Helium energy levels including $m\alpha^6$ corrections

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The $m\alpha^6$ correction to energy is expressed in terms of an effective Hamiltonian $H^{(6)}$ for an arbitrary state of helium. Numerical calculations are performed for $n=2$ levels, and the previous result for the $2\,^3P$ centroid is corrected. While the resulting theoretical predictions for the ionization energy are in moderate agreement with experimental values for $2\,^3S_1$, $2\,^3P$, and $2\,^1S_0$ states, they are in significant disagreement for the singlet state 2^1P_1.

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High precision calculations of helium energy levels including relativistic and QED effects is a complicated task [1]. It has been recognized early on that the two-electron Dirac-Coulomb Hamiltonian is only an approximate Hamiltonian, as it includes negative energy spectra and does not account for magnetic and higher order interactions between electrons. The proper approach has to be based on quantum electrodynamic theory. For heavy few-electron ions the interactions between electrons can be treated perturbatively, on the same footing as the electron self-energy and vacuum polarization. Highly accurate results have been obtained for heavy helium- and lithium-like ions [2,3], and a convenient formulation of this $1/Z$ expansion has been introduced a few years ago by Shabaev in Ref. [4]. For systems with a larger number of electrons the zeroth order Hamiltonian will include an effective local potential to approximately account for interactions between electrons. This approach is being developed by Sapirstein *et al.* [5], and more recently by Shabaev and collaborators [6]. One of the most interesting results obtained so far was the calculation of QED corrections to parity violation in the cesium atom [6].

For light atomic systems relativistic and QED effects are only a small correction to the nonrelativistic Hamiltonian, and for this reason they can be treated perturbatively. More precisely, this perturbative approach relies on expansion of the binding energy in powers of the fine structure constant α,

$$E(\alpha) = E^{(2)} + E^{(4)} + E^{(5)} + E^{(6)} + E^{(7)} + O(\alpha^8), \tag{1}$$

where $E^{(n)}=m\alpha^n\mathcal{E}^{(n)}$ is a contribution of order α^n. However, this expansion is nonanalytic, inasmuch as some of the $\mathcal{E}^{(n)}$ coefficients contain $\ln\alpha$ [see, for example, Eq. (4)]. Each $\mathcal{E}^{(n)}$ can be expressed in terms of the expectation value of some effective Hamiltonian $H^{(n)}$ with the nonrelativistic wave function [7]. This approach allows for a consistent inclusion of all relativistic and QED effects order by order in α. We present in this work high precision calculations of $n=2$ energy levels in helium including the contribution $E^{(6)}$. This contribution has already been derived separately for triplet states in Refs. [8,9], and for singlet states in Refs. [10,11]. Here we obtain $H^{(6)}$ valid for all helium states, and present numerical results for $2\,^3S_1$, $2\,^3P$, 2^1S_0, and $2\,^1P_1$ energy levels.

The leading term in the expansion of the energy in powers of α, $\mathcal{E}^{(2)}=\mathcal{E}$, is the nonrelativistic energy, the eigenvalue of the nonrelativistic Hamiltonian, which in atomic units is

$$H^{(2)} \equiv H = \sum_a \left[\frac{\vec{p}_a^{\,2}}{2} - \frac{Z}{r_a}\right] + \sum_{a>b}\frac{1}{r_{ab}}. \tag{2}$$

The relativistic correction $\mathcal{E}^{(4)}$ is the expectation value of the Breit-Pauli Hamiltonian $H^{(4)}$ [12]

$$\begin{aligned}H^{(4)} = \sum_a \left\{-\frac{\vec{p}_a^{\,4}}{8} + \frac{\pi Z}{2}\delta^3(r_a) + \frac{Z}{4}\vec{\sigma}_a\cdot\frac{\vec{r}_a}{r_a^3}\times\vec{p}_a\right\} \\ + \sum_{a>b}\left\{\pi\delta^3(r_{ab}) - \frac{1}{2}p_a^i\left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i r_{ab}^j}{r_{ab}^3}\right)p_b^j\right. \\ + \frac{\sigma_a^i\sigma_b^j}{4r_{ab}^3}\left(\delta^{ij} - 3\frac{r_{ab}^i r_{ab}^j}{r_{ab}^2}\right) + \frac{1}{4r_{ab}^3}[2(\vec{\sigma}_a\cdot\vec{r}_{ab}\times\vec{p}_b \\ \left. - \vec{\sigma}_b\cdot\vec{r}_{ab}\times\vec{p}_a) + (\vec{\sigma}_b\cdot\vec{r}_{ab}\times\vec{p}_b - \vec{\sigma}_a\cdot\vec{r}_{ab}\times\vec{p}_a)]\right\}.\end{aligned} \tag{3}$$

$\mathcal{E}^{(5)}$ is the leading QED correction. Apart from the anomalous magnetic moment correction to the spin-orbit and spin-spin interactions, which we neglect here, as we consider singlet or spin-orbit averaged (centroid) levels, it includes the following terms [1]:

$$\begin{aligned}\mathcal{E}^{(5)} = \sum_{a>b}\left\langle\left[\frac{164}{15} + \frac{14}{3}\ln\alpha\right]\delta^3(r_{ab}) - \frac{7}{6\pi}\frac{1}{r_{ab}^3}\right\rangle \\ + \sum_a\left[\frac{19}{30} + \ln(\alpha^{-2}) - \ln k_0\right]\frac{4Z}{3}\langle\delta^3(r_a)\rangle,\end{aligned} \tag{4}$$

where

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$$\left\langle \frac{1}{r^3} \right\rangle \equiv \lim_{a\to 0} \int d^3r\,\phi^*(\vec r)\,\phi(\vec r)\left[\frac{1}{r^3}\Theta(r-a) + 4\pi\delta^3(r)\times(\gamma + \ln a)\right], \tag{5}$$

$$\ln k_0 = \frac{\left\langle \sum_a \vec p_a (H-\mathcal{E})\ln[2(H-\mathcal{E})]\sum_b \vec p_b \right\rangle}{2\pi Z\left\langle \sum_c \delta^3(r_c)\right\rangle}. \tag{6}$$

The next order contribution $\mathcal{E}^{(6)}$ is much more complicated. It can be represented in general as

$$\mathcal{E}^{(6)} = \langle H^{(6)}\rangle + \left\langle H^{(4)}\frac{1}{(\mathcal{E}-H)'}H^{(4)}\right\rangle, \tag{7}$$

but separate matrix elements of the first and the second term in the above are divergent. The spin dependent terms which contribute to fine structure are finite, and have been derived by Douglas and Kroll in Ref. [8]. These contributions are not included here because we consider spin-orbit averaged levels. The singularities of matrix elements in Eq. (7) can be eliminated by algebraic transformations [11] in a similar way for both singlet and triplet states. Therefore we extend the result obtained in Ref. [11] to arbitrary states of helium, and the contribution $\mathcal{E}^{(6)}$ can be represented as

$$\begin{aligned}
\mathcal{E}^{(6)} = \Bigg\langle & -\frac{\mathcal{E}^3}{2} + \left[\left(-\mathcal{E} + \frac{3}{2}\vec p_2^{\,2} + \frac{1-2Z}{r_2}\right)\frac{Z\pi}{4}\delta^3(r_1) + (1\leftrightarrow 2)\right] + \frac{\vec P^2}{6}\pi\delta^3(r) - \frac{(3+\vec\sigma_1\cdot\vec\sigma_2)}{24}\pi\vec p\,\delta^3(r)\vec p - \left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)\frac{\pi}{2}\delta^3(r)\\
&+\left(\frac{13}{12} + \frac{8}{\pi^2} - \frac{3}{2}\ln(2) - \frac{39\zeta(3)}{4\pi^2}\right)\pi\delta^3(r) + \frac{\mathcal{E}^2 + 2\mathcal{E}^{(4)}}{4r} - \frac{\mathcal{E}}{r^2}\frac{(31+5\vec\sigma_1\cdot\vec\sigma_2)}{32} - \frac{\mathcal{E}}{2r}\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right) + \frac{\mathcal{E}}{4}\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)^2 - \frac{1}{r^2}\left(\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{1}{r}\right)\\
&\times\frac{(23+5\vec\sigma_1\cdot\vec\sigma_2)}{32} - \frac{1}{4r}\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)^2 + \frac{Z^2}{2r_1r_2}\left(\mathcal{E} + \frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{r}\right) - Z\left(\frac{\vec r_1}{r_1^3} - \frac{\vec r_2}{r_2^3}\right)\cdot\frac{\vec r}{r^3}\frac{(13+5\vec\sigma_1\cdot\vec\sigma_2)}{64} + \frac{Z}{4}\left(\frac{\vec r_1}{r_1^3} - \frac{\vec r_2}{r_2^3}\right)\cdot\frac{\vec r}{r^2}\\
&-\frac{Z^2}{8}\frac{r_1^i}{r_1^3}\frac{(r^ir^j - 3\delta^{ij}r^2)}{r}\frac{r_2^j}{r_2^3} + \left[\frac{Z^2}{8}\frac{1}{r_1^2}\vec p_2^{\,2} + \frac{Z^2}{8}\vec p_1\frac{1}{r_1^2}\vec p_1 + \vec p_1\frac{1}{r^2}\vec p_1\frac{(47+5\vec\sigma_1\cdot\vec\sigma_2)}{64} + (1\leftrightarrow 2)\right] + \frac{1}{4}p_1^i\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)\frac{(r^ir^j + \delta^{ij}r^2)}{r^3}p_2^j\\
&+P^i\frac{(3r^ir^j - \delta^{ij}r^2)}{r^5}P^j\frac{(-3+\vec\sigma_1\cdot\vec\sigma_2)}{192} - \left[\frac{Z}{8}p_2^k\frac{r_1^i}{r_1^3}\left(\delta^{jk}\frac{r^i}{r} - \delta^{ik}\frac{r^j}{r} - \delta^{ij}\frac{r^k}{r} - \frac{r^ir^jr^k}{r^3}\right)p_2^j + (1\leftrightarrow 2)\right] - \frac{\mathcal{E}}{8}p_1^2p_2^2 - \frac{1}{4}p_1^2\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)p_2^2\\
&+\frac{1}{4}\vec p_1\times\vec p_2\frac{1}{r}\vec p_1\times\vec p_2 + \frac{1}{8}p_1^kp_2^l\left(-\delta^{jl}\frac{r^ir^k}{r^3} - \delta^{ik}\frac{r^jr^l}{r^3} + 3\frac{r^ir^jr^kr^l}{r^5}\right)p_1^ip_2^j\Bigg\rangle + E_{\rm sec} + E_{R1} + E_{R2} - \ln(\alpha)\pi\langle\delta^3(r)\rangle,
\end{aligned} \tag{8}$$

where $\vec P = \vec p_1 + \vec p_2$, $\vec p = (\vec p_1 - \vec p_2)/2$, $\vec r = \vec r_1 - \vec r_2$, and

$$E_{\rm sec} = \left\langle H_A'\frac{1}{(\mathcal{E}-H)'}H_A'\right\rangle + \left\langle H_B\frac{1}{(\mathcal{E}-H)'}H_B\right\rangle + \left\langle H_C\frac{1}{\mathcal{E}-H}H_C\right\rangle + \left\langle H_D\frac{1}{(\mathcal{E}-H)'}H_D\right\rangle. \tag{9}$$

The operators H_A', H_B, H_C, and H_D are parts of the $H^{(4)}$ Hamiltonian from Eq. (3), which was transformed [11] to eliminate singularities from second order matrix elements,

$$H_A' = -\frac{1}{2}(\mathcal{E}-V)^2 - p_1^i\frac{1}{2r}\left(\delta^{ij} + \frac{r^ir^j}{r^2}\right)p_2^j + \frac{1}{4}\vec\nabla_1^2\vec\nabla_2^2 - \frac{Z}{4}\frac{\vec r_1}{r_1^3}\cdot\vec\nabla_1 - \frac{Z}{4}\frac{\vec r_1}{r_1^3}\cdot\vec\nabla_1, \tag{10}$$

$$H_B = \left[\frac{Z}{4}\left(\frac{\vec r_1}{r_1^3}\times\vec p_1 + \frac{\vec r_2}{r_2^3}\times\vec p_2\right) - \frac{3}{4}\frac{\vec r}{r^3}\times(\vec p_1 - \vec p_2)\right]\frac{\vec\sigma_1 + \vec\sigma_2}{2}, \tag{11}$$

$$H_C = \left[\frac{Z}{4}\left(\frac{\vec r_1}{r_1^3}\times\vec p_1 - \frac{\vec r_2}{r_2^3}\times\vec p_2\right) + \frac{1}{4}\frac{\vec r}{r^3}\times(\vec p_1 + \vec p_2)\right]\frac{\vec\sigma_1 - \vec\sigma_2}{2}, \tag{12}$$

$$H_D = \frac{1}{4}\left(\frac{\vec\sigma_1\vec\sigma_2}{r^3} - 3\frac{\vec\sigma_1\cdot\vec r\,\vec\sigma_2\cdot\vec r}{r^5}\right), \tag{13}$$

where $\vec\nabla_1^2\,\vec\nabla_2^2$ in H_A' in Eq. (10) is understood as a differentiation of ϕ on the right-hand side as a function [omitting $\delta^3(r)$]. E_{R1} and E_{R2} are one- and two-loop electron self-energy and vacuum polarization corrections, respectively [10,11],

$$E_{R1} = Z^2\left[\frac{427}{96} - 2\ln(2)\right]\pi\langle\delta^3(r_1) + \delta^3(r_2)\rangle + \left[\frac{6\zeta(3)}{\pi^2} - \frac{697}{27\pi^2} - 8\ln(2) + \frac{1099}{72}\right]\pi\langle\delta^3(r)\rangle, \tag{14}$$

$$E_{R2} = Z\left[-\frac{9\zeta(3)}{4\pi^2} - \frac{2179}{648\pi^2} + \frac{3\ln(2)}{2} - \frac{10}{27}\right]\pi\langle\delta^3(r_1)+\delta^3(r_2)\rangle + \left[\frac{15\zeta(3)}{2\pi^2} + \frac{631}{54\pi^2} - 5\ln(2) + \frac{29}{27}\right]\pi\langle\delta^3(r)\rangle. \quad (15)$$

The higher order contribution $\mathcal{E}^{(7)}$ is known only to some approximation. Following Ref. [13] the hydrogenic values for one-, two-, and three-loop contributions [14] at order $m\alpha^7$ are extrapolated to helium, according to

$$\mathcal{E}^{(7)} = [\mathcal{E}^{(7)}(1S,\mathrm{He}^+) + \mathcal{E}^{(7)}(nX,\mathrm{He}^+)] \times \frac{\langle\delta^3(r_1)+\delta^3(r_2)\rangle_{\mathrm{He}}}{\langle\delta^3(r)\rangle_{1S,\mathrm{He}^+} + \langle\delta^3(r)\rangle_{nX,\mathrm{He}^+}} - \mathcal{E}^{(7)}(1S,\mathrm{He}^+) \quad (16)$$

for $X=S$, and for states with higher angular momenta $\mathcal{E}^{(7)}(nX,\mathrm{He}^+)$ is neglected.

We pass now to the calculation of matrix elements. The wave function is expressed in terms of explicitly correlated exponential functions ϕ_i,

$$\phi_i = e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12}} \pm (r_1 \leftrightarrow r_2), \quad (17)$$

$$\vec{\phi}_i = \vec{r}_1 e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12}} \pm (r_1 \leftrightarrow r_2), \quad (18)$$

with random α_i, β_i, γ_i [15]. This basis set is a very effective representation of the two-electron wave function, so much so that the nonrelativistic energies with 1500 basis functions are accurate to about 18 digits. Moreover, matrix elements of operators for relativistic and higher order corrections can all be obtained analytically in terms of rational, logarithmic and dilogarithmic functions, for example,

$$\frac{1}{16\pi^2}\int d^3r_1 \int d^3r_2 \frac{e^{-\alpha r_1 - \beta r_2 - \gamma r}}{r_1 r_2 r} = \frac{1}{(\alpha+\beta)(\beta+\gamma)(\gamma+\alpha)}. \quad (19)$$

Numerical results for matrix elements of $m\alpha^6$ operators with singlet and triplet P states are presented in Table I, due to the singularity of these operators we had to use octuple precision arithmetic. The $m\alpha^6$ correction to the energy also involves second order matrix elements E_{sec}. If we write

$$H'_A = Q_A, \quad (20)$$

$$H_B = \vec{Q}_B \cdot \vec{s}, \quad (21)$$

$$H_C = \vec{Q}_C \cdot \frac{(\vec{\sigma}_1 - \vec{\sigma}_2)}{2}, \quad (22)$$

$$H_D = Q_D^{ij} s^i s^j, \quad (23)$$

where $\vec{s}=(\vec{\sigma}_1+\vec{\sigma}_2)/2$, then one obtains for singlet states

$$E(2\,^1S_0)_{\mathrm{sec}} = \langle 2\,^1S|Q_A \frac{1}{\mathcal{E}-H} Q_A|2\,^1S\rangle + \langle 2\,^1S|Q_C^j \frac{1}{\mathcal{E}-H} Q_C^j|2\,^1S\rangle, \quad (24)$$

TABLE I. Expectation values of operators entering $H^{(6)}$ for the $2\,^1P_1$ and $2\,^3P$ centroid.

Operator	$2\,^1P_1$	$2\,^3P$
$4\pi\delta^3(r_1)$	16.014 493	15.819 309
$4\pi\delta^3(r)$	0.009 238	0.0
$4\pi\delta^3(r_1)/r_2$	3.934 080	4.349 766
$4\pi\delta^3(r_1)p_2^2$	3.866 237	4.792 830
$4\pi\delta^3(r)/r_1$	0.012 785	0.0
$4\pi\delta^3(r)P^2$	0.070 787	0.0
$4\pi\vec{p}\delta^3(r)\vec{p}$	0.0	0.077 524
$1/r$	0.245 024	0.266 641
$1/r^2$	0.085 798	0.094 057
$1/r^3$	0.042 405	0.047 927
$1/r_1^2$	4.043 035	4.014 865
$1/(r_1 r_2)$	0.491 245	0.550 342
$1/(r_1 r)$	0.285 360	0.317 639
$1/(r_1 r_2 r)$	0.159 885	0.198 346
$1/(r_1^2 r_2)$	1.063 079	1.196 631
$1/(r_1^2 r)$	1.002 157	1.109 463
$1/(r_1 r^2)$	0.105 081	0.121 112
$(\vec{r}_1\cdot\vec{r})/(r_1^3 r^3)$	0.010 472	0.030 284
$(\vec{r}_1\cdot\vec{r})/(r_1^3 r^2)$	0.043 524	0.075 373
$r_1^i r_2^j (r^i r^j - 3\delta^{ij} r^2)/(r_1^3 r_2^3 r)$	−0.004 745	0.090 381
p_2^2/r_1^2	1.127 058	1.410 228
$\vec{p}_1/r_1^2\vec{p}_1$	16.067 214	15.925 672
$\vec{p}_1/r^2\vec{p}_1$	0.190 797	0.279 229
$p_1^i(r^i r^j + \delta^{ij} r^2)/(r_1 r^3) p_2^j$	0.053 432	−0.097 364
$P^i(3r^i r^j - \delta^{ij} r^2)/r^5 P^j$	0.013 743	−0.060 473
$p_2^k r_1^i/r_1^3(\delta^{jk} r^i/r - \delta^{ik} r^j/r - \delta^{ij} r^k/r - r^i r^j r^k/r^3) p_2^j$	−0.039 975	0.071 600
$p_1^2 p_2^2$	0.973 055	1.198 492
$p_1^2/r_1 p_2^2$	3.102 248	3.883 404
$\vec{p}_1\times\vec{p}_2/r\,\vec{p}_1\times\vec{p}_2$	0.216 869	0.399 306
$p_1^k p_2^l(-\delta^{jl} r^i r^k/r^3 - \delta^{ik} r^j r^l/r^3 + 3r^i r^j r^k r^l/r^5) p_1^i p_2^j$	−0.126 416	−0.187 304

$$E(2\,^1P_1)_{\mathrm{sec}} = \langle 2\,^1P^i|Q_A \frac{1}{\mathcal{E}-H} Q_A|2\,^1P^i\rangle + \langle 2\,^1P^i|Q_C^j \frac{1}{\mathcal{E}-H} Q_C^j|2\,^1P^i\rangle, \quad (25)$$

and the contributions from H_B and H_D vanish. The result for the $2\,^3S_1$ state is

$$E(2\,^3S_1)_{\mathrm{sec}} = \langle 2\,^3S|Q_A \frac{1}{\mathcal{E}-H} Q_A|2\,^3S\rangle + \frac{2}{3}\langle 2\,^3S|Q_B^j \frac{1}{\mathcal{E}-H} Q_B^j|2\,^3S\rangle + \frac{1}{3}\langle 2\,^3S|Q_C^j \frac{1}{\mathcal{E}-H} Q_C^j|2\,^3S\rangle$$

TABLE II. Contributions to ionization energy $\mathcal{E}^{(6)}$ for $n=2$ states of the helium atom. E_Q is a sum of operators in Eq. (8), in comparison to Ref. [11] it includes the contribution E_H. E_{LG} is the logarithmic contribution, last term in Eq. (8). The sum $E_B+E_C+E_D$ of spin dependent, second order corrections for $2\,^3P$ centroid is taken from Ref. [18].

$m\alpha^6$	$2\,^1S$	$2\,^1P$	$2\,^3S$	$2\,^3P$
E_Q	12.287 491	12.236 966	13.052 109	11.963 305
E'_A	−16.280 186(10)	−16.084 034(5)	−17.189 809(10)	−15.848 510(2)
E_B	0.0	0.0	−0.018 722	
E_C	−0.033 790	0.201 363	−0.001 108	−0.168 704(2)
E_D	0.0	0.0	−0.003 848	
$-E_{\rm Dirac}(\mathrm{He}^+)$	4.000 000	4.000 000	4.000 000	4.000 000
Subtotal	−0.026 485(10)	0.354 296(5)	−0.161 377(10)	−0.053 908(3)
E_{R1}	2.999 960	0.106 839	3.625 397	−1.106 416
E_{R2}	0.016 860	0.000 112	0.032 331	−0.009 867
$E_{\rm LG}$	0.133 682	0.011 364	0.0	0.0
Total	3.124 017(10)	0.472 611(5)	3.496 351(10)	−1.170 191(3)

$$+\frac{1}{3}\langle 2\,^3S|Q_D^{ij}\frac{1}{\mathcal{E}-H}Q_D^{ij}|2\,^3S\rangle. \qquad (26)$$

The result for the $2\,^3P$ centroid, defined by

$$E(2\,^3P)=\tfrac{1}{9}[E(2\,^3P_0)+3E(2\,^3P_1)+5E(2\,^3P_2)], \qquad (27)$$

is

$$E(2\,P^3)_{\rm sec}=\langle 2\,^3P^i|Q_A\frac{1}{\mathcal{E}-H}Q_A|2\,^3P^i\rangle + \frac{2}{3}\langle 2\,^3P^i|Q_B^j\frac{1}{\mathcal{E}-H}Q_B^j|2\,^3P^i\rangle + \frac{1}{3}\langle 2\,^3P^i|Q_C^j\frac{1}{\mathcal{E}-H}Q_C^j|2\,^3P^i\rangle + \frac{1}{3}\langle 2\,^3P^i|Q_D^{jk}\frac{1}{\mathcal{E}-H}Q_D^{jk}|2\,^3P^i\rangle. \qquad (28)$$

Numerical results for second order matrix elements are presented in Table II. One notices a strong cancellation between $m\alpha^6$ contributions and the Dirac energy for the He^+ ion, the subtotal line in Table II. Because of this cancellation, the dominant contribution is the one loop radiative correction, with the exception of the $2\,^1P_1$ state, where the wave function at the nucleus happens to be very close to 16, the He^+ value, see Table I.

The summary of all important contributions to ionization energies is presented in Table III. We include the first and second order mass polarization correction to the nonrelativistic energy, as well as first order nuclear recoil corrections $\alpha^4 m^2/M$ and $\alpha^5 m^2/M$. We expect higher order terms in the

TABLE III. Contributions to ionization energy of $n=2$ helium states in MHz. Physical constants from [23], $R_\infty=10\,973\,731.568\,525(73)$ m^{-1}, $\alpha=1/137.035\,999\,11(46)$, $\lambda\!\!\!^{-}_e=386.159\,267\,8(26)$ fm, $m_\alpha/m_e=7294.299\,536\,3(32)$, $c=299\,792\,458$. $E_{\rm fs}$ is a finite nuclear size correction with the charge radius $r_\alpha=1.673$ fm.

	$\nu(2\,^1S)$	$\nu(2\,^1P)$	$\nu(2\,^3S)$	$\nu(2\,^3P)$
$\mu\alpha^2$	−960 331 428.61	−814 736 669.94	−1 152 795 881.77	−876 058 183.13
$\mu^2/M\alpha^2$	8 570.43	41 522.20	6 711.19	−58 230.36
$\mu^3/M^2\alpha^2$	−16.72	−20.80	−7.11	−25.33
$E_{\rm fs}$	1.99	0.06	2.59	−0.79
$m\alpha^4$	−11 971.45	−14 024.05	−57 629.31	11 436.88
$m^2/M\alpha^4$	−3.34	−2.81	4.28	11.05
$m\alpha^5$	2 755.76	38.77	3 999.43	−1 234.73
$m^2/M\alpha^5$	−0.63	1.91	−0.80	−0.62
$m\alpha^6$	58.29	8.82	65.24	−21.83
$m\alpha^7$	−3.85(1.90)	−0.16(16)	−5.31(1.00)	1.93(40)
$E_{\rm the}$	−960 332 038.13(1.90)	−814 709 145.99(16)	−1 152 842 741.56(1.00)	−876 106 246.93(40)
$E_{\rm exp}$	−960 332 040.86(15)	−814 709 153.0(3.0)	−1 152 842 742.97(0.06)	−876 106 247.35(6)

mass ratio to be much below the 0.01 MHz level, the precision of calculated contributions (see Table III). Results for nonrelativistic as well as for leading relativistic corrections are in agreement with those obtained previously by Drake [13,16]. Corrections of order $m\alpha^5$ were calculated using the Drake and Goldman [17] values for Bethe logarithms. The $m\alpha^6$ correction is calculated in this work. All but $m\alpha^7$ contributions are calculated exactly. This last one, $m\alpha^7$, is estimated on the basis of the hydrogenic value according to Eq. (16). It is the only source of uncertainty of theoretical predictions, as the achieved numerical precision for each correction is below 0.01 MHz.

The value for the $2\,^1S_0$ state has already been presented in our former work [11]; here we display in more detail all the contributions. The value for the $2\,^3S_1$ state is in agreement with our previous calculation in [9], where we obtained $\mathcal{E}^{(6)}=3.496\,93(50)$. This provides justification of the correctness of the obtained result, since the two derivations of the $m\alpha^6$ operators were performed in a different way. However, the result for the $2\,^3P$ state is in disagreement with our result from Ref. [18]. For this reason we checked Ref. [18], and found a mistake. The derived set of operators representing $\mathcal{E}^{(6)}$ was correct, but the expectation value of H'_{EN}, in the notation of Ref. [18], was in error. The correct result is $\langle H'_{EN}\rangle=11.903\,751$. With the second order matrix element $-15.838\,656(9)$ and subtracting He$^+$ $m\alpha^6$ energy $-Z^6/16$, it is equal to $0.049\,702(9)$, while the former result was $0.140\,689(9)$, see Table II of [18]. Together with other corrections from that table the total $m\alpha^6$ contribution becomes $-1.170\,188(9)$, in agreement with the result obtained here.

We find a moderate agreement with experimental ionization energies for the $2\,^1S_0$, $2\,^3S_1$, and $2\,^3P$ states but a significant disagreement for the $2\,^1P_1$ state. Following Ref. [13], the result for the $2\,^3S_1$ state was obtained by combining the $2\,^3S_1-3\,^3D_1$ measurement by Dorrer *et al.* [19] 786 823 850.002(56) MHz with the theoretical $3\,^3D_1$ ionization energy 366 018 892.97(2) MHz calculated by Drake [13,16]. The ionization energy of the $2\,^3P$ state was obtained from the measurement of the $2\,^3S_1-2\,^3P$ transition by Cancio *et al.* [20] of 276 736 495.6246(24) MHz and the previously obtained $2\,^3S_1$ ionization energy. The ionization energy of the $2\,^1S$ state was obtained from measurements of $2\,^1S-n\,^1D$ transitions by Lichten *et al.* [21] with $n=7-20$ and Drake's calculations for $n\,^1D$ states [13,16]. Finally, the result for $2\,^1P$ ionization energy is determined by combining the $2\,^1P-3\,^1D_2$ transition 448 791 404.0(30) MHz by Sansonetti and Martin [22] (including correction of 0.6 MHz [13]), with calculated [13,16] $3\,^1D_2$ energy 365 917 749.02(2) MHz. The significant disagreement with theoretical predictions for $2\,^1P$ state calls for an independent calculation of the $m\alpha^6$ term and, on the other hand, for the direct frequency measurement of $2\,^1P-3\,^1D_2$ or $2\,^1P-2\,^1S$ transitions.

Further improvement of theoretical predictions can be achieved by the calculation of $m\alpha^7$ contributions. The principal problem here will be the numerical evaluation of the relativistic corrections to Bethe-logarithms and the derivation of remaining operators. Such a calculation has recently been performed for helium fine structure [24]. Therefore, in view of newly proposed experiments [25], calculations for other states of helium, although not simple, can be achieved.

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