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

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Abstract

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 [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 [8, 9], and for singlet states in [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]

$$
\begin{aligned}
H^{(4)} \;=\; & \sum_a \biggl\{ -\frac{\vec p_a^{\,4}}{8} + \frac{\pi\, Z}{2}\, \delta^3(r_a) + \frac{Z}{4}\, \vec\sigma_a \cdot \frac{\vec r_a}{r_a^3} \times \vec p_a \biggr\} \\
& + \sum_{a>b} \biggl\{ \pi\, \delta^3(r_{ab}) - \frac{1}{2}\, p_a^i \left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i\, r_{ab}^j}{r_{ab}^3} \right) p_b^j + \frac{\sigma_a^i\, \sigma_b^j}{4\, r_{ab}^3} \left(\delta^{ij} - 3\, \frac{r_{ab}^i\, r_{ab}^j}{r_{ab}^2} \right) \\
& + \frac{1}{4\, r_{ab}^3} \Bigl[2 \left(\vec\sigma_a \cdot \vec r_{ab} \times \vec p_b - \vec\sigma_b \cdot \vec r_{ab} \times \vec p_a \right) + \left(\vec\sigma_b \cdot \vec r_{ab} \times \vec p_b - \vec\sigma_a \cdot \vec r_{ab} \times \vec p_a \right) \Bigr] \biggr\}\,. \qquad (3)
\end{aligned}
$$

$\mathcal{E}^{(5)}$ 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]

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

where

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

$$
\ln k_0 \;=\; \frac{\Bigl\langle \sum_a \vec p_a\, (H-\mathcal{E})\, \ln\bigl[2\,(H-\mathcal{E})\bigr]\, \sum_b \vec p_b \Bigr\rangle}{2\,\pi\, Z \Bigl\langle \sum_c \delta^3(r_c) \Bigr\rangle}. \qquad (6)
$$

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

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

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 [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 [11] to arbitrary states of helium, and the contribution $\mathcal{E}^{(6)}$ can be represented as

$$
\begin{aligned}
\mathcal{E}^{(6)} \;=\; & \biggl\langle -\frac{\mathcal{E}^3}{2} + \biggl[\biggl(-\mathcal{E} + \frac{3}{2}\,\vec{p}_2^{\,2} + \frac{1-2\,Z}{r_2}\biggr)\,\frac{Z\,\pi}{4}\,\delta^3(r_1) + (1\leftrightarrow 2)\biggr] \\
& + \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} - \biggl(\frac{Z}{r_1}+\frac{Z}{r_2}\biggr)\,\frac{\pi}{2}\,\delta^3(r) \\
& + \biggl(\frac{13}{12} + \frac{8}{\pi^2} - \frac{3}{2}\,\ln(2) - \frac{39\,\zeta(3)}{4\,\pi^2}\biggr)\,\pi\,\delta^3(r) + \frac{\mathcal{E}^2 + 2\,\mathcal{E}^{(4)}}{4\,r} \\
& - \frac{\mathcal{E}}{r^2}\,\frac{(31+5\,\vec{\sigma}_1\cdot\vec{\sigma}_2)}{32} - \frac{\mathcal{E}}{2\,r}\,\biggl(\frac{Z}{r_1}+\frac{Z}{r_2}\biggr) + \frac{\mathcal{E}}{4}\,\biggl(\frac{Z}{r_1}+\frac{Z}{r_2}\biggr)^2 \\
& - \frac{1}{r^2}\,\biggl(\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{1}{r}\biggr)\,\frac{(23+5\,\vec{\sigma}_1\cdot\vec{\sigma}_2)}{32} - \frac{1}{4\,r}\,\biggl(\frac{Z}{r_1}+\frac{Z}{r_2}\biggr)^2 \\
& + \frac{Z^2}{2\,r_1\,r_2}\,\biggl(\mathcal{E} + \frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{r}\biggr) - Z\,\biggl(\frac{\vec{r}_1}{r_1^3} - \frac{\vec{r}_2}{r_2^3}\biggr)\cdot\frac{\vec{r}}{r^3}\,\frac{(13+5\,\vec{\sigma}_1\cdot\vec{\sigma}_2)}{64} \\
& + \frac{Z}{4}\,\biggl(\frac{\vec{r}_1}{r_1^3} - \frac{\vec{r}_2}{r_2^3}\biggr)\cdot\frac{\vec{r}}{r^2} - \frac{Z^2}{8}\,\frac{r_1^i}{r_1^3}\,\frac{(r^i r^j - 3\,\delta^{ij}\,r^2)}{r}\,\frac{r_2^j}{r_2^3} \\
& + \biggl[\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)\biggr] \\
& + \frac{1}{4}\,p_1^i\,\biggl(\frac{Z}{r_1}+\frac{Z}{r_2}\biggr)\,\frac{(r^i\,r^j + \delta^{ij}\,r^2)}{r^3}\,p_2^j + P^i\,\frac{(3\,r^i\,r^j - \delta^{ij} r^2)}{r^5}\,P^j\,\frac{(-3+\vec{\sigma}_1\cdot\vec{\sigma}_2)}{192} \\
& - \biggl[\frac{Z}{8}\,p_2^k\,\frac{r_1^i}{r_1^3}\,\biggl(\delta^{jk}\,\frac{r^i}{r} - \delta^{ik}\,\frac{r^j}{r} - \delta^{ij}\,\frac{r^k}{r} - \frac{r^i\,r^j\,r^k}{r^3}\biggr)\,p_2^j + (1\leftrightarrow 2)\biggr] \\
& - \frac{\mathcal{E}}{8}\,p_1^2\,p_2^2 - \frac{1}{4}\,p_1^2\,\biggl(\frac{Z}{r_1}+\frac{Z}{r_2}\biggr)\,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^k\,p_2^l\,\biggl(-\delta^{jl}\,\frac{r^i\,r^k}{r^3} - \delta^{ik}\,\frac{r^j\,r^l}{r^3} + 3\,\frac{r^i\,r^j\,r^k\,r^l}{r^5}\biggr)\,p_1^i\,p_2^j\biggr\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

$$
\begin{aligned}
E_{\rm sec} \;=\; & \biggl\langle H'_A\,\frac{1}{(\mathcal{E}-H)'}\,H'_A\biggr\rangle + \biggl\langle H_B\,\frac{1}{(\mathcal{E}-H)'}\,H_B\biggr\rangle \\
& + \biggl\langle H_C\,\frac{1}{\mathcal{E}-H}\,H_C\biggr\rangle + \biggl\langle H_D\,\frac{1}{(\mathcal{E}-H)'}\,H_D\biggr\rangle
\end{aligned} \tag{9}
$$

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

$$H_A' = -\frac{1}{2}\,(\mathcal{E}-V)^2 - p_1^i\,\frac{1}{2\,r}\left(\delta^{ij}+\frac{r^i\,r^j}{r^2}\right)p_2^j + \frac{1}{4}\,\vec{\nabla}_1^2\,\vec{\nabla}_2^2 - \frac{Z}{4}\,\frac{\vec{r}_1}{r_1^3}\cdot\vec{\nabla}_1 - \frac{Z}{4}\,\frac{\vec{r}_1}{r_1^3}\cdot\vec{\nabla}_1 \quad (10)$$

$$H_B = \left[\frac{Z}{4}\left(\frac{\vec{r}_1}{r_1^3}\times\vec{p}_1+\frac{\vec{r}_2}{r_2^3}\times\vec{p}_2\right)-\frac{3}{4}\,\frac{\vec{r}}{r^3}\times(\vec{p}_1-\vec{p}_2)\right]\frac{\vec{\sigma}_1+\vec{\sigma}_2}{2}\,, \quad (11)$$

$$H_C = \left[\frac{Z}{4}\left(\frac{\vec{r}_1}{r_1^3}\times\vec{p}_1-\frac{\vec{r}_2}{r_2^3}\times\vec{p}_2\right)+\frac{1}{4}\,\frac{\vec{r}}{r^3}\times(\vec{p}_1+\vec{p}_2)\right]\frac{\vec{\sigma}_1-\vec{\sigma}_2}{2}\,, \quad (12)$$

$$H_D = \frac{1}{4}\left(\frac{\vec{\sigma}_1\,\vec{\sigma}_2}{r^3}-3\,\frac{\vec{\sigma}_1\cdot\vec{r}\,\vec{\sigma}_2\cdot\vec{r}}{r^5}\right). \quad (13)$$

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],

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

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

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

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

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 $\alpha_i, \beta_i, \gamma_i$ [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

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

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 $E_{\rm sec}$. If we write

$$H'_A = Q_A \tag{20}$$

$$H_B = \vec{Q}_B\cdot\vec{s} \tag{21}$$

$$H_C = \vec{Q}_C\cdot\frac{(\vec\sigma_1-\vec\sigma_2)}{2} \tag{22}$$

$$H_D = Q^{ij}_D\, s^i\, s^j \tag{23}$$

then one obtains for singlet states

$$E(2^1S_0)_{\rm sec} = \langle 2^1S|Q_A\,\frac{1}{\mathcal{E}-H}\,Q_A|2^1S\rangle + \langle 2^1S|Q^j_C\,\frac{1}{\mathcal{E}-H}\,Q^j_C|2^1S\rangle \tag{24}$$

$$E(2^1P_1)_{\rm sec} = \langle 2^1P^i|Q_A\,\frac{1}{\mathcal{E}-H}\,Q_A|2^1P^i\rangle + \langle 2^1P^i|Q^j_C\,\frac{1}{\mathcal{E}-H}\,Q^j_C|2^1P^i\rangle \tag{25}$$

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

$$\begin{aligned} E(2^3S_1)_{\rm sec} =\; & \langle 2^3S|Q_A\,\frac{1}{\mathcal{E}-H}\,Q_A|2^3S\rangle + \frac{2}{3}\,\langle 2^3S|Q^j_B\,\frac{1}{\mathcal{E}-H}\,Q^j_B|2^3S\rangle \\ & + \frac{1}{3}\,\langle 2^3S|Q^j_C\,\frac{1}{\mathcal{E}-H}\,Q^j_C|2^3S\rangle + \frac{1}{3}\,\langle 2^3S|Q^{ij}_D\,\frac{1}{\mathcal{E}-H}\,Q^{ij}_D|2^3S\rangle \end{aligned} \tag{26}$$

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

$$E(2^3P) = \frac{1}{9}\,\bigl[E(2^3P_0) + 3\,E(2^3P_1) + 5\,E(2^3P_2)\bigr] \tag{27}$$

is

$$\begin{aligned} E(2^3P)_{\rm sec} =\; & \langle 2^3P^i|Q_A\,\frac{1}{\mathcal{E}-H}\,Q_A|2^3P^i\rangle + \frac{2}{3}\,\langle 2^3P^i|Q^j_B\,\frac{1}{\mathcal{E}-H}\,Q^j_B|2^3P^i\rangle \\ & + \frac{1}{3}\,\langle 2^3P^i|Q^j_C\,\frac{1}{\mathcal{E}-H}\,Q^j_C|2^3P^i\rangle + \frac{1}{3}\,\langle 2^3P^i|Q^{jk}_D\,\frac{1}{\mathcal{E}-H}\,Q^{jk}_D|2^3P^i\rangle \end{aligned} \tag{28}$$

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
$r_1^i\,r_2^j\,(r^ir^j-3\,\delta^{ij}\,r^2)/(r_1^3\,r_2^3\,r)$	−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
$P^i\,(3\,r^i\,r^j-\delta^{ij}r^2)/r^5\,P^j$	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
$p_1^k\,p_2^l\,(-\delta^{jl}\,r^i\,r^k/r^3-\delta^{ik}\,r^j\,r^l/r^3+3\,r^i\,r^j\,r^k\,r^l/r^5)\,p_1^i\,p_2^j$	−0.126 416	−0.187 304

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 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	$-0.003\,848$	
$-E_{\rm Dirac}({\rm He}^+)$	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_{LG}	0.133 682	0.011 364	0.0	0.0
Total	$3.124\,017(10)$	$0.472\,611(5)$	$3.496\,351(10)$	$-1.170\,191(3)$

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 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

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}, $\alpha = 1/137.03599911(46)$, $\lambda\!\!\!^{-}_e = 386.1592678(26)$ fm, $m_\alpha/m_e = 7294.2995363(32)$, $c = 299792458$. $E_{\rm fs}$ 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	0.47	-0.80	-0.62
$m\,\alpha^6$	58.29	8.82	65.24	-21.83
$m\,\alpha^7$	$-3.85(1.90)$	$-0.16(16)$	$-5.31(1.00)$	$1.93(40)$
$E_{\rm the}$	$-960\,332\,038.13(1.90)$	$-814\,709\,147.44(16)$	$-1\,152\,842\,741.56(1.00)$	$-876\,106\,246.93(40)$
$E_{\rm exp}$	$-960\,332\,040.86(15)$	$-814\,709\,153.0(3.0)$	$-1\,152\,842\,742.97(0.06)$	$-876\,106\,247.35(6)$

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 [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 [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 [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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