Complete $m\,\alpha^6$ contribution to helium 2^3P_J energy

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Abstract. The complete calculation of the $m\,\alpha^6$ contribution to helium ionization energy of 2^3P_J states is presented. The result beyond the previously known radiative corrections amounts to 0.4046 MHz and significantly reduces theoretical uncertainties. The computational method is based on the effective Hamiltonian derived from relativistic quantum electrodynamic theory. The current status of theoretical predictions is summarized and comparison with latest experimental results is performed.

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1. Introduction

High precision calculation of atomic energy levels allows us, by comparison with measurements, to verify QED and our understanding of relativistic atomic structure. In heavy systems like cesium or francium very interesting weak interaction physics becomes visible through PNC (parity nonconservation) effects [1]. Precise knowledge of atomic structure, from one hand could determine nuclear properties like the weak charge or anapole moment, which are responsible for atomic PNC, but from the other hand, helps to search for appearance of electric dipole moment: the effect related to the violation of time reversal symmetry, the origin of which is not yet well understood. The common problem in the high precision atomic calculations is the inclusion of electron correlations and QED effects. Various computational methods, such as multi-configurational Dirac-Fock, configuration interaction, or many body perturbation theory and coupled cluster have been developed for many electron atoms [2]. In none of these methods have QED (Quantum Electrodynamics) effects been consistently included. In heavy few-electron ions the electron-electron interactions could be initially neglected and later incorporated as a small perturbation on the same footing as the QED effects. This treatment was shown to be very successful for the case of helium and lithium like heavy ions by Shabayev, Sapirstein, Mohr, Lindgren, Soff and others as well, see for example [3] and references therein. However, for atomic systems like helium, the electron-electron interaction is as important as the electron-nucleus one. Therefore the inclusion of relativistic, QED and electron correlation effects at the same time is necessary, which is a challenging computational problem. The formal solution employed the Bethe-Salpeter equation which was practically used only for positronium [4], the bound system of electron and positron. The solution for the case of light atomic systems was developed many years ago in the context of helium fine structure, i.e. the splitting between 2^3P_J levels, by Douglas and Kroll in [5]. While it is well known that leading relativistic effects are included in the Breit-Pauli Hamiltonian, the higher order relativistic effects could also be included through the use of some effective higher order Hamiltonian. Douglas and Kroll were first to derive higher order terms contributing to helium fine structure. It was generally believed the Breit-Pauli Hamiltonian could not be extended to higher order for arbitrary states because it leads to singular, divergent matrix elements. What has been shown recently is that these divergences cancel out between matrix elements of higher order effective Hamiltonian and the second order contribution from the Hamiltonian of lower order. This higher order effective Hamiltonian has already been derived for both triplet and singlet S states of helium in [6] and [7]. In this work we consider triplet P states. The effective Hamiltonian here is a sum of spin independent terms which are the same as for triplet S-states and spin dependent one, which were derived by Douglas and Kroll in their original work [5]. They include relativistic and QED effects as well, and therefore lead to the complete correction to energy of order of $m\,\alpha^6$. All lower order terms, including leading QED effects as anomalous electron magnetic moment or Bethe-log have already been calculated with sufficiently high precision [8, 9]. In this work we follow closely a similar calculation of the $m\,\alpha^6$ correction to the ionization energy of 2^3S_1 [10] and calculate this correction for 2^3P_J states. In the next section we present these effective operators in a form suitable for numerical calculations. Next, we explain numerical methods and present results for matrix elements. A summary, comparison with experiments, and brief concluding remarks are left to the very end.

2. Effective Hamiltonian

The idea of the effective Hamiltonian approach for the calculation of bound state energies relies on the replacement of Hamiltonian of the complete quantum electrodynamics with a simplified Hamiltonian H_{EF} which acts only in the subspace of few-particle states with all momenta being of the order of the inverse of the size of the bound state [6]. This new simplified Hamiltonian depends on an artificial parameter λ which preserves finiteness of matrix elements. The particular form of this regularization does not play a role, since all divergences cancel out algebraically, and therefore we will not write it explicitly. H_{EF} is obtained by an expansion of the resolvent in the electron-nucleus and electron-electron interactions up to third order and by an expansion in momenta. It has the general form

$$H_{EF} = H_0 + H^{(4)} + H^{(5)} + H^{(6)}\,, \tag{1}$$

where H_0 is a nonrelativistic Hamiltonian for helium in the nonrecoil limit

$$H_0 = \frac{p_1^2}{2\,m} + \frac{p_2^2}{2\,m} - \frac{Z\,\alpha}{r_1} - \frac{Z\,\alpha}{r_2} + \frac{\alpha}{r}\,, \tag{2}$$

and $\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2$. $H^{(4)}$ is the leading relativistic Breit Hamiltonian and $H^{(5)}, H^{(6)}$ are higher order corrections in $m\,\alpha^5$ and $m\,\alpha^6$ orders respectively. The correction to the energy in the order $m\,\alpha^6$ can be written as

$$E^{(6)} = \left\langle \phi \left| H^{(4)} \frac{1}{(E_0 - H_0)'} H^{(4)} \right| \phi \right\rangle + \langle \phi | H^{(6)} | \phi \rangle \,. \tag{3}$$

where prime in the denominator means the exclusion of the state ϕ in the operator inversion. The Breit Hamiltonian $H^{(4)}$, neglecting terms proportional to $\delta^3(r)$, which vanish for triplet states, is, in atomic units,

$$H^{(4)} = H_{NF} + H_{FS} \,, \tag{4}$$

$$H_{NF} = -\frac{1}{8}(p_1^4 + p_2^4) + \frac{Z\,\pi}{2}[\delta^3(r_1) + \delta^3(r_2)] - \frac{1}{2} p_1^i \left(\frac{\delta^{ij}}{r} + \frac{r^i\,r^j}{r^3}\right) p_2^j \,, \tag{5}$$

$$\begin{aligned} H_{FS} = {} & \left[\frac{Z}{4}\left(\frac{\boldsymbol{r}_1}{r_1^3} \times \boldsymbol{p}_1 + \frac{\boldsymbol{r}_2}{r_2^3} \times \boldsymbol{p}_2\right) - \frac{3}{4}\frac{\boldsymbol{r}}{r^3} \times (\boldsymbol{p}_1 - \boldsymbol{p}_2)\right] \frac{\boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2}{2} \\ & + \left[\frac{Z}{4}\left(\frac{\boldsymbol{r}_1}{r_1^3} \times \boldsymbol{p}_1 - \frac{\boldsymbol{r}_2}{r_2^3} \times \boldsymbol{p}_2\right) + \frac{1}{4}\frac{\boldsymbol{r}}{r^3} \times (\boldsymbol{p}_1 + \boldsymbol{p}_2)\right] \frac{\boldsymbol{\sigma}_1 - \boldsymbol{\sigma}_2}{2} \\ & + \frac{1}{4}\left(\frac{\boldsymbol{\sigma}_1\,\boldsymbol{\sigma}_2}{r^3} - 3\,\frac{\boldsymbol{\sigma}_1\cdot\boldsymbol{r}\,\boldsymbol{\sigma}_2\cdot\boldsymbol{r}}{r^5}\right) \,. \end{aligned} \tag{6}$$

The corresponding correction to the energy at order $m\,\alpha^6$ is

$$E_{NF} = \langle H_{NF} \frac{1}{(E_0 - H_0)'} H_{NF} \rangle \,, \tag{7}$$

$$E_{FS} = \langle H_{FS} \frac{1}{(E_0 - H_0)'} H_{FS} \rangle + 2\,\langle H_{NF} \frac{1}{(E_0 - H_0)'} H_{FS} \rangle \,. \tag{8}$$

The expression for $H^{(6)}$ is much more complex. It consists of electron–nucleus terms, electron–electron terms, and the radiative correction. The spin dependent part, as we have already mentioned, was derived by Douglas and Kroll in [5]. Their calculation was verified in a different approach by Zhang in [11] and us in [12]. Corresponding matrix elements were calculated by many groups and the most recent results are published in [13, 14]. The spin independent terms are the same as for n^3S_1 states, and are of form:

$$H^{(6)} = H_{EN}(1) + H_{EN}(2) + H_V + H_{RC1} + H_{RC2} \,, \tag{9}$$

where

$$H_{EN}(i) = \frac{p_i^6}{16} - \frac{1}{8}\left[\boldsymbol{p}_i; \frac{Z}{r_i}\right]^2 - \frac{5}{128}\left[p_i^2; \left[p_i^2; \frac{Z}{r_i}\right]\right] - \frac{3}{32} p_i^2 \left[\boldsymbol{p}_i; \left[\boldsymbol{p}_i; \frac{Z}{r_i}\right]\right] , \tag{10}$$

$$\begin{aligned} H_V = {} & \frac{13}{12\,r^4} - \frac{11}{36}\pi\nabla^2\delta^3(r) - \frac{5\,Z}{12}\frac{\boldsymbol{r}}{r^3}\left(\frac{\boldsymbol{r}_1}{r_1^3} - \frac{\boldsymbol{r}_2}{r_2^3}\right) \\ & + \frac{1}{4}(p_1^2 + p_2^2)\,p_1^i \left(\frac{\delta^{ij}}{r} + \frac{r^i\,r^j}{r^3}\right) p_2^j + \frac{23}{48} p_1^i \left(\frac{\delta^{ij}}{r^3} - 3\,\frac{r^i\,r^j}{r^5}\right) p_1^j \\ & - \frac{3}{16} p_1^i \left(\frac{\delta^{ij}}{r^3} - 3\,\frac{r^i\,r^j}{r^5}\right) p_2^j + \frac{1}{4} p_1^i \left(\frac{\delta^{ij}}{r^2} + 3\,\frac{r^i\,r^j}{r^4}\right) p_1^j \\ & - \left\{\frac{1}{8}[p_1^i\,;\,H_0]\left(\frac{r^i\,r^j}{r} - 3\,\delta^{ij}\,r\right)[H_0\,;\,p_2^j] \right. \end{aligned}$$

$$
\begin{aligned}
&+\frac{1}{16}\,[p_1^i\,;\,H_0]\left[p_2^2\,;\,\frac{r^i\,r^j}{r}-3\,\delta^{ij}\,r\right]p_2^j \\
&+\frac{1}{16}\,p_1^i\left[\frac{r^i\,r^j}{r}-3\,\delta^{ij}\,r\,;\,p_1^2\right][H_0\,;\,p_2^j] \\
&+\frac{1}{32}\,p_1^i\left[p_2^2\,;\left[\frac{r^i\,r^j}{r}-3\,\delta^{ij}\,r\,;\,p_1^2\right]\right]p_2^j\Big\}\,, \qquad (11)
\end{aligned}
$$

$$
H_{RC1} = \pi\,Z^2\left(\frac{139}{32}-2\,\ln(2)+\frac{5}{48}\right)[\delta^3(r_1)+\delta^3(r_2)]\,, \qquad (12)
$$

$$
H_{RC2} = \frac{Z}{\pi}\left(-\frac{4358}{1296}-\frac{10}{27}\,\pi^2+\frac{3}{2}\,\pi^2\,\ln(2)-\frac{9}{4}\,\zeta(3)\right)[\delta^3(r_1)+\delta^3(r_2)]. \qquad (13)
$$

These effective operators have been originally derived in [6] and presented in this form in [10]. As they stand, they are valid for any triplet state of helium. An additional transformation is required for E_{NF} and H_{EN}, since both of these terms are divergent, but in such a way that this divergence cancels out in the sum. Let us define new Hamiltonians H'_{NF} and H'_{EN} with $\delta V = (\frac{Z}{r_1}+\frac{Z}{r_2})/4$:

$$
H'_{NF} = H_{NF}-\delta V\,(H_0-E_0)-(H_0-E_0)\,\delta V\,, \qquad (14)
$$

$$
\begin{aligned}
H'_{EN} &= H_{EN}(1)+H_{EN}(2)-\delta V\,(E_0-H_0)\,\delta V \\
&\quad+\delta V\,H_A+H_A\,\delta V-2\,\delta V\,\langle H_A\rangle\,. \qquad (15)
\end{aligned}
$$

The correction to the energy

$$
E'_{NF} = \langle H'_{NF}\,\frac{1}{(E-H)'}\,H'_{NF}\rangle+\langle H'_{EN}\rangle \qquad (16)
$$

is finite for separate terms and equal to the original expression $E_{NF}+\langle H_{EN}(1)+H_{EN}(2)\rangle$.

3. Numerical calculation of matrix elements

Analogous numerical calculations have been performed for helium fine structure in [13, 14], ionization energy of 2^3S_1 state in [10] and 1^1S_0 ground state in [7]. We use here a similar basis set, which was developed by Korobov in [15] of exponential functions of the form

$$
\boldsymbol{\phi}(r_1,r_2,r)=\sum_i v_i[\boldsymbol{r}_1\,e^{-\alpha_i r_1-\beta_i r_2-\gamma_i r}-(r_1\leftrightarrow r_2)], \qquad (17)
$$

where α_i, β_i and γ_i are obtained according to:

$$
\begin{aligned}
\alpha &= A_2\,X+A_1 \\
\beta &= B_2\,Y+B_1 \\
\gamma &= C_2\,Z+C_1 \qquad (18)
\end{aligned}
$$

and X, Y, Z are independent pseudo random numbers with uniform distribution in the range $\langle 0,1\rangle$. The parameters A_i, B_i, C_i are determined by minimization of the energy of the state of interest. In order to obtain a more precise wave function we used double basis set of the form (17) with different parameters A_i, B_i, C_i to account for electron correlations at small distances. The coefficients v_i in Eq. (17) form a vector v which is a solution of the generalized eigenvalue problem

$$\hat{H} v = E \hat{N} v, \tag{19}$$

where $\hat{H}$ is a matrix of the Hamiltonian in this basis set, $\hat{N}$ is a normalization matrix, and E an eigenvalue, the energy of the state corresponding to v. For the solution of the eigenvalue problem with a typical value of $N = 1200$ we used an inverse iteration method with standard LU decomposition, however in nonstandard quadruple or sixtuple precision arithmetic [16]. As a result for the nonrelativistic energy of helium 2^3P state in the nonrecoil limit we got

$$E(2^3P) = -2.133\,164\,190\,779\,283\,19(1)\,. \tag{20}$$

The calculation of all matrix elements can be performed with the use of one formula:

$$\frac{1}{16\,\pi^2}\int d^3r_1 \int d^3r_2\,\frac{e^{-\alpha r_1-\beta r_2-\gamma r}}{r_1\,r_2\,r} = \frac{1}{(\alpha+\beta)(\beta+\gamma)(\gamma+\alpha)}. \tag{21}$$

The result with any additional r in the numerator can be obtained by differentiation with respect to the corresponding parameter α, β or γ. Any additional r in the denominator can be obtained by integration with respect to its associated parameter. This leads to the appearance of logarithmic and dilogarithmic functions. It is the advantage of this basis set, that matrix elements could be easily calculated algebraically. Having algebraic expression which sometimes is pretty large, the numerical computation requires the use of at least quadruple arithmetic due to numerical instabilities in calculating long rational expressions. With the exception of the term in braces in Eq. (11), all matrix elements in H_V were calculated as described above. That term in braces was too complicated for the analytic calculation of matrix element. Instead, we calculated the r_i integrals numerically using Gaussian method. The resulting precision was only a few digits less with comparison to the analytic integration.

Much more computationally intensive were second order corrections. The spin dependent part E_{FS} have been calculated previously and we rewrite in Table 1 results as presented in [14] (although in different units). The spin independent part E'_{NF} in Eq. (16) requires a special treatment. From the state $H'_{NF}|\phi\rangle$ one projects out anything parallel to ϕ. Then, a prime in the reduced resolvent $1/(H_0-E_0)'$ could be dropped and inversion of $H_0 - E_0$ is performed in the similar basis set as for the 2^3P wave function, but with well optimized distribution of parameters α, β, and γ. Due to singularity of H'_{NF} we used the quadruple basis set. The first one had uniform distribution as in Eq. (18). The second one was:

$$\begin{aligned}
\alpha &= A_2\,(X^{-5}-1) + A_1\\
\beta &= B_2\,Y + B_1\\
\gamma &= C_2\,Z + C_1
\end{aligned} \tag{22}$$

The third and fourth basis sets are given by analogous formulas. This strongly nonuniform distribution toward very large values of α, β or γ accounts for singularities in H'_{NF} at small r_1, r_2 and r values. To find the optimized parameters A_i, B_i and C_i we minimize with respect to them this second order matrix element. Results of these calculations including $\langle H'_{EN}\rangle$ are presented in Table 2. The estimated numerical uncertainty of E'_{NF} is the dominant theoretical uncertainty of this calculation, however it is quite small, namely 0.17 kHz.

4. Summary

The summary of numerical results for $m\,\alpha^6$ contributions to the 2^3P_J centroid is presented in Table 2. By centroid E_C we mean

$$E_C(2^3P) = \frac{E(2^3P_0) + 3\,E(2^3P_1) + 5\,E(2^3P_2)}{9} \tag{23}$$

a spin averaged value of ionization energies. The value for any particular state could be than obtained from the centroid E_C and the known fine structure [14]. In the following we use the 1998 CODATA [17] value of the Rydberg constant

$$\mathrm{Ry}_\infty c = 3.289\ 841\ 960\ 368(25)\,10^9\,\mathrm{MHz}, \tag{24}$$

and the fine structure constant α

$$\alpha^{-1} = 137.035\ 999\ 76(50)\,. \tag{25}$$

The new term calculated here, beyond the previously known radiative corrections E_{RC} is

$$\Sigma = m\,\alpha^6\,0.02169 = 0.40465\ \mathrm{MHz}\,. \tag{26}$$

This result is surprisingly small, but significantly improves precision of final theoretical predictions. Other contributions to helium ionization energy have already been calculated and are presented in Table 3. Therefore, we are now at the position to give an improved value for the helium 2^3P ionization energy (centroid). We base our analysis on a work of Drake and Martin [8]. The nonrelativistic energies of helium low lying states are known with precision highly exceeding any other contribution. The relativistic correction of relative order α^2, which is given by the matrix element of the Breit-Pauli Hamiltonian, is also known very accurately. The complete non-QED value for ionization energy, including the effect of the finite mass and size of the nucleus, is denoted by E_N in Table 3. The leading QED contribution of order α^3 includes the so called Bethe logarithms, the logarithmic average excitation energy. This term has been recently calculated with high precision by Drake and Goldman [9] for triplet P-states. This contribution includes also recoil effects, which are obtained only approximately with 20 kHz uncertainty. It was the $E^{(6)}$ correction which limited the precision of theoretical predictions of He ionization energies. It includes radiative correction that scales exactly with Dirac δ functions and the term Σ calculated here. At the current precision level it is necessary to include higher order QED effects, which are known to be significant in hydrogenic atoms. These higher order terms were estimated in [8], we use that value here and denote in Table 3 as $E^{(7)}$. We associate uncertainty of 0.4 MHz to this correction and this is now the dominant source of theoretical error provided the calculation presented in this paper is correct. The numerical uncertainties are much smaller, of order of 0.17 kHz, mainly from E'_{NF}.

From the precise measurements of $2^3S - 2^3P$ [18] and $2^3S_1 - 3^3D_1$ [19], one gets 2^3P ionization energy by subtraction of the theoretically well known value for the 3^3D_1 state, E_{exp} in Table 3. It does not agree well with the theoretical value, the difference being 1.85(0.40)(0.09) MHz. Curiously enough a disagreement of few σ shows up also in the fine splitting $E(2^3P_1 - 2^3P_2)$ [14] and it may indicate underestimation of some as yet unknown effect. At present the most probable explanation is the very approximate calculation of $E^{(7)}$ and we emphasize that the theoretical uncertainty is chosen quite arbitrarily. It is also important to stress at this point that the numerical calculation of the $m\,\alpha^6$ contribution as presented in this paper, and the former derivation of corresponding operators [6], requires an independent confirmation: a possible mistake, difficult to avoid in such an involved analytic derivation and numerical calculations, could easily have been made. Further improvements of precision in theoretical predictions of helium ionization energies would require the complete calculation of the $m\,\alpha^7$ term, which is a difficult task.

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State	^3P	^1P	^3D	^1D	^3F
$J=0$	-0.325801(5)	0.0	0.0	0.0	0.0
$J=1$	-0.063484(3)	-0.353500(5)	-0.001412	0.0	0.0
$J=2$	0.020639(3)	0.0	-0.004118	-0.001190	-0.002800

Table 1. Spin dependent second order contribution E_{FS} for each J and each intermediate state in units $m\,\alpha^6$.

contribution	$m\,\alpha^6$
E_V	0.049702
$E'_{NF} + Z^6/16$	0.140689(9)
E_{FS}	$-0.168703(2)$
Σ	0.021688(9)
$E_{RC} - E_{RC}(^{+}\mathrm{He})$	-1.116283
Σ_{tot}	$-1.094595(9)$

Table 2. Numerical results for $m\,\alpha^6$ contributions to 2^3P (centroid) ionization energy, E_V is the expectation value of H_V given by Eq, (13), E'_{NF} by Eq. (16), and E_{RC} is equal to $\langle H_{RC1} + H_{RC2}\rangle$

contribution	value in MHz
E_N	$-876\,104\,991.69$
$E^{(5)}$	$-1\,235.33(2)$
$E^{(6)}$	-20.42
$E^{(7)}$	$2.00(40)$
$-E_{th}$	$-876\,106\,245.44(40)$
$-E_{exp}$	$-876\,106\,247.29(9)$

Table 3. Summary of contributions to 2^3P (centroid) ionization energy and comparison with experiment. E_N is the nonrelativistic energy and leading relativistic corrections including nuclear recoil and finite size. $E^{(n)}$ is a correction to energy of order $m\,\alpha^n$.