range effects involving overlap integrals with the inner 1s electron [36,40], rather than long-range polarization terms proportional to $\langle x^{-4}\rangle_{nL}$. Since the short-range effects decrease exponentially with L, the leading asymptotic term alone rapidly improves in accuracy as illustrated previously for the $n=10$ states of helium (see

TABLE VII. Variational matrix elements $\pi\langle\delta(\mathbf{r}_{12})\rangle=d_{12}+(\mu/M)d_{12}^{\mathrm{X}}$ (in units of 10^{-6} a.u.).

State	$d_{12}(n\,^1L)$	$d_{12}^{\mathrm{X}}(n\,^1L)$	State	$d_{12}(n\,^1L)$	$d_{12}^{\mathrm{X}}(n\,^1L)$
2S	27 169.868(4)	5 550.(3)	5G	0.000 015 868(4)	−0.000 128 3(2)
			6G	0.000 017 666(1)	−0.000 15(3)
2P	2 309.601 8(8)	−10 854.41(1)	7G	0.000 015 209(2)	−0.000 2(1)
3P	791.729(2)	−3 367.130(2)	8G	0.000 012 211(1)	−0.000 091 64(1)
4P	350.176(2)	−1 419.69(2)	9G	0.000 009 635(3)	−0.000 064(2)
5P	183.2091(1)	−723.(1)	10G	0.000 007 607(3)	−0.000 046(5)
6P	107.283 31(8)	−415.2(8)			
7P	68.048 56(2)	−256.14(6)	6H	0.000 000 013 71(1)	−0.000 000 1864(1)
8P	45.804 1(1)	−171.3(9)	7H	0.000 000 018 886(4)	−0.000 000 07(8)
9P	32.276 24(8)	−121.(2)	8H	0.000 000 018 91(3)	−0.000 000 2(5)
10P	23.585 8(4)	−90.(2)	9H	0.000 000 017 00(9)	−0.000 000 139(1)
			10H	0.000 000 014 481(8)	−0.000 000 1(2)
3D	7.186 37(1)	−30.59(8)			
4D	4.230 74(8)	−17.787(6)	7I	0.000 000 000 0093(2)	−0.000 000 0003(2)
5D	2.461 13(4)	−10.333(6)	8I	0.000 000 000 0152(4)	−0.000 000 0010(7)
6D	1.518 51(2)	−6.17(5)	9I	0.000 000 000 0174(4)	−0.000 000 0008(3)
7D	0.992 34(8)	−4.10(7)	10I	0.000 000 000 0174(4)	0.000 000 000(3)
8D	0.680 57(5)	−2.9(2)			
9D	0.485 58(2)	−2.08(6)			
10D	0.357 98(1)	−1.36(7)			
4F	0.013 053(1)	−0.082 7(9)			
5F	0.011 079 8(7)	−0.065 289(1)			
6F	0.008 001 4(2)	−0.047(2)			
7F	0.005 687 46(1)	−0.034(1)			
8F	0.004 104 1(4)	−0.025(1)			
9F	0.003 028 0(6)	−0.020(2)			
10F	0.002 284 7(7)	−0.014(1)			

Table 19 of Ref. [5]). As a consequence, high accuracy can be expected from multiconfiguration Hartree-Fock calculations for these terms [41,42]. However, the same is not true for the spin-independent terms where polarization effects are important.

The spin-dependent matrix elements for the $2\,^3P_J$ states are of particular interest because comparisons with high-precision measurements of the fine-structure splittings may eventually lead to an atomic-physics value for the fine-structure constant. This was the motivation for a long sequence of calculations beginning with Schwartz [43], continuing with the operators for the higher-order spin-dependent terms derived by Douglas and Kroll [44], and culminating with the second-order terms evaluated by Lewis and Serafino [31]. However, the accuracy of neither theory nor experiment was sufficient to compete with α obtained from the quantum Hall effect or the electron magnetic moment [45]. The convergence study presented in Table XVIII shows that the lowest-order matrix elements are now known to an accuracy of about 3 parts in 10^9 for the sum of the three terms. This improves by 3 orders of magnitude the previous results of Schwartz [43], who evidently overestimated the accuracy of his calculation (see the table). In the present work, the entire amount of the extrapolation is taken as a conservative estimate of the uncertainty.

Further work is in progress to achieve a similar improvement in the higher-order corrections. Lewis and Serafino [31] have considered all contributions to the fine-structure splittings up to order α^4 a.u. To this order, self-energy and vacuum-polarization effects are spin independent, and so do not contribute. However, self-

TABLE VIII. Comparison of spin-averaged variational matrix elements with the asymptotic values [see Eq. (62)] for $\langle B_1+B_4\rangle$ (in units of MHz, with $\alpha^2e^2/a_\mu=350\,329.1022\pm0.031$ MHz).

State	Variational	U_1[a]	U_2[b]	U_1+U_2	Difference
$3D$	−884.747(1)	−875.024 601	−17.480 413	−893(14)	8(14)
$4D$	−541.807 0(1)	−536.491 751	−10.060 415	−547(8)	5(8)
$5D$	−329.345 8(4)	−326.370 636	−5.773 710	−332(5)	3(5)
$6D$	−210.664 8(4)	−208.877 304	−3.525 309	−212(3)	2(3)
$7D$	141.701 24(8)	−140.555 999	−2.284 442	−143(2)	1(2)
$8D$	−99.472 8(2)	−98.699 621	−1.555 854	−100(1)	1(1)
$9D$	−72.346 6(2)	−71.801 756	−1.103 714	−72.9(9)	0.6(9)
$10D$	−54.189(2)	−53.792 219	−0.809 667	−54.6(7)	0.4(7)
$4F$	−261.802 89(9)	−261.293 690	−0.479 545	−261.77(9)	−0.03(9)
$5F$	−186.245 6(4)	−185.884 412	−0.343 251	−186.23(7)	−0.02(7)
$6F$	−127.945 86(6)	−127.705 314	−0.229 536	−127.93(4)	−0.01(4)
$7F$	−89.650 0(2)	−89.486 953	−0.155 930	−89.64(3)	−0.01(3)
$8F$	−64.622 14(7)	−64.508 075	−0.109 177	−64.62(2)	−0.00(2)
$9F$	−47.880 09(7)	−47.797 871	−0.078 818	−47.88(2)	−0.00(2)
$10F$	−36.359 7(3)	−36.298 548	−0.058 500	−36.36(1)	−0.00(1)
$5G$	−100.208 73(1)	−100.171 288	−0.035 532	−100.207(3)	−0.002(3)
$6G$	−78.207 7(1)	−78.177 231	−0.028 672	−78.206(3)	−0.002(3)
$7G$	−58.347 9(3)	−58.325 471	−0.021 194	−58.347(2)	−0.001(2)
$8G$	−43.661 03(8)	−43.644 573	−0.015 547	−43.660(1)	−0.001(1)
$9G$	−33.162 870(1)	−33.150 664	−0.011 550	−33.162(1)	−0.001(1)
$10G$	−25.633 080(3)	−25.623 809	−0.008 737	−25.6325(8)	−0.0005(8)
$6H$	−45.869 1(2)	−45.864 402	−0.004 557	−45.869 0(2)	−0.000 2(3)
$7H$	−37.992 42(1)	−37.988 312	−0.003 954	−37.992 3(2)	−0.000 2(2)
$8H$	−30.028 50(1)	−30.025 238	−0.003 133	−30.028 4(2)	−0.000 1(2)
$9H$	−23.590 4(2)	−23.587 765	−0.002 433	−23.590 2(1)	−0.000 2(2)
$10H$	−18.655 72(6)	−18.653 703	−0.001 893	−18.655 6(1)	−0.000 1(1)
$7I$	−23.794 82(1)	−23.793 961	−0.000 833	−23.794 79(3)	−0.000 02(3)
$8I$	−20.519 26(2)	−20.518 484	−0.000 757	−20.519 24(3)	−0.000 02(3)
$9I$	−16.912 66(3)	−16.912 000	−0.000 631	−16.912 63(2)	−0.000 03(2)
$10I$	−13.788 19(1)	−13.787 661	−0.000 512	−13.788 17(2)	−0.000 01(2)
$8K$	−13.524 110(3)	−13.523 911	−0.000 195	−13.524 106(7)	−0.000 004(6)
$9K$	−12.000 2753(5)	−12.000 090	−0.000 183	−12.000 273(7)	−0.000 002(5)
$10K$	−10.207 353(3)	−10.207 192	−0.000 158	−10.207 351(6)	−0.000 003(5)

[a] $U_1=h_1(nL)+\Delta B_1(\alpha_{\rm rel})$.
[b] $U_2=\Delta B_1(\phi_1)$ [see Eqs. (62)–(65)].

energy terms of order $\alpha^5 Z^6 \ln(Z\alpha)^{-2}$ in the one-electron Lamb shift [46–48] become spin dependent for p states. The spin dependence follows from the fact that the small component of the $p_{1/2}$ state is s-like, and so does not vanish at the origin, while the small component of $p_{3/2}$ is d-like which does vanish at the origin. The spin dependence carries over to the two-electron case where, in an unscreened hydrogenic approximation, it contributes at the ± 0.5-MHz level of accuracy [5]. This is undoubtedly an overestimate, but a proper two-electron treatment will be required for a high-precision comparison with experimental fine-structure splittings in helium.

C. Total energies

The main purpose of this work is to present a tabulation of energy levels for all states of helium up to $n=10$ which systematically includes all contributions of orders α^2, α^3, $\alpha^2\mu/M$, $(\mu/M)^2$, and $\alpha^3\mu/M$. Because of the nonperturbative method of treating mass polarization, the results actually contain terms of all orders in μ/M, along with the major part of the $(\alpha\mu/M)^2$ term. Collecting the results of the preceding sections, the total energy is

TABLE IX. Variational matrix elements $\langle B_2\rangle = b_2 + (\mu/M) b_2^X$ (in units of $10^{-3}\alpha^2$ a.u.).

State	$b_2(n\,^1L)$	$b_2^X(n\,^1L)$	$b_2(n\,^3L)$	$b_2^X(n\,^3L)$
2S	−9.253 046 19(5)	142.257 41(4)	−1.628 430 061(2)	23.528 198 5(5)
2P	−20.330 474 10(2)	104.505 483(2)	35.080 886 83(4)	152.372 647(1)
3P	−6.697 368 94(7)	35.411 026 6(5)	10.344 716 185(4)	42.731 990 4(3)
4P	−2.918 278 35(6)	15.815 361 4(7)	4.309 336 988 0(9)	17.857 171 3(1)
5P	−1.516 084 310(6)	8.369 76(3)	2.186 478 863(2)	9.148 602(1)
6P	−0.884 359 852(3)	4.950 67(2)	1.257 237 441 8(6)	5.309 512(3)
7P	−0.559 628 897 2(3)	3.166 44(1)	0.788 014 456(2)	3.354 20(7)
8P	−0.376 116 535(8)	2.146 28(7)	0.526 022 75(3)	2.253 5(2)
9P	−0.264 755 498(5)	1.521 15(5)	0.368 407 518(3)	1.586 935(1)
10P	−0.193 325 91(2)	1.117 1(1)	0.267 963 890(5)	1.159 526(2)
3D	0.121 649 030 2(4)	10.925 689(2)	0.132 279 499 5(6)	9.345 09(4)
4D	0.055 448 022(9)	6.045 59(1)	0.061 389 771(6)	5.137 67(9)
5D	0.029 361 923(2)	3.526 993(1)	0.032 732 686 0217(2)	3.004 600(3)
6D	0.017 296 269 4(8)	2.205 24(1)	0.019 347 096 3(4)	1.884 821(3)
7D	0.011 007 287(7)	1.461 824(2)	0.012 336 011 4(3)	1.253 158 0(1)
8D	0.007 423 938(5)	1.015 78(1)	0.008 330 027 81(9)	0.872 981(5)
9D	0.005 238 034(1)	0.733 23(1)	0.005 881 996 56(4)	0.631 483(2)
10D	0.003 830 987 4(6)	0.546 001 7(8)	0.004 304 353 54(3)	0.471 092 2(7)
4F	0.009 502 665 7(1)	2.806 007 514(1)	0.009 503 888 432(4)	2.805 826 348 3(4)
5F	0.005 420 774 50(8)	1.837 601 740(2)	0.005 421 752 71(2)	1.837 454 27(1)
6F	0.003 310 486 11(4)	1.218 026 103 7(1)	0.003 311 168 732(5)	1.217 922 0(1)
7F	0.002 150 350 885(8)	0.836 551(1)	0.002 150 825 82(4)	0.836 479(1)
8F	0.001 469 024 93(8)	0.595 342 4(2)	0.001 469 362 72(3)	0.595 290 01(7)
9F	0.001 045 422 2(3)	0.437 198 2(7)	0.001 045 669 1(1)	0.437 159 6(6)
10F	0.000 769 236 7(1)	0.329 839 2(6)	0.000 769 421 45(5)	0.329 808 7(6)
5G	0.001 298 129 293 8(3)	1.068 750 148 3(3)	0.001 298 120 604 98(4)	1.068 750 251 39(2)
6G	0.000 834 020 379 6(1)	0.772 941 70(3)	0.000 834 010 759 18(8)	0.772 941 81(3)
7G	0.000 556 538 867(1)	0.556 214 5(2)	0.000 556 530 613(2)	0.556 214 6(2)
8G	0.000 386 427 750 7(1)	0.407 518 081(8)	0.000 386 421 130 026(5)	0.407 518 152(4)
9G	0.000 277 934 795(7)	0.305 274 487(3)	0.000 277 929 582 2(2)	0.305 274 562 0(4)
10G	0.000 206 018 195(2)	0.233 661 0(1)	0.000 206 014 077(6)	0.233 661 12(5)
6H	0.000 264 234 003 215(1)	0.491 437 790 06(2)	0.000 264 233 989 965(3)	0.491 437 790 28(3)
7H	0.000 183 406 809 88(1)	0.378 919 171(9)	0.000 183 406 791 504(4)	0.378 919 155 9(2)
8H	0.000 130 247 632 43(2)	0.288 734 98(2)	0.000 130 247 614 4(1)	0.288 734 984(7)
9H	0.000 095 025 244(1)	0.221 845 25(2)	0.000 095 025 229(5)	0.221 845 230(6)
10H	0.000 071 121 727 7(6)	0.172 839 082 8(6)	0.000 071 121 713 8(3)	0.172 839 082 3(2)
7I	0.000 070 240 254 53(6)	0.256 412 819 0(5)	0.000 070 240 254 65(7)	0.256 412 818 1(4)
8I	0.000 051 486 186 50(4)	0.206 660 708 64(3)	0.000 051 486 186 49(5)	0.206 660 708 9(2)
9I	0.000 038 290 884 84(4)	0.164 199 706 53(1)	0.000 038 290 884 82(4)	0.164 199 706 9(3)
10I	0.000 029 023 920 14(8)	0.130 814 409 0(9)	0.000 029 023 920 1(1)	0.130 814 406(4)
8K	0.000 022 579 147 920(0)	0.146 519 236 07(0)	0.000 022 579 147 920(0)	0.146 519 236 07(0)
9K	0.000 017 235 050 114(0)	0.121 959 251 72(0)	0.000 017 235 050 114(0)	0.121 959 251 76(5)
10K	0.000 013 281 713 075(1)	0.100 020 514 9(9)	0.000 013 281 713 10(1)	0.100 020 514 6(1)

$$E_{\rm tot}=E_{\rm NR}+\Delta E_M^{(1)}+\Delta E_M^{(2)}+\Delta E_{\rm rel}+\Delta E_{\rm anom}+\Delta E_{st}+(\Delta E_{\rm RR})_M+(\Delta E_{\rm RR})_{\rm X}+\Delta E_{\rm nuc}+\Delta E_{L,1}+\Delta E_{L,2}\ . \tag{125}$$

The meaning of each of the terms is defined below, and, as an aid in identifying the physical effects included, each term is expressed in terms of its corresponding asymptotic expansion. All terms are expressed relative to $\mathrm{He}^+(1s)$ (where applicable), so that each is a contribution to the negative ionization energy.

$E_{\rm NR}$ is the nonrelativistic energy without mass polarization, expressed in the form

$$E_{\rm NR}=-(4+1/n^2)R_M+\Delta E_{\rm NR}\ , \tag{126}$$

where $R_M=(1-y)R_\infty$ is the finite-mass Rydberg. To save tabulating excessively many figures, only $\Delta E_{\rm NR}$ is given in the tables. For convenience, the values of R_M/n^2 which must be added to $\Delta E_{\rm NR}$ and $\Delta E_{\rm tot}$ are listed in Table XIX. The asymptotic expansion for $\Delta E_{\rm NR}$ has recently been worked out by Drachman [21] up to terms of order $\langle x^{-10}\rangle_{nL}$. For completeness, the coefficients of $\frac{1}{2}\langle x^{-9}\rangle_{nL}$ and $\frac{1}{2}\langle x^{-10}\rangle_{nL}$ are [26]

$$c_9^{(0)}=-Z^{10}[\tfrac{921\,873}{1008}(Z-1)+\tfrac{14\,307}{8}]\ ,$$

$$c_{10}^{(0)}=Z^{-12}[-\tfrac{436\,835}{128}+\tfrac{33\,295}{4}Z^2+\tfrac{33\,275}{4}Z^2L(L+1)]$$

[cf. Eq. (14)], and the total energy contains the second-order term $(1-6\beta_2/\alpha_1)e_{2,0}^{(1,2)}$, where $e_{2,0}^{(1,2)}$ is defined in Eq. (16), and the multiplying factor is a nonadiabatic correction.

$\Delta E_M^{(1)}$ and $\Delta E_M^{(2)}$ are the first- and second-order mass-polarization corrections with asymptotic expansions corresponding to Eqs. (14) and (15) [including the small y dependence expressed by Eq. (115)].

$\Delta E_{\rm rel}$ is the relativistic correction of order α^2 defined by Eq. (39), with the $\mathrm{He}^+(1s)$ contribution of $-\alpha^2Z^4/8$ a.u. subtracted. From Eqs. (62), (77), and (106) the asymptotic value is thus

$$\Delta E_{\rm rel}\to h_1(nL)+\Delta B_1(\alpha_{\rm rel})+\Delta B_1(\phi_1)+\langle B_2\rangle+[Z-3+2S_L(J)]T_{nL}(J)\delta_{S,1}\ . \tag{127}$$

TABLE X. Comparison of spin-averaged variational matrix elements with the asymptotic values [see Eq. (77)] for $\langle B_2\rangle$, in MHz.

State	Variational	Asymptotic	Difference
3D	44.479 277	48.(6.)	−4.(6.)
4D	20.465 840(4)	23.(3.)	−2.(3.)
5D	10.876 774(1)	12.(2.)	−1.(2.)
6D	6.418 619	7.(1.)	−1.(1.)
7D	4.088 918(2)	4.7(8)	−0.6(8)
8D	2.759 536(2)	3.2(5)	−0.4(5)
9D	1.947 835(1)	2.2(4)	−0.3(4)
10D	1.425 023	1.6(3)	−0.2(3)
4F	3.329 275	3.3(2)	0.1(2)
5F	1.899 226	1.9(1)	0.0(1)
6F	1.159 879	1.14(7)	0.02(7)
7F	0.753 414	0.74(5)	0.01(5)
8F	0.514 701	0.51(3)	0.01(3)
9F	0.366 285	0.36(2)	0.00(2)
10F	0.269 518	0.27(2)	0.00(2)
5G	0.454 771	0.44(1)	0.01(1)
6G	0.292 180	0.286(9)	0.006(9)
7G	0.194 970	0.191(6)	0.004(6)
8G	0.135 376	0.133(4)	0.003(4)
9G	0.097 368	0.095(3)	0.002(3)
10G	0.072 173	0.071(2)	0.001(2)
6H	0.092 569	0.091(2)	0.002(2)
7H	0.064 253	0.063(1)	0.001(1)
8H	0.045 630	0.044 9(9)	0.000 8(9)
9H	0.033 290	0.032 7(7)	0.000 6(7)
10H	0.024 916	0.024 5(5)	0.000 4(5)
7I	0.024 607	0.024 3(3)	0.000 3(3)
8I	0.018 037	0.017 8(2)	0.000 2(2)
9I	0.013 414	0.013 2(2)	0.000 2(2)
10I	0.010 168	0.010 0(1)	0.000 1(1)
8K	0.007 910	0.007 83(7)	0.000 08(7)
9K	0.006 038	0.005 98(6)	0.000 06(6)
10K	0.004 653	0.004 60(5)	0.000 05(5)

TABLE XI. Comparison of spin-averaged variational matrix elements with the asymptotic values [see Eq. (93)] for $\langle B_1^{\rm X}+B_4^{\rm X}\rangle$, in kHz.

State	Variational	Asymptotic	Difference
3D	5.01(4)	11(23)	−5(23)
4D	1.5(7)	4(14)	−3(14)
5D	0.8(1)	2(8)	−1(8)
6D	−0.1(4)	1(5)	−1(5)
7D	0.20(7)	1(3)	−1(3)
8D	−0.0(4)	1(2)	−1(2)
9D	0.3(3)	0(2)	−0(2)
10D	−1(2)	0(1)	−1(2)
4F	0.6(5)	0.5(1)	0.1(5)
5F	0.3(4)	0.3(1)	0.1(4)
6F	0.2(2)	0.13(7)	0.0(3)
7F	0.1(2)	0.07(5)	0.0(2)
8F	0.1(1)	0.03(4)	0.0(1)
9F	0.03(9)	0.01(3)	0.01(9)
10F	0.04(7)	0.00(2)	0.04(8)
5G	−0.137(2)	−0.132(5)	−0.005(5)
6G	−0.105(2)	−0.101(4)	−0.004(5)
7G	−0.084(1)	−0.081(3)	−0.003(4)
8G	−0.068(1)	−0.066(2)	−0.003(3)
9G	−0.0568(9)	−0.055(2)	−0.002(2)
10G	−0.052(1)	−0.046(1)	−0.006(2)
6H	−0.15752(4)	−0.1571(4)	−0.0005(4)
7H	−0.11757(6)	−0.1171(4)	−0.0004(4)
8H	−0.0910(3)	−0.0909(3)	−0.0001(4)
9H	−0.07309(6)	−0.0727(2)	−0.0003(2)
10H	−0.05958(9)	−0.0595(2)	−0.0000(2)
7I	−0.12832(6)	−0.12822(5)	−0.00010(7)
8I	−0.09874(9)	−0.09864(5)	−0.0001(1)
9I	−0.078325(8)	−0.07828(4)	−0.00005(4)
10I	−0.06367(1)	−0.06364(3)	−0.00003(3)
8K	−0.101313(2)	−0.101298(8)	−0.000014(8)
9K	−0.080228(1)	−0.080216(8)	−0.000012(8)
10K	−0.0555(8)	−0.065093(7)	−0.0004(8)

In this and the following terms, the J-dependent part sums to zero on taking a statistically weighted spin average of the energies.

$\Delta E_{\rm anom}$ is the J-dependent part of the anomalous magnetic-moment correction [see Eq. (61)], including finite-mass contributions. From Eqs. (109) and (110), the asymptotic form is

$$\Delta E_{\rm anom} \to 2\gamma_e\{Z-2+(2+\gamma_e)S_L(J) -y[Z-2+4S_L(J)]\}T_{nL}(J)\ . \qquad (128)$$

ΔE_{st} is the singlet-triplet mixing term obtained by diagonalizing all other contributions in the $n\,^3L_L$, $n\,^1L_L$ two-dimensional subset of states. From Eqs. (109) and (110), the total off-diagonal matrix element is asymptotically

$$\langle n\,^3L_L|B_{\rm tot}|n\,^1L_L\rangle \to (Z+1-2y+2\gamma_e Z-2\gamma_e yZ) \times[L(L+1)]^{1/2}T_{nL}(J)\ , \qquad (129)$$

and the diagonal singlet-triplet splitting 2κ can be estimated to sufficient accuracy from the variational results to be

$$2\kappa = \left[1+\left[\frac{3}{2L-1}\right]^{1/2}\right]\pi\langle\delta(\mathbf{r}_{12})\rangle_{\rm singlet} \qquad (130)$$

with $\pi\langle\delta(\mathbf{r}_{12})\rangle$ given by Eq. (111), including $g(Z)$ (cf. Table 5 of Ref. [5]).

$(\Delta E_{\rm RR})_M$ is the relativistic reduced-mass correction given by [cf. Eq. (49)]

$$(\Delta E_{\rm RR})_M = -y\langle 3(B_1+B_4)+2B_2-B_4\rangle+\Delta_2 -2y\langle B_{3,e}+B_5+B_6\rangle+\Delta_3\ . \qquad (131)$$

With the use of Eqs. (62), (77), (98), (100), and (106), the asymptotic form is thus

$$(\Delta E_{\rm RR})_M \to -3y[h_1(nL)+\Delta B_1(\alpha_{\rm rel})+\Delta B_1(\phi_1)]+y\left[Zh_2(nL)+\frac{325}{16Z^2}\alpha^2[1+(Z-2)/6]\langle x^{-4}\rangle_{nL}\right] +y\alpha^2\left[-\frac{31}{4Z^2}\langle x^{-4}\rangle_{nL}+\frac{1447}{32Z^4}\langle x^{-6}\rangle_{nL}\right]-2y\{\langle B_2\rangle+[Z-3+1+2S_L(J)]T_{nL}(J)\delta_{S,1}\}\ . \qquad (132)$$

$(\Delta E_{\rm RR})_{\rm X}$ is the relativistic-recoil cross term between relativistic operators and the mass-polarization operator given

TABLE XII. Variational matrix elements $\langle\Delta_2\rangle+16\alpha^2\mu/M$ (in units of $10^{-3}\alpha^2\mu/M$ a.u.).

State	$\Delta_2(n\,^1L)$	$\Delta_2(n\,^3L)$	State	$\Delta_2(n\,^1L)$	$\Delta_2(n\,^3L)$
2S	−656.864 09(1)	905.330 873 70(4)	5G	−2.107 795 7(1)	−2.107 794 69(1)
			6G	−1.526 864 3(9)	−1.526 864(1)
2P	−286.504 04(2)	241.317 789 40(9)	7G	−1.099 758(2)	−1.099 759(3)
3P	−101.710 88(2)	55.401 39(7)	8G	−0.806 247 4(5)	−0.806 246 1(8)
4P	−46.113 51(2)	19.947 44(1)	9G	−0.604 231 276(1)	−0.604 230 69(2)
5P	−24.555 659(2)	9.193 57(1)	10G	−0.462 641 8(4)	−0.462 640 966(1)
6P	−14.567 360 4(6)	4.937 295(9)			
7P	−9.331 936(8)	2.940 36(1)	6H	−0.976 763(2)	−0.976 763(1)
8P	−6.330 439(9)	1.886 296(1)	7H	−0.753 604 7(1)	−0.753 604 6(1)
9P	−4.488 790(6)	1.279 749(2)	8H	−0.574 466 9(1)	−0.574 467 0(1)
10P	−3.297 113(9)	0.906 915 2(8)	9H	−0.441 503(2)	−0.441 502(1)
			10H	−0.344 041 0(5)	−0.344 040 4(5)
3D	−17.271 572(9)	−17.493 370(6)			
4D	−9.774 938(1)	−9.911 584 94(2)	7I	−0.511 191 01(6)	−0.511 191 00(9)
5D	−5.776 394 211(3)	−5.857 236(4)	8I	−0.412 124 96(9)	−0.412 125 0(2)
6D	−3.642 282(1)	−3.692 528(4)	9I	−0.327 510 5(3)	−0.327 510 5(2)
7D	−2.428 937(1)	−2.461 890 36(1)	10I	−0.260 955 26(7)	−0.260 955 2(1)
8D	−1.695 359 6(3)	−1.717 997(2)			
9D	−1.228 027(2)	−1.244 191(2)	8K	−0.292 511 07(2)	−0.292 511 07(2)
10D	−0.917 02(2)	−0.928 949(9)	9K	−0.243 516 326(3)	−0.243 516 321(5)
			10K	−0.199 731 30(2)	−0.199 731 30(3)
4F	−5.398 868(1)	−5.398 603 6(3)			
5F	−3.554 138(3)	−3.553 919(3)			
6F	−2.362 249 4(6)	−2.362 097 6(2)			
7F	−1.625 210(2)	−1.625 103 7(5)			
8F	−1.157 984 1(2)	−1.157 907 5(9)			
9F	−0.851 132 9(5)	−0.851 076 6(1)			
10F	−0.642 563(3)	−0.642 520 (2)			

by Eqs. (54) and (55). With use of Eqs. (93), (99), and (106), the asymptotic form is

$$(\Delta E_{\rm RR})_{\rm X}\rightarrow y\alpha^2\left[Z^2(Z-1)\alpha_{1,\rm rel}-\frac{20}{9Z^2}+\frac{25}{16Z^2}\right]\langle x^{-4}\rangle_{nL}-yh_2(nL)$$
$$+2y(Z-1)\Delta B_1(\phi_1)-(4\pm1)y\alpha^2\langle x^{-6}\rangle_{nL}-2yT_{nL}(J)+y^2\left[-\frac{5}{12}\left[\frac{\alpha Z(Z-1)}{n}\right]^2+4h_1(nL)\right]+(\delta E_{\rm RR})_{\rm X}\,. \tag{133}$$

The term $(\delta E_{\rm RR})_{\rm X}$ is introduced because of the term defined in Eq. (116) which was not included in the variational calculations. Thus the correct value is zero, but the variational calculations correspond to the value

$$(\delta E_{\rm RR})_{\rm X}=\tfrac{1}{6}y^2\left[\frac{\alpha Z(Z-1)}{n}\right]^2. \tag{134}$$

In other words, $(\delta E_{\rm RR})_{\rm X}\simeq 4.39/n^2$ kHz should be subtracted from the tabulated variational energies to make them asymptotically correct. This has no effect on $\Delta n=0$ transitions, and is otherwise negligible at current levels of accuracy. The sum $(\Delta E_{\rm RR})_M+(\Delta E_{\rm RR})_{\rm X}$ is asymptotically small and nearly independent of L for a given n, as expected from Eqs. (52) and (102).

$\Delta E_{\rm nuc}$ is the finite-nuclear-size correction given by

$$\Delta E_{\rm nuc}=\tfrac{2}{3}\pi Z(R/a_0)^2[\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle-Z^3/\pi]$$
$$\rightarrow\tfrac{2}{3}(R/a_0)^2\left[-\frac{31}{2Z^2}\langle x^{-4}\rangle_{nL}+\frac{1447}{16Z^4}\langle x^{-6}\rangle_{nL}\right], \tag{135}$$

where R is the rms nuclear radius. For ^{4}He, $R=1.673\pm0.001$ fm [49].

$\Delta E_{L,1}$ is the essentially one-electron part of the Lamb shift, including two-electron corrections to the Bethe logarithm and to the electron density at the nucleus. Goldman and Drake [6] have recently calculated the correction of order $\langle x^{-4}\rangle_{nL}$ in the asymptotic expansion of the Bethe logarithm due to the electric-field perturbation of the Rydberg electron on the Lamb shift of the 1s electron. For $L\geq 1$, the additional contribution to the energy is

TABLE XIII. Variational Q matrix elements (in units of $10^{-3}\alpha^3$ a.u.).

State	$Q(n\,^1L)$	$Q(n\,^3L)$	State	$Q(n\,^1L)$	$Q(n\,^3L)$
2S	5.406 997(6)	3.092 498 767 110(6)	5G	0.007 094 112 708(3)	0.007 094 109 818 41(4)
			6G	0.004 108 374 240 1(6)	0.004 108 371 038 98(3)
2P	3.374 496 4(9)	3.813 917 912(5)	7G	0.002 588 321 185 0(8)	0.002 588 318 434 03(5)
3P	0.997 136(3)	1.037 395 044(4)	8G	0.001 734 458 024 1(5)	0.001 734 455 813 1(2)
4P	0.421 013(2)	0.422 102 578(1)	9G	0.001 218 397 474(2)	0.001 218 395 729 76(4)
5P	0.215 756 4(2)	0.211 998 588 365(1)	10G	0.000 888 332 186(2)	0.000 888 330 808 35(9)
6P	0.124 953 24(9)	0.121 250 612 6(1)			
7P	0.078 735 46(2)	0.075 758 038(3)	6H	0.002 235 437 758 45(0)	0.002 235 437 755 820(1)
8P	0.052 772 0(1)	0.050 468 431(3)	7H	0.001 408 142 065 24(0)	0.001 408 142 061 610(2)
9P	0.037 078 02(8)	0.035 297 693 6(2)	8H	0.000 943 519 269 346(1)	0.000 943 519 265 740(3)
10P	0.027 038 9(4)	0.025 648 944 1(5)	9H	0.000 662 747 169 313(0)	0.000 662 747 166 06(5)
			10H	0.000 483 186 017 671(1)	0.000 483 186 014 925(1)
3D	0.205 966 01(1)	0.205 279 017 03(3)			
4D	0.087 663 07(7)	0.087 241 332 6(7)	7I	0.000 850 311 944 538(0)	0.000 850 311 944 532(6)
5D	0.045 054 99(3)	0.044 804 016 7(2)	8I	0.000 569 717 408 995(0)	0.000 569 717 408 993(0)
6D	0.026 125 08(1)	0.025 967 977 7(1)	9I	0.000 400 166 633 183(1)	0.000 400 166 633 180(1)
7D	0.016 470 86(7)	0.016 367 158 2(9)	10I	0.000 291 740 127 913(0)	0.000 291 740 127 910(1)
8D	0.011 042 15(4)	0.010 970 520 3(3)			
9D	0.007 758 99(1)	0.007 707 590 8(4)	8K	0.000 370 171 398 911(0)	0.000 370 171 398 911(0)
10D	0.005 658 19(1)	0.005 620 139 1(2)	9K	0.000 260 000 663 720(0)	0.000 260 000 663 720(0)
			10K	0.000 189 549 557(1)	0.000 189 549 559(2)
4F	0.029 888 962(1)	0.029 886 876 415(8)			
5F	0.015 339 669 3(5)	0.015 337 900 34(1)			
6F	0.008 888 452 9(2)	0.008 887 176 000(4)			
7F	0.005 601 647 51(1)	0.005 600 739 943(3)			
8F	0.003 754 498 3(3)	0.003 753 842 921(6)			
9F	0.002 637 778 2(5)	0.002 637 294 60(1)			
10F	0.001 923 392 4(5)	0.001 923 027 260(9)			

$$\Delta E_{L,\beta} = -\frac{4\alpha^3}{3Z^5}\langle \delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle 0.316\,26\langle x^{-4}\rangle_{nL}$$
$$\to -\frac{4\alpha^3}{3\pi Z^2}0.316\,26\langle x^{-4}\rangle_{nL}\ . \qquad (136)$$

For $L=1$, the value is taken to be $0.5\Delta E_{L,\beta}$ with $\pm 0.5\Delta E_{L,\beta}$ as the uncertainty. For $L>1$, the values are $\Delta E_{L,\beta}$ with $\pm 1.5\Delta E_{L,\beta}\langle x^{-6}\rangle_{nL}/\langle x^{-4}\rangle_{nL}$ as an estimate of the contribution from higher-order terms. This substantially reduces the previous theoretical uncertainties [4], which were taken to be 4% of $\Delta E_{L,1}$. Including this term, the full asymptotic expansion for $\Delta E_{L,1}$ is

$$\Delta E_{L,1} \to \frac{4\alpha^3 Z}{3\pi}\Bigg\{ \left(Z^3 - \tfrac{31}{2}Z^{-3}\langle x^{-4}\rangle_{nL} + \tfrac{1447}{16}Z^{-5}\langle x^{-6}\rangle_{nL}\right) \times \left[\ln(Z\alpha)^{-2} + \tfrac{19}{30} - \beta_{1s} - \left[\frac{Z-1}{Z}\right]^4 n^{-3}\beta_{nL} - 0.316\,26Z^{-6}\langle x^{-4}\rangle_{nL} + 2.296\pi\alpha Z + O(\alpha^2 Z^2) + yC_M\right]\Bigg\} - \Delta E_L(1s)\ , \qquad (137)$$

TABLE XIV. Variational matrix elements $\langle B_{3,Z}\rangle = b_{3,Z} + (\mu/M)b_{3,Z}$ (in units of $10^{-3}\alpha^2$ a.u.).

State	$b_{3,Z}(n\,^3L_L)$	$b^{X}_{3,Z}(n\,^3L_L)$	$b_{3,Z}(n\,^3L_L - n\,^1L_L)$	$b^{X}_{3,Z}(n\,^3L_L - n\,^1L_L)$
2*P*	−34.659 207 46(2)	−116.450 8(3)	−17.886 579 99(3)	9.162 33(5)
3*P*	−10.052 576 79(9)	−27.604 94(7)	−5.248 036 80(5)	3.712 21(6)
4*P*	−4.177 955 98(4)	−10.455 5(3)	−2.201 449 16(5)	1.675 1(1)
5*P*	−2.118 552 751(5)	−5.035 4(8)	−1.123 090 697 8(3)	0.878 8(5)
6*P*	−1.217 922 615(1)	−2.802 74(7)	−0.648 331 089 61(3)	0.514 11(3)
7*P*	−0.763 303 32(5)	−1.718 2(3)	−0.407 543 30(3)	0.325 8(1)
8*P*	−0.509 504 54(2)	−1.129(2)	−0.272 648 06(1)	0.219 1(6)
9*P*	−0.356 830 058 2(2)	−0.781 13(6)	−0.191 283 118(3)	0.154 110(4)
10*P*	−0.259 539 25(2)	−0.562 5(2)	−0.139 324 18(4)	0.112 46(5)
3*D*	−1.253 936 932(3)	−0.568 432(3)	−0.882 271 458(1)	0.418 403 043(9)
4*D*	−0.530 396 012 80(3)	−0.229 403(6)	−0.372 636 705 2(2)	0.175 223(3)
5*D*	−0.271 843 243(1)	−0.115 033 05(6)	−0.190 864 037 4(2)	0.089 422(2)
6*D*	−0.157 392 102(2)	−0.065 820(6)	−0.110 469 724(2)	0.051 657(6)
7*D*	−0.099 140 059 5(1)	−0.041 175(2)	−0.069 57052334(6)	0.032 500(4)
8*D*	−0.066 424 942 115(2)	−0.027 463 9(7)	−0.046 607 359 14(6)	0.021 760(3)
9*D*	−0.046 655 828 77(1)	−0.019 233 8(5)	−0.032 733 632 5(2)	0.015 278 9(1)
10*D*	−0.034 013 509 850(2)	−0.013 991 6(2)	−0.023 862 475 2(3)	0.011 133 369 3(1)
4*F*	−0.186 288 156 35(8)	−0.093 802 25(5)	−0.131 681 442 79(3)	0.065 366 845(7)
5*F*	−0.095 404 200 928(6)	−0.048 084 42(1)	−0.067 429 304 485(3)	0.033 429 09(2)
6*F*	−0.055 217 756 03(1)	−0.027 842 55(7)	−0.039 023 628 20(1)	0.019 333 992(8)
7*F*	−0.034 775 098 501(6)	−0.017 538 6(4)	−0.024 575 228 10(3)	0.012 171 0(2)
8*F*	−0.023 297 542 106(9)	−0.011 751 514(5)	−0.016 463 661 10(1)	0.008 151 918 5(9)
9*F*	−0.016 363 016 854(3)	−0.008 254 35(3)	−0.011 563 007 926 45(2)	0.005 724 550(6)
10*F*	−0.011 928 829 58(3)	−0.006 017 92(4)	−0.008 429 443 80(1)	0.004 172 80(2)
5*G*	−0.044 457 362 185(8)	−0.022 280 002(1)	−0.031 434 295 887(6)	0.015 686 016(7)
6*G*	−0.025 728 898 919(3)	−0.012 897 66(2)	−0.018 191 585 105 6(9)	0.009 075 4430(3)
7*G*	−0.016 202 894 306(3)	−0.008 123 68(3)	−0.011 456 060 115(2)	0.005 714 41(4)
8*G*	−0.010 854 849 186(3)	−0.005 442 831(1)	−0.007 674 711 800(2)	0.003 827 879(3)
9*G*	−0.007 623 785 564(1)	−0.003 822 959 4(4)	−0.005 390 212 644 8(2)	0.002 688 297 75(5)
10*G*	−0.005 557 777 132 4(8)	−0.002 787 064 52(5)	−0.003 929 471 556 8(4)	0.001 959 689 30(8)
6*H*	−0.014 030 321 600 04	−0.007 024 533 77	−0.009 920 791 601 46(2)	0.004 955 211 453(7)
7*H*	−0.008 835 535 551 7(3)	−0.004 423 990(6)	−0.006 247 537 331 2(4)	0.003 120 294 3(8)
8*H*	−0.005 919 164 886 8(3)	−0.002 963 890(9)	−0.004 185 377 073 9(4)	0.002 090 274(6)
9*H*	−0.004 157 239 529(1)	−0.002 081 715(3)	−0.002 939 530 152 0(8)	0.001 468 034(2)
10*H*	−0.003 030 637 776 9(4)	−0.001 517 604 0(4)	−0.002 142 920 068 8(2)	0.001 070 175 6(1)
7*I*	−0.005 339 807 865 6(1)	−0.002 672 816 3(2)	−0.003 775 796 540 13(8)	0.001 886 367 6(1)
8*I*	−0.003 577 269 284 2(1)	−0.001 790 628(2)	−0.002 529 494 425 01(8)	0.001 263 694 3(5)
9*I*	−0.002 512 437 436 7(1)	−0.001 257 638 89(9)	−0.001 776 547 148 04(8)	0.000 887 520 90(6)
10*I*	−0.001 831 570 275 6(3)	−0.000 916 832 4(1)	−0.001 295 103 928 6(2)	0.000 646 998 1(2)
8*K*	−0.002 325 176 073 824	−0.001 163 765 867 44	−0.001 644 144 756 049	0.000 821 466 788 10
9*K*	−0.001 633 048 129 96(1)	−0.000 817 358 79(3)	−0.001 154 736 437 90	0.000 576 938 038 50
10*K*	−0.001 190 493 400 44(2)	−0.000 595 858 9(1)	−0.000 841 803 331 98	0.000 420 585 7(1)

where the β_{nL} are hydrogen-atom Bethe logarithms [50], the term yC_M denotes finite-mass corrections [5,46–48], and $\Delta E_L(1s)$ is the $He^+(1s)$ Lamb shift which is subtracted. For $L \leq 3$, the asymptotic expansion represented by first group of terms in parentheses should be replaced by the correct matrix element $\langle \delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle$. For low-lying states, the corrections of relative $O(\alpha^2 Z^2)$ are also important, and are included in the calculations in a one-electron approximation as described in Ref. [5]. Equation (136) does not apply to S states. In this case, a $1/Z$ expansion is used instead for the Bethe logarithm [5,23,51,52]. Very accurate values for the $1\,^1S$ and $2\,^1S$ states have recently been calculated by Baker *et al.* [53].

Finally, $\Delta E_{L,2}$ denotes the Araki-Sucher electron-electron QED energy shift given by Eq. (118). The asymptotic expansion follows simply by inserting Eq. (119) for Q, and neglecting the $\langle \delta(\mathbf{r}_{12})\rangle$ terms.

The result of adding all the above contributions is summarized in Table XX for the states up to $n=10$ and $L=7$. A detailed listing of the individual terms in Eq. (125) is given in Ref. [5]. The $2\,^1S$ and $2\,^3S$ states are renormalized to the high-precision measurements of the $2\,^1S_0$-$n\,^1D_2$ [54] and $2\,^3S_1$-$n\,^3D_1$ [55] transition frequencies. The comparison with theory allows a precise determination of the S-state energies because the theoretical uncertainties are relatively much smaller for the D states

TABLE XV. Variational matrix elements $\langle B_{3,e}\rangle = b_{3,e}+(\mu/M)b^{X}_{3,e}$ (in units of $10^{-3}\alpha^2$ a.u.).

State	$b_{3,e}(n\,^3L_L)$	$b^X_{3,e}(n\,^3L_L)$	$b_{3,e}(n\,^3L_L - n\,^1L_L)$	$b^X_{3,e}(n\,^3L_L - n\,^1L_L)$
2*P*	51.478 075 56(4)	159.911 91(2)	−6.460 340 383(6)	5.340 187 27(2)
3*P*	14.697 663 101 9(3)	36.691 06(1)	−1.796 214 099(5)	1.774 3914(2)
4*P*	6.072 474 598(1)	13.723 36(4)	−0.739 628 814(2)	0.761 251(5)
5*P*	3.070 671 52(7)	6.566 6(1)	−0.374 132 216 5(2)	0.390 876(9)
6*P*	1.762 603 91(4)	3.640 28(1)	−0.214 986 917 2(7)	0.226 18(1)
7*P*	1.103 657 55(2)	2.225 5(2)	−0.134 769 320(4)	0.142 344(1)
8*P*	0.736 252 928 9467(4)	1.460(1)	−0.090 000 449(6)	0.095 25(5)
9*P*	0.515 422 689(3)	1.008 35(6)	−0.063 065 064(4)	0.066 87(1)
10*P*	0.374 782 01(8)	0.725 4(2)	−0.045 894 449(7)	0.048 71(1)
3*D*	10.877 615 241 1(9)	1.741 123(2)	−0.433 637 925 51(2)	0.425 325 98(6)
4*D*	0.794 033 195(3)	0.713 162(3)	−0.182 117 193 0(1)	0.178 131(2)
5*D*	0.406 931 042 4233(7)	0.360 153(6)	−0.093 032 955 0(2)	0.090 887 16(9)
6*D*	0.235 595 491 4(7)	0.206 878 6(8)	−0.053 768 264 3(1)	0.052 496 7(3)
7*D*	0.148 396 142(7)	0.129 704 0(2)	−0.033 831 935 5(2)	0.033 021(2)
8*D*	0.099 425 529(2)	0.086 63(2)	−0.022 652 083 0(2)	0.022 104 45(5)
9*D*	0.069 834 185(2)	0.060 728(1)	−0.015 902 947 9(3)	0.015 517 62(3)
10*D*	0.050 910 856(1)	0.044 218(2)	−0.011 589 829 1(3)	0.011 3064 757(3)
4*F*	0.279 250 206 049 5(4)	0.279 873 44(3)	−0.065 749 728 329(5)	0.065 604 96(2)
5*F*	0.142 976 294 47(3)	0.143 282 35(6)	−0.033 648 680 555(7)	0.033 571 08(2)
6*F*	0.082 739 646 27(2)	0.082 908 1(3)	−0.019 467 347 857(3)	0.019 421 76(4)
7*F*	0.052 103 367 16(4)	0.052 204 6(4)	−0.012 257 182 505(2)	0.012 228 3(1)
8*F*	0.034 904 632 45(2)	0.034 970(1)	−0.008 210 376 17(1)	0.008 191 06(7)
9*F*	0.024 514 300 91(9)	0.024 558 9(3)	−0.005 765 918 23(3)	0.005 752 381 2(6)
10*F*	0.017 870 713 95(4)	0.017 902 9(4)	−0.004 203 088 674(8)	0.004 193 25(3)
5*G*	0.066 678 518 297 69(2)	0.066 740 200 3404	−0.015 713 692 250 67(2)	0.015 701 551 8030
6*G*	0.038 587 085 852 6(4)	0.038 625 415 6(9)	−0.009 092 914 312 22(2)	0.009 085 836(1)
7*G*	0.024 299 646 815 6(4)	0.024 324 63(3)	−0.005 725 871 436 2(2)	0.005 721 425(5)
8*G*	0.016 278 795 107(1)	0.016 295 878(6)	−0.003 835 755 935 03(3)	0.003 832 795 9(6)
9*G*	0.011 433 072 245 1(1)	0.011 445 238(2)	−0.002 693 907 451 48(1)	0.002 691 840 1(3)
10*G*	0.008 334 680 076(2)	0.008 343 593 385(1)	−0.001 963 822 214 4(1)	0.001 962 325 8(1)
6*H*	0.002 1 044 897 027 262	0.021 056 652 4671	−0.004 960 127 672 240	0.004 957 556 4513
7*H*	0.013 252 773 943 91(1)	0.013 260 432 63(3)	−0.003 123 526 153 029	0.003 121 900 3041
8*H*	0.008 878 320 097 77(4)	0.008 883 551 4(3)	−0.002 092 492 807 42(1)	0.002 091 404 248 9
9*H*	0.006 235 523 424 2(9)	0.006 239 238 6(5)	−0.001 469 611 196 255	0.001 468 848 2(1)
10*H*	0.004 545 692 830 407(2)	0.004 548 422 6(2)	−0.001 071 339 154 86(2)	0.001 070 784 242(9)
7*I*	0.008 009 639 945 31(1)	0.008 013 352 5(1)	−0.001 887 865 368 769	0.001 887 015 196 56
8*I*	0.005 365 835 473 893	0.005 368 357 257 04	−0.001 264 715 866 287	0.001 264 145 133 18
9*I*	0.003 768 597 928 47(1)	0.003 770 384 30(5)	−0.000 888 246 909 51(0)	0.000 887 845 947(5)
10*I*	0.002 747 307 540 223(3)	0.002 748 617 03(2)	−0.000 647 530 040 294	0.000 647 237 86(1)
8*K*	0.003 487 751 991 873	0.003 489 261 703 51	−0.000 822 066 829 645	0.000 821 715 263 94
9*K*	0.002 449 560 245702	0.002 450 626 705 42	−0.000 577 362 748 041	0.000 577 115 568 21
10*K*	0.001 785 729 532 702	0.001 786 510 025 63	−0.000 420 896 827 379	0.000 420 716 574(8)

TABLE XVI. Variational matrix elements $\langle B_5 \rangle = b_5 + (\mu/M) b_5^X$ (in units of $10^{-3}\alpha^2$ a.u.).

State	$b_5(n\,^3L_L)$	$b_5^X(n\,^3L_L)$	State	$b_5(n\,^3L_L)$	$b_5^X(n\,^3L_L)$
$2P$	−22.520 165 85(1)	−54.068 86(1)	$5G$	−0.044 444 887 727 817(5)	−0.000 041 882 8(2)
$3P$	−6.157 504 600(1)	−11.639 505(4)	$6G$	−0.025 718 502 596 952(6)	−0.000 026 329(2)
$4P$	−2.509 269 934 6(1)	−4.236 54(1)	$7G$	−0.016 195 094 855 4(2)	−0.000 017 31(2)
$5P$	−1.261 112 06(2)	−1.996 16(4)	$8G$	−0.010 849 067 153 6(8)	−0.000 011 881 9(1)
$6P$	−0.721 53649(1)	−1.095 507(7)	$9G$	−0.007 619 452 487(2)	−0.000 008 476(2)
$7P$	−0.450 914 432(5)	−0.664 98(6)	$10G$	−0.005 554 474 955 2(9)	−0.000 006 235 532 7(6)
$8P$	−0.300 430 273 13(4)	−0.433 9(4)			
$9P$	−0.210 140 607 3(6)	−0.298 45(2)	$6H$	−0.014 029 355 809 429	−0.000 007 850 884 091
$10P$	−0.152 707 90(2)	−0.214 04(7)	$7H$	−0.008 834 661 831 84(1)	−0.000 005 122 7(6)
			$8H$	−0.005 918 459 627 55(3)	−0.000 003 502 03(3)
$3D$	−1.229 609 720 0(2)	−0.005 851(2)	$9H$	−0.004 156 685 020 9(2)	−0.000 002 490 2(1)
$4D$	−0.516 865 792(2)	−0.002 27872(2)	$10H$	−0.003 030 202 159 079(1)	−0.000 001 830 371 386
$5D$	−0.264 140 663 9(1)	−0.001 278(4)			
$6D$	−0.152 690 983 1(4)	−0.000 809(1)	$7I$	−0.005 339 689 422 330	−0.000 002 475 412 823
$7D$	−0.096 087 155(2)	−0.000 546 5(4)	$8I$	−0.003 577 156 428 906	−0.000 001 681 769 463
$8D$	−0.064 339 586 8(4)	−0.000 382 5(7)	$9I$	−0.002 512 341 431 804	−0.000 001 191 548 688
$9D$	−0.045 171 905 9(6)	−0.000 280(2)	$10I$	−0.001 831 491 336 303(3)	−0.000 000 865 984 456
$10D$	−0.032 921 672 9(4)	−0.000 213(2)			
			$8K$	−0.002 325 156 103 409	−0.000 001 002 917 144
$4F$	−0.185 960 647 706(7)	−0.000 584 26(2)	$9K$	−0.001 633 028 437 480	−0.000 000 711 005 402
$5F$	−0.095 166 933 47(2)	−0.000 343 8(2)	$10K$	−0.001 190 475 983 466	−0.000 000 517 636 417
$6F$	−0.055 057 905 123(9)	−0.000 212 20(3)			
$7F$	−0.034 665 731 39(2)	−0.000 138 4(7)			
$8F$	−0.023 220 452 22(4)	−0.000 094 6(6)			
$9F$	−0.016 307 021 32(9)	0.000 067 17(7)			
$10F$	−0.011 887 038 32(3)	−0.000 049 6(2)			

TABLE XVII. Variational matrix elements $\langle \Delta_3 \rangle$ (in units of $10^{-3}\alpha^2\mu/M$ a.u.).

State	$\Delta_3(n\,^3L_L)$	$\Delta_3(n\,^3L_L - n\,^1L_L)$	State	$\Delta_3(n\,^3L_L)$	$\Delta_3(n\,^3L_L - n\,^1L_L)$
$2P$	99.554 499 868(2)	−12.744 210 4(1)	$5G$	0.044 459 434 0(1)	−0.031 427 388 25(1)
$3P$	29.319 957 23(8)	−3.575 818 6(3)	$6G$	0.025 730 566(2)	−0.018 185 828(3)
$4P$	12.213 608(1)	−1.476 273 8(4)	$7G$	0.016 204 13(2)	−0.011 451 76(2)
$5P$	6.197 176 8(3)	−0.747 483 0(4)	$8G$	0.010 855 763(1)	−0.007 671 516(1)
$6P$	3.563 514 01(1)	−0.429 712 7(1)	$9G$	0.007 624 465(3)	−0.005 387 820(7)
$7P$	2.233 594(2)	−0.269 435 3(6)	$10G$	0.005 558 295 01(7)	−0.003 927 648 7(9)
$8P$	1.491 005(1)	−0.179 952 1(9)			
$9P$	1.044 261 22(2)	−0.126 107 52(4)	$6H$	0.014 030 498 9(1)	−0.009 920 255 78(2)
$10P$	0.759 557 5(6)	−0.091 777 03(8)	$7H$	0.008 835 693 6(1)	−0.006 247 052 27(3)
			$8H$	0.005 919 291 1(1)	−0.004 184 984 87(1)
$3D$	1.202 745 6(1)	−0.867 276 123(1)	$9H$	0.004 157 344(4)	−0.002 939 226(3)
$4D$	0.500 392 1(1)	−0.364 234 56(1)	$10H$	0.003 030 717(4)	−0.002 142 679(3)
$5D$	0.254 432 379 7(7)	−0.186 065 886(5)			
$6D$	0.146 663 787(5)	−0.107 535 9(2)	$7I$	0.005 339 830 1(2)	−0.003 775 730 82(2)
$7D$	0.092 135 78(3)	−0.067 663 66(5)	$8I$	0.003 577 290 415(2)	−0.002 529 431 806(1)
$8D$	0.061 624 2(4)	−0.045 304 3(2)	$9I$	0.002 512 455 080(5)	−0.001 776 493 658(4)
$9D$	0.043 231 9(1)	−0.031 806 12(3)	$10I$	0.001 831 585 4(3)	−0.001 295 060 5(1)
$10D$	0.031 490 27(2)	−0.023 179 76(2)			
			$8K$	0.002 325 179 85(1)	−0.001 644 133 661(9)
$4F$	0.186 290 136(2)	−0.131 499 464(2)	$9K$	0.001 633 051 862(1)	−0.001 154 725 509(1)
$5F$	0.095 399 44(2)	−0.067 297 36(2)	$10K$	0.001 190 496 48(3)	−0.000 841 793 51(2)
$6F$	0.055 212 61(4)	−0.038 934 70(2)			
$7F$	0.034 770 77(2)	−0.024 514 34(2)			
$8F$	0.023 294 13(2)	−0.016 420 718 1(6)			
$9F$	0.016 360 371(7)	−0.011 531 808 93(2)			
$10F$	0.011 926 768(8)	−0.008 406 16(2)			

TABLE XVIII. Convergence of the spin-dependent matrix elements $\langle 2\,^3P_1|B_i|2\,^3P_1\rangle$ for helium, and comparison with previous calculations (in units of $10^{-3}\alpha^2$ a.u.).

N[a]	$\langle B_{3,Z}\rangle$	$\langle B_{3,e}\rangle$	$\langle B_5\rangle$
104	−34.659 788 995	51.477 882 212	−2.252 033 317 7
145	−34.659 291 413	51.477 935 509	−2.252 018 835 8
197	−34.659 222 961	51.478 041 652	−2.252 016 877 8
264	−34.659 214 323	51.478 116 882	−2.252 018 058 4
342	−34.659 209 437	51.478 086 912	−2.252 016 979 3
436	−34.659 209 239	51.478 080 805	−2.252 016 769 5
539	−34.659 207 952	51.478 076 407	−2.252 016 615 6
658	−34.659 207 782	51.478 075 998	−2.252 016 600 7
724	−34.659 207 542	51.478 075 713	−2.252 016 590 5
804	−34.659 207 475	51.478 075 603	−2.252 016 586 8
Extrapolation	−34.659 207 456(19)	51.478 075 561(42)	−2.252 016 585 5(13)
Lewis and Serafino[b]	−34.659 107	51.476 434	−2.251 977
$\langle B_{3,Z}\rangle+\langle B_{3,e}\rangle$	16.818 868 105(46)		
Schwartz[c]	16.818 822(5)		−2.252 016 3(5)

[a]N is the number of terms in the doubled basis sets corresponding to $\Omega=4,5,\ldots,13$ in Table 2 of Ref. [5].
[b]Reference [31].
[c]Reference [43].

(±100 kHz or less, see the table).

Table XXI compares the spin-averaged energy shifts calculated variationally with those obtained entirely from the asymptotic expansions described above. This short table is of key importance because it establishes the degree of convergence of the asymptotic expansions, in addition to verifying the correctness of the much more elaborate variational matrix elements. The agreement to within 100 Hz for the K states indicates that the asymptotic expansions are substantially more accurate than ±100 Hz for the L and M states. For this reason, the variational calculations have not been pursued beyond the K states.

With the above results in hand, one can confidently take the asymptotic expansions as correct to better than ±100 Hz for the L and M states. The detailed results for the various contributions are presented in Table XXII in the same format as used previously for the variational calculations [5]. Note that the relatively large uncertainty from ΔE_{st} should not be included in the spin-averaged energy because it cancels on taking the average. The other uncertainties are common to all four components and so should only be included once in the spin average. It is useful to remember that, with the exception of ΔE_{st}, the singlet value for each quantity equals the spin-averaged value in the asymptotic limit.

Except for the higher-lying S states, Table XXII completes the tabulation of energies for all states of helium up to $n=10$. A paper on the S states is in preparation.

TABLE XIX. Values of R_M/n^2 (in MHz) for ^{4}He.

n	R_M/n^2
1	3 289 391 007.44(54)
2	822 347 751.86(13)
3	365 487 889.716(60)
4	205 586 937.965(34)
5	131 575 640.298(22)
6	91 371 972.429(15)
7	67 130 428.723(11)
8	51 396 734.491 3(84)
9	40 609 765.524 0(67)
10	32 893 910.074 4(54)
11	27 185 049.648 3(45)
12	22 842 993.107 2(37)

V. COMPARISON WITH EXPERIMENT

Reference [5] presents a detailed discussion of recent high-precision experiments, which will not be repeated here. In summary, measured singlet and triplet transition frequencies of the type 2S-2P, 2S-3P, and 2S-nD are in generally satisfactory agreement with theory at the ±2-MHz level of accuracy or better when the 2S states are renormalized to the values shown in Table XX. For the $2\,^3S_1$ state, the renormalization is 12.70±2.4 MHz, and, using the new Bethe logarithm of Baker *et al.* [53], the renormalization for the $2\,^1S_0$ state is only 0.75±0.15 MHz. The agreement is as good as can be expected, and further theoretical progress will require a complete evaluation of the $O(\alpha^4)$ QED contributions.

The one experiment requiring further discussion is the work of Hessels *et al.* [1] on the transition frequencies among the $n=10$ states of helium. As shown in Table XXIII, the differences between theory (including the $\Delta V''_{\rm ret}$ retardation correction) and experiment remain substantially larger than the $\Delta V''_{\rm ret}$ term listed separately in the table. Unfortunately, the new result for the 10L energy in Table XXI does not give a predicted $10K$-$10L$ transition frequency which fits the previous pattern of monotonically decreasing differences from experiment (although the experimental uncertainty is larger in this case). Since the theoretical uncertainties have now been markedly reduced with the evaluation of the $\Delta E_{L,\beta}$ term in Eq. (136), there does not appear to be a ready explanation for the differences. As a representative example of higher-order terms, the last column of Table XXIII lists contributions from the spin-averaged Dirac energies of order $\alpha^4(Z-1)^6$ given by

$$\Delta E_D^{(4)} = -\alpha^4(Z-1)^6 \left[\frac{L^{-2}+(L+1)^{-2}}{8n^3(2L+1)} + \frac{3}{8n^4 L(L+1)} - \frac{3}{4n^5(L+\frac{1}{2})} + \frac{5}{16n^6} \right] . \tag{138}$$

TABLE XX. Total calculated energies of helium, relative to $^4He^+(1s)$, in units of MHz. The quantity R_M/n^2 from Table XIX must be subtracted from the entries.

State	$E(n\,^1L_L)$	$E(n\,^3L_{L-1})$	$E(n\,^3L_L)$	$E(n\,^3L_{L+1})$
2S	−137 984 289.00(15)[a]		−330 494 992.7(2.4)[a]	
2P	7 638 599.5(1.8)	−53 730 894.1(1.8)	−53 760 517.5(1.8)	−53 762 811.0(1.8)
3P	2 699 920.4(6)	−16 622 013.8(6)	−16 630 129.1(6)	−16 630 788.5(6)
4P	1 189 726.7(3)	−7 071 103.4(3)	−7 074 411.0(3)	−7 074 680.8(3)
5P	620 098.18(13)	−3 627 803.20(13)	−3 629 465.46(13)	−3 629 601.02(13)
6P	362 161.73(8)	−2 100 069.37(8)	−2 101 020.39(8)	−2 101 097.90(8)
7P	229 301.10(5)	−1 322 158.07(5)	−1 322 752.38(5)	−1 322 800.79(5)
8P	154 147.04(3)	−885 357.65(3)	−885 753.61(3)	−885 785.85(3)
9P	108 519.09(2)	−621 517.79(2)	−621 794.75(2)	−621 817.29(2)
10P	79 244.730(17)	−452 874.336(17)	−453 075.597(17)	−453 091.976(17)
3D	−429 859.386(17)	−531 003.220(17)	−532 328.336(17)	−532 403.665(17)
4D	−196 997.901(10)	−255 609.936(10)	−256 165.167(10)	−256 201.188(10)
5D	−104 571.673(6)	−138 403.635(6)	−138 687.195(6)	−138 706.416(6)
6D	−61 683.435(3)	−82 468.176(3)	−82 632.057(3)	−82 643.402(3)
7D	−39 288.450(2)	−52 835.868(2)	−52 938.988(2)	−52 946.212(2)
8D	−26 513.662 7(15)	−35 788.758 3(16)	−35 857.803 4(16)	−35 862.677 3(16)
9D	−18 714.752 9(11)	−25 324.925 9(11)	−25 373.400 2(11)	−25 376.839 3(11)
10D	−13691.8482(17)	−18560.6844(12)	−18596.0123(12)	−18598.5276(12)
4F	−33 859.226 4(7)	−34 091.683 5(7)	−34 564.100 1(7)	−34 350.055 8(7)
5F	−19 401.232 6(5)	−19 554.966 3(6)	−19 779.472 4(6)	−19 687.185 4(6)
6F	−11 879.622 6(3)	−11 981.892 4(3)	−12 106.491 2(3)	−12 058.385 2(3)
7F	−7 729.848 7(3)	−7 799.850 0(2)	−7 876.357 2(2)	−7 848.011 3(2)
8F	−5 287.149 15(19)	−5 336.630 2(2)	−5 387.054 4(2)	−5 368.890 3(2)
9F	−3 765.993 97(14)	−3 802.040 09(12)	−3 837.062 79(12)	−3 824.695 34(12)
10F	−2 773.029 2(4)	−2 799.999 6(4)	−2 825.329 7(4)	−2 816.514 2(4)
5G	−4 679.864 28(16)	−4 730.677 94(17)	−4 889.250 25(17)	−4 806.192 06(17)
6G	−3 025.552 40(16)	−3 055.009 08(16)	−3 146.727 46(16)	−3 098.705 10(16)
7G	−2 027.239 2(2)	−2 045.813 3(3)	−2 103.548 8(3)	−2 073.328 6(3)
8G	−1 411.758 10(8)	−1 424.213 0(1)	−1 462.880 1(1)	−1 442.645 2(1)
9G	−1 017.683 7(1)	−1 026.437 33(7)	−1 053.588 52(7)	−1 039.382 47(7)
10G	−755.703 81(4)	−762.088 58(4)	−781.878 56(4)	−771.525 36(4)
6H	−968.203 6(2)	−989.404 9(1)	−1 049.121 6(1)	−1 017.818 1(1)
7H	−680.306 88(4)	−693.658 38(4)	−731.263 92(4)	−711.550 82(4)
8H	−487.099 45(5)	−496.044 04(6)	−521.236 63(6)	−508.030 38(6)
9H	−357.521 0(2)	−363.803 1(1)	−381.496 6(1)	−372.221 4(1)
10H	−268.842 54(5)	−273.422 27(5)	−286.320 72(5)	−279.559 15(5)
7I	−263.771 61(2)	−273.781 11(2)	−300.206 62(2)	−286.380 00(2)
8I	−197.463 24(2)	−204.168 86(2)	−221.871 84(2)	−212.609 07(2)
9I	−149.001 83(3)	−153.711 42(2)	−166.144 76(2)	−159.639 21(2)
10I	−114.173 95(1)	−117.607 25(1)	−126.671 14(1)	−121.928 59(1)
8K	−88.254 76(1)	−93.449 69(1)	−106.573 06(1)	−99.723 48(1)
9K	−69.582 60(1)	−73.231 18(1)	−82.448 13(1)	−77.637 45(1)
10K	−54.859 90(1)	−57.519 72(1)	−64.238 87(1)	−60.731 88(1)

[a]Renormalized to the $2S$-nD transition frequencies (see text).

TABLE XXI. Comparison of the variational and asymptotic results for the total spin-averaged energy shifts of helium (in units of MHz). The $(\delta E_{\mathrm{RR}})_{\mathrm{X}}$ term in Eq. (133) is included in the asymptotic values.

State	Variational	Asymptotic	Difference
$6H$	−1007.428 6(2)	−1007.440(2)	0.001(2)
$7H$	−705.008 29(4)	−705.013(7)	0.005(7)
$8H$	−503.647 46(5)	−503.651(8)	0.004(8)
$9H$	−369.143 2(2)	−369.146(7)	0.003(7)
$10H$	−277.315 12(5)	−277.318(6)	0.003(6)
$7I$	−281.519 41(2)	−281.519 5(3)	0.000 1(3)
$8I$	−209.352 87(2)	−209.353 0(2)	0.000 1(2)
$9I$	−157.352 30(3)	−157.352 4(2)	0.000 1(2)
$10I$	−120.261 44(1)	−120.261 6(2)	0.000 1(2)
$8K$	−97.209 37(1)	−97.209 39(6)	0.000 02(6)
$9K$	−75.871 72(1)	−75.871 73(5)	0.000 01(5)
$10K$	−59.444 66(1)	−59.444 67(4)	0.000 01(4)
$9L$		−39.722 87(1)	
$10L$		−32.268 75(1)	
$10M$		−18.648 443(3)	

The contributions are 2 orders of magnitude too small and of the wrong sign to account for the differences. Although a fully screened nuclear charge is used in the above, the corresponding terms of order $\alpha^2(Z-1)^4$ given by Eq. (63) are an excellent approximation to the correct ΔE_{rel}.

It is perhaps worth while to enquire what additional energy terms of the form $\langle x^{-j}\rangle_{nL}$ might be arbitrarily added to account for the discrepancies. Values of $j<3$ do not produce corrections which decrease fast enough with L, and values of $j>3$ produce intolerably large corrections for the low-lying states. For example, a term of the form $2.1\alpha^3\langle x^{-4}\rangle_{nL}$ a.u. would account for the discrepancies (except for the D-F and K-L transitions), but it also shifts the $2P$ and $3P$ states by 256 and 84 MHz, respectively. Although the polarization picture is of low accuracy for P states, at least the order of magnitude should be correct to within a factor of 2. For the case $j=3$, a term of the form $\alpha^3\langle x^{-3}\rangle_{nL}/(2\pi)$ is a possible candidate, but even this would produce shifts of 17 and 5 MHz, respectively, for the above P states. Such shifts would clearly disrupt the existing agreement between theory and experiment for the P states at the ± 2 MHz level, and it seems unlikely that higher-order QED terms would be large enough to compensate. For example, Eq. (138) with a screened nuclear charge is only $\Delta E_D^{(4)} \simeq -0.14$ MHz for the $2P$ state. In addition, a new contribution of the asymptotic form $\alpha^3\langle x^{-3}\rangle_{nL}$ would imply that the Araki-Sucher terms are incomplete, and a major readjustment of theory would be required.

VI. APPLICATION TO QUANTUM-DEFECT ANALYSIS

The $1/n^2$ terms contained in the asymptotic expansions (14) and (93) for $\varepsilon_M^{(2)}$ and $\langle B_1^{\mathrm{X}}+B_4^{\mathrm{X}}\rangle$ have important implications for the quantum-defect method widely used in the analysis of experimental data and extrapolations to the series limit [56]. In the quantum-defect method, the term energies for a Rydberg series of states is written in the form

$$T_n = -R_M(Z-1)^2/n^{*2} \tag{139}$$

where $n^* = n - \delta(n^*)$, and the quantum defect $\delta(n^*)$ is a slowly-varying function of n^* often expressed in the Ritz form

$$\delta = \delta_0 + \delta_2/(n-\delta)^2 + \delta_4/(n-\delta)^4 + \cdots \tag{140}$$

(see Drake and Swainson [57] for a recent discussion). The significant point is that the above functional form is valid for the fixed experimental value of R_M only if the leading term $-R_M(Z-1)^2/n^2$ fully accounts for the $1/n^2$ dependence of the T_n. This will only be true if the higher-order terms in $1/n^2$ are subtracted from T_n; i.e., T_n should be replaced by $T_n - \delta T_n$ where, from Eqs. (14) and (93),

$$\delta T_n = -R_M(Z-1)^2 y^2(1+\tfrac{5}{6}\alpha^2 Z^2)/n^{*2} . \tag{141}$$

Equivalently, if the quantum defect δ is small, one could define an effective Rydberg to be

$$\tilde{R}_M = R_M[1+y^2+\tfrac{5}{6}(y\alpha Z)^2] . \tag{142}$$

For ^{4}He, the correction factor is $1+1.879\,27\times 10^{-8}$, which is certainly significant at current levels of experimental precision of one or two parts in 10^{10} [54,58,59]. Without this adjustment, a quantum-defect fit may still appear to be adequate, but the higher-order terms in Eq. (140) will be abnormally large and loose their physical significance.

The physical significance of the $1+y^2$ correction is that the nucleus and inner electron can be thought of as a single composite particle with mass $M+m$. This increases the effective reduced mass for the Rydberg electron, and hence produces deeper binding. Note that for the variational calculations presented here, the coefficient $\frac{5}{6}$ in Eq. (142) should be replaced by $\frac{1}{2}$ as explained in connection with Eq. (116). Quantum-defect analyses of the total energies will be presented in a future publication [59].

VII. SUMMARY AND CONCLUSIONS

The results presented here complete the tabulation of nonrelativistic energies, and lowest-order relativistic and QED corrections for all states of helium up to $n=10$, with the exception of the higher-lying S states. The precision that has been achieved makes the helium spectrum up to $n=10$ as well understood as hydrogen for all practical purposes, at least in the nonrelativistic limit. As a consequence, helium now becomes a candidate for fundamental studies of higher-order QED effects in the same sense as hydrogen is, since the lowest-order terms can now be reliably subtracted from experimental data. The results for the $2\,^3P$ states are of special significance because of the possibility of determining α from the fine-structure splittings. Further work is in progress to determine the higher-order corrections to a similarly improved accuracy.

The comparison with the extended asymptotic expansions for the nonrelativistic and relativistic energies summarized in Table XXI clearly establishes the equivalence of the SAT and LRI pictures defined by Hessels *et al.* [1] in the limit of high L, provided that the $\Delta V''_{\rm ret}$ and $\Delta E_{L,1}$ terms are treated consistently in both pictures. For lower L, the differences are due entirely to the lack of convergence of the asymptotic expansions, rather than to a difference in physical content. The comparison also resolves questions raised [34] concerning the adequacy of the Breit operators used in SAT relative to those of LRI. With the addition of $\Delta V''_{\rm ret}$ to SAT, both are equally justified (or unjustified) in the high-L limit.

The other significant conclusion from Table XXI is that variational calculations need not be extended beyond $L=7$ because the asymptotic expansions provide more than sufficient precision for current levels of experimental accuracy. The detailed asymptotic results for L and M states are those listed in Table XXII.

Finally, the interpretation of the experimental results for transition frequencies among the $n=10$ in Table XXIII remains puzzling. The present result for the $10L$ state gives a predicted K-L transition frequency which appears to fall outside the pattern of deviations shown by the previous ones. In addition, it is difficult to arbitrarily add a new $\langle x^{-j}\rangle$ term to account for the discrepancies without disrupting the existing agreement between theory and experiment for the lower-lying states. Even the case $j=3$ leads to an implausibly large shift for the $2S$-$2P$ transitions. Perhaps future experiments on Rydberg states, especially a remeasurement of the least accurately

TABLE XXII. Contributions to the energies of ^{4}He, relative to He$^+(1s)$ in MHz.

Term	$9\ ^1L_8$	$9\ ^3L_7$	$9\ ^3L_8$	$9\ ^3L_9$
$\Delta E_{\rm nr}$	−30.712 304	−30.712 304	−30.712 304	−30.712 304
$\Delta E_{\rm M}^{(1)}$	−0.008 414	−0.008 414	−0.008 414	−0.008 414
$\Delta E_{\rm M}^{(2)}$	−0.763 037	−0.763 037	−0.763 037	−0.763 037
$\Delta E_{\rm rel}$	−8.235 266(9)	−6.232 928(9)	−8.431 574(9)	−9.640 416(9)
$\Delta E_{\rm anom}$	0.000 000	0.000 547	−0.000 911	0.000 384
$\Delta E_{\rm st}$	4.906 83(2)	0.000 000	−4.906 83(2)	0.000 000
$(\Delta E_{\rm RR})_{\rm M}$	−0.005 219	−0.006 252	−0.005 219	−0.004 403
$(\Delta E_{\rm RR})_{\rm X}$	0.004 225	0.004 709	0.004 279	0.003 795
$\Delta E_{\rm nuc}$	−0.000 001	−0.000 001	−0.000 001	−0.000 001
$\Delta E_{\rm L,1}$	−0.000 722(3)	−0.000 722(3)	−0.000 722(3)	−0.000 722(3)
$\Delta E_{\rm L,2}$	−0.002 128	−0.002 128	−0.002 128	−0.002 128
Total	−34.816 03(2)	−37.720 53(1)	−44.826 87(2)	−41.127 25(1)
Term	$10\ ^1L_8$	$10\ ^3L_7$	$10\ ^3L_8$	$10\ ^3L_9$
$\Delta E_{\rm nr}$	−24.178 633	−24.178 633	−24.178 633	−24.178 633
$\Delta E_{\rm M}^{(1)}$	−0.006 623	−0.006 623	−0.006 623	−0.006 623
$\Delta E_{\rm M}^{(2)}$	−0.618 060	−0.618 060	−0.618 060	−0.618 060
$\Delta E_{\rm rel}$	−7.462 659(8)	−6.002 954(8)	−7.605 767(8)	−8.487 013(8)
$\Delta E_{\rm anom}$	0.000 000	0.000 398	−0.000 664	0.000 280
$\Delta E_{\rm st}$	3.577 08(1)	0.000 000	−3.577 08(1)	0.000 000
$(\Delta E_{\rm RR})_{\rm M}$	−0.004 271	−0.005 025	−0.004 271	−0.003 677
$(\Delta E_{\rm RR})_{\rm X}$	0.003 607	0.003 960	0.003 646	0.003 293
$\Delta E_{\rm nuc}$	0.000 000	0.000 000	0.000 000	0.000 000
$\Delta E_{\rm L,1}$	−0.000 557(3)	−0.000 557(3)	−0.000 557(3)	−0.000 557(3)
$\Delta E_{\rm L,2}$	−0.001 551	−0.001 551	−0.001 551	−0.001 551
Total	−28.691 67(2)	−30.809 045(9)	−35.989 56(2)	−33.292 541(9)
Term	$10\ ^1M_9$	$10\ ^3M_8$	$10\ ^3M_9$	$10\ ^3M_{10}$
$\Delta E_{\rm nr}$	−12.727 808	−12.727 808	−12.727 808	−12.727 808
$\Delta E_{\rm M}^{(1)}$	−0.003 488	−0.003 488	−0.003 488	−0.003 488
$\Delta E_{\rm M}^{(2)}$	−0.618 059	−0.618 059	−0.618 059	−0.618 059
$\Delta E_{\rm rel}$	−5.297 028(3)	−4.152 161(3)	−5.399 463(3)	−6.131 145(3)
$\Delta E_{\rm anom}$	0.000 000	0.000 280	−0.000 475	0.000 204
$\Delta E_{\rm st}$	2.868 615(6)	0.000 000	−2.868 615(6)	0.000 000
$(\Delta E_{\rm RR})_{\rm M}$	−0.003 380	−0.003 975	−0.003 380	−0.002 898
$(\Delta E_{\rm RR})_{\rm X}$	0.002 715	0.002 995	0.002 743	0.002 462
$\Delta E_{\rm nuc}$	0.000 000	0.000 000	0.000 000	0.000 000
$\Delta E_{\rm L,1}$	−0.000 285(2)	−0.000 285(2)	−0.000 285(2)	−0.000 285(2)
$\Delta E_{\rm L,2}$	−0.001 110	−0.001 110	−0.001 110	−0.001 110
Total	−15.779 827(7)	−17.503 610(3)	−21.619 941(7)	−19.482 127(3)

TABLE XXIII. Comparison of theory (including $\Delta V''_{\mathrm{ret}}$) and experiment for the spin-averaged transition frequencies among the $n=10$ states of helium (in MHz).

Transition	Experiment	Theory	Difference	$\Delta V''_{\mathrm{ret}}$ [a]	$\Delta E_D^{(4)}$
D-F	14 560.651(34)[b]	14 560.652 3(18)	0.001(35)	−0.002 397	0.000 153
F-G	2 036.559 0(22)[c]	2 036.573 25(40)	−0.014 3(23)	−0.001 223	0.000 046
G-H	491.005 23(49)[c]	491.007 51(7)	−0.002 28(49)	−0.000 714	0.000 018
H-I	157.052 41(23)[c]	157.053 23(5)	−0.000 82(23)	−0.000 453	0.000 009
I-K	60.815 95(20)[c]	60.816 471(14)	−0.000 52(20)	−0.000 304	0.000 004
K-L	27.174 72(52)[c]	27.175 706(10)	−0.000 99(52)	−0.000 213	0.000 002

[a]Au and Mesa [11].
[b]Farley, MacAdam, and Wing [60] global fit.
[c]Hessels *et al.* [1].

known 10D-10F transition, will shed additional light on the subject, and ultimately lead to a confirmation of the Casimir-Polder effect.

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APPENDIX: ASYMPTOTIC RELATIONSHIPS AMONG SPIN-DEPENDENT RECOIL CORRECTIONS

This appendix derives a number of useful asymptotic relationships among the relativistic-recoil corrections to the spin-dependent terms in the Breit interaction. It also demonstrates that the same results can be obtained either by a direct perturbation calculation involving the mass-polarization operator, or by a transformation to Jacobi coordinates. The results are obtained in detail for $B_{3,Z}$ and Δ_3. An exactly parallel transformation to Jacobi coordinates gives the corresponding asymptotic limits for $B_{3,e}$ shown in Eqs. (106) and (107).

Applying the Jacobi transformation (3)–(5) to $B_{3,Z}$ yields immediately

$$B_{3,Z}=\frac{Z\alpha^2}{2}\left[\frac{1}{r^3}(\mathbf{r}\times\mathbf{p}_r)\cdot\mathbf{s}_1+\frac{1}{|\mathbf{x}+y\mathbf{r}|^3}(\mathbf{x}\times\mathbf{p}_x)\cdot\mathbf{s}_2\right]+\frac{Z\alpha^2}{2}y\left[-\frac{1}{r^3}(\mathbf{r}\times\mathbf{p}_x)\cdot\mathbf{s}_1+\frac{1}{x^3}(\mathbf{x}\times\mathbf{p}_x)\cdot\mathbf{s}_2\right], \tag{A1}$$

up to terms linear in $y=\mu/M$. With use of the expansion

$$\frac{1}{|\mathbf{x}+y\mathbf{r}|^3}=\frac{1}{x^3}\left[1-\frac{3y}{x^2}\mathbf{r}\cdot\mathbf{x}+\cdots\right] \tag{A2}$$

and $(\mathbf{r}\cdot\mathbf{x})_{\mathrm{av}}=0$, the first line of (A1) reduces to the lowest-order spin-orbit interaction, and the second line is the recoil correction $B_{3,Z}^{\mathrm{X}}$ linear in y. In the asymptotic approximation $x\gg r$, only the first term of the second line contributes. Comparison with Eq. (48) gives immediately

$$\Delta_3\to -2yB_{3,Z}^{\mathrm{X}} \tag{A3}$$

in conformity with the asymptotic limits displayed in Eqs. (106) and (107).

The alternative perturbation calculation proceeds as follows. Denoting the screened hydrogenic wave function for an infinite nuclear mass $1snL$ state by Ψ_{SH} and the mass-polarization correction by $\delta\Psi$, the recoil correction to $\langle B_{3,Z}\rangle$ is

$$\langle B_{3,Z}^{\mathrm{X}}\rangle=\langle\Psi_{\mathrm{SH}}|B_{3,Z}|\delta\Psi\rangle+\langle\delta\Psi|B_{3,Z}|\Psi_{\mathrm{SH}}\rangle\ , \tag{A4}$$

where, in terms of spectral representations,

$$\langle\delta\Psi|B_{3,Z}|\Psi_{\mathrm{SH}}\rangle=y\sum_{\substack{n',l'\\ n'',l''}}\frac{\langle\Psi_{\mathrm{SH}}|\mathbf{p}_1\cdot\mathbf{p}_2|n'l',n''l''\rangle\langle n'l',n''l''|B_{3,Z}|\Psi_{\mathrm{SH}}\rangle}{E(1s,nl)-E(n'l',n''l'')}\ . \tag{A5}$$

With use of

$$\mathbf{p}_r=i[h_r(Z),\mathbf{r}]\ , \tag{A6}$$

where $h_r(Z)$ is the one-electron Hamiltonian for the unscreened inner electron with coordinate $\mathbf{r}$ and

$$E(1s,nl)-E(n'l',n''l'')\simeq E(1s)-E(n'l') \tag{A7}$$

in the adiabatic approximation, the commutator approximately cancels the energy difference in the denominator of (A5). The sums over intermediate states can then be completed by closure. Combining the two terms in (A4) gives

$$\langle B_{3,Z}^{\mathrm{X}}\rangle=y\langle\Psi_{\mathrm{SH}}|[\mathbf{r}_1\cdot\nabla_2,B_{3,Z}]|\Psi_{\mathrm{SH}}\rangle\ . \tag{A8}$$

Evaluation of the commutator gives the final result

$$\langle B^{X}_{3,Z}\rangle=\tfrac{1}{2}Z\alpha^2 y\left\langle\Psi_{\rm SH}\left|-\frac{1}{r^3}(\mathbf{r}\times\mathbf{p}_x)\cdot\mathbf{s}_1+\frac{1}{x^3}(\mathbf{r}\times\mathbf{p}_x)\cdot\mathbf{s}_2\right.\right.$$

$$\left.\left.-\frac{3\mathbf{r}\cdot\mathbf{x}}{x^5}(\mathbf{r}\times\mathbf{p}_x)\cdot\mathbf{s}_2\right|\Psi_{\rm SH}\right\rangle \quad \text{(A9)}$$

in agreement with the corresponding terms from (A1) obtained from the Jacobi transformation.

The expectation value $\langle\Delta_3\rangle$ vanishes in any one-electron approximation because of the symmetry of the $\mathbf{r}\cdot\mathbf{p}_x$ operator. The leading nonvanishing contribution comes from perturbations to the screened hydrogenic wave function due to the dipole term

$$V_1=\frac{r}{x^2}\cos(\hat{\mathbf{r}}\cdot\hat{\mathbf{x}}) \quad \text{(A10)}$$

in Eq. (11). Denoting the wave-function correction by $\delta\Psi'$, the matrix element is

$$\langle\Delta_3\rangle=\langle\Psi_{\rm SH}|\Delta_3|\delta\Psi'\rangle+\langle\delta\Psi'|\Delta_3|\Psi_{\rm SH}\rangle\ , \quad \text{(A11)}$$

where, in parallel with Eq. (A5),

$$\langle\delta\Psi'|\Delta_3|\Psi_{\rm SH}\rangle =\sum_{\substack{n',l'\\ n'',l''}}\frac{\langle\Psi_{\rm SH}|V_1|n'l',n''l''\rangle\langle n'l',n''l''|\Delta_3|\Psi_{\rm SH}\rangle}{E(1s,nl)-E(n'l',n''l'')}\ . \quad \text{(A12)}$$

With use of

$$Z\frac{\mathbf{r}}{r^3}=i[\mathbf{p}_r,h_r(Z)] \quad \text{(A13)}$$

to replace the corresponding factors in the dominant r^{-3} part of Δ_3, the same steps as those leading to Eq. (A8) yield

$$\langle\Delta_3\rangle\to -i\alpha^2 y\langle\Psi_{\rm SH}|\mathbf{s}_1\cdot[\mathbf{p}_r\times\mathbf{p}_x,V_1]|\Psi_{\rm SH}\rangle \quad \text{(A14)}$$

in the adiabatic approximation. Evaluation of the commutator and discarding terms proportional to $\mathbf{r}\times\mathbf{p}_r$, $\mathbf{r}\times\mathbf{p}_x$, and $\mathbf{x}\times\mathbf{p}_r$ that vanish for $1snl$ states gives

$$\langle\Delta_3\rangle\to -\alpha^2\frac{\mu}{M}\left\langle\Psi_{\rm SH}\left|\frac{1}{x^3}(\mathbf{x}\times\mathbf{p}_x)\cdot\mathbf{s}_1\right|\Psi_{\rm SH}\right\rangle\ . \quad \text{(A15)}$$

Comparing with Eq. (34) and using $\mathbf{r}_1\simeq\mathbf{r},\mathbf{r}_2\simeq\mathbf{x}$, it is evident that for diagonal triplet matrix elements

$$\langle 1snl\,^3L|\Delta_3|1snl\,^3L\rangle \to -2Z^{-1}y\langle 1snl\,^3L|B_{3,Z}|1snl\,^3L\rangle\ , \quad \text{(A16)}$$

and for off-diagonal matrix elements

$$\langle 1snl\,^3L|\Delta_3|1snl\,^1L\rangle \to 2Z^{-1}y\langle 1snl\,^3L|B_{3,Z}|1snl\,^1L\rangle \quad \text{(A17)}$$

in agreement with Eqs. (106) and (107).

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