Improved Result for Helium 2^3S_1 Ionization Energy

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A complete calculation of relativistic and quantum electrodynamic effects to order $m\alpha^6$ on the energy of the 2^3S_1 state in helium is presented. The result, beyond the previously known radiative corrections, amounts to $-3.00(1)$ MHz, and significantly reduces the theoretical uncertainty. The improved theoretical predictions are compared to the best available experimental result for the 2^3S_1 state.

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The helium atom is one of the simplest systems in which quantum electrodynamics (QED) can be studied with high precision [1]. The presence of the electron-electron interaction is an essential ingredient in the comparison of helium to hydrogenic systems and brings QED calculations to the next level of complexity. While the numerical solution of the Schrödinger equation can be obtained with precision far beyond experimental accuracy, relativistic and quantum electrodynamics effects are known with much less precision. A series of measurements involving the triplet 2^3S_1 state, in particular, those by Shiner *et al.* [2], by the Florence group [3], and by the Paris group [4], have stimulated advances in the theory of bound state quantum electrodynamics. Recently, the so-called Bethe log, a mean excitation energy that forms part of the leading radiative correction, has been precisely calculated in [5–7] for low lying states of helium. In this paper, we present the complete result for the next to leading quantum electrodynamics effects on the 2^3S_1 ionization energy. It is achieved by the calculation of matrix elements of effective operators in the appropriate basis set of functions. We first present these effective operators and rewrite them in a form suitable for numerical calculations. Next, we explain numerical methods and present results for matrix elements. Brief concluding remarks with the prospects of further QED tests are left to the very end.

The key idea of the effective Hamiltonian approach for the calculation of bound state energies is the replacement of the Hamiltonian of the full quantum electrodynamics with a simplified Hamiltonian $H_{\rm eff}$ which acts only in the subspace of two-particle states with all momenta being of the order of the inverse of the size of the bound state [8]. This new simplified Hamiltonian depends on an artificial parameter λ to keep its matrix element finite. The particular form of this regularization does not play a role, since all divergences will be canceled out algebraically, and therefore we will not write it explicitly. $H_{\rm eff}$ 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

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

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

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

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

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

where the prime in the denominator means the exclusion of the ϕ state in the operator inversion. It should be mentioned that for the helium fine structure splitting this expression has been derived many years ago in the traditional (Bethe-Salpeter) approach by Douglass and Kroll [9].

The Breit Hamiltonian $H^{(4)}$, neglecting terms proportional to $\delta^3(r)$, which vanish for triplet states, is, in atomic units,

$$H^{(4)} = H_A + H_B + H_C + H_D, \tag{4}$$

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

$$H_B = \left[\frac{Z}{4} \left(\frac{\boldsymbol{r}_1}{r_1^3} \times \boldsymbol{p}_1 + \frac{\boldsymbol{r}_2}{r_2^3} \times \boldsymbol{p}_2 \right) - \frac{3}{4} \frac{\boldsymbol{r}}{r^3} \times (\boldsymbol{p}_1 - \boldsymbol{p}_2) \right] \frac{\boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2}{2}, \tag{6}$$

$$H_C = \left[\frac{Z}{4} \left(\frac{\boldsymbol{r}_1}{r_1^3} \times \boldsymbol{p}_1 - \frac{\boldsymbol{r}_2}{r_2^3} \times \boldsymbol{p}_2 \right) + \frac{1}{4} \frac{\boldsymbol{r}}{r^3} \times (\boldsymbol{p}_1 + \boldsymbol{p}_2) \right] \frac{\boldsymbol{\sigma}_1 - \boldsymbol{\sigma}_2}{2}, \tag{7}$$

$$H_D = \frac{1}{4} \left(\frac{\boldsymbol{\sigma}_1 \boldsymbol{\sigma}_2}{r^3} - 3 \frac{\boldsymbol{\sigma}_1 \cdot \boldsymbol{r} \boldsymbol{\sigma}_2 \cdot \boldsymbol{r}}{r^5} \right). \tag{8}$$

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

$$E_I = \left\langle H_I \frac{1}{(E_0 - H_0)'} H_I \right\rangle, \tag{9}$$

for $I = A, B, C, D$. The expression for $H^{(6)}$ is much more complex. It consists of electron-nucleus terms, electron-electron terms, and the radiative correction,

$$H^{(6)} = H_{e\text{-}n}(1) + H_{e\text{-}n}(2) + H_V + H_{\mathrm{RC}1} + H_{\mathrm{RC}2}\,, \tag{10}$$

where

$$H_{e\text{-}n}(i) = \frac{p_i^6}{16} - \frac{1}{8}\left[\boldsymbol{p}_i;\frac{Z}{r_i}\right]^2 - \frac{5}{128}\left[p_i^2;\left[p_i^2;\frac{Z}{r_i}\right]\right] - \frac{3}{32}\,p_i^2\left[\boldsymbol{p}_i;\left[\boldsymbol{p}_i;\frac{Z}{r_i}\right]\right], \tag{11}$$

$$\begin{aligned} H_V = {} & \frac{13}{12r^4} - \frac{11}{36}\,\pi\nabla^2\delta^3(r) - \frac{5Z}{12}\,\frac{\boldsymbol{r}}{r^3}\left(\frac{\boldsymbol{r}_1}{r_1^3} - \frac{\boldsymbol{r}_2}{r_2^3}\right) + \frac{1}{4}\,(p_1^2 + p_2^2)\,p_1^i\left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\right)p_2^j + \frac{23}{48}\,p_1^i\left(\frac{\delta^{ij}}{r^3} - 3\,\frac{r^i r^j}{r^5}\right)p_1^j \\ & - \frac{3}{16}\,p_1^i\left(\frac{\delta^{ij}}{r^3} - 3\,\frac{r^i r^j}{r^5}\right)p_2^j + \frac{1}{4}\,p_1^i\left(\frac{\delta^{ij}}{r^2} + 3\,\frac{r^i r^j}{r^4}\right)p_1^j \\ & - \left\{\frac{1}{8}\,[p_1^i;H_0]\left(\frac{r^i r^j}{r} - 3\delta^{ij}r\right)[H_0;p_2^j] + \frac{1}{16}\,[p_1^i;H_0]\left[p_2^2;\frac{r^i r^j}{r} - 3\delta^{ij}r\right]p_2^j\right. \\ & \left. + \frac{1}{16}\,p_1^i\left[\frac{r^i r^j}{r} - 3\delta^{ij}r;p_1^2\right][H_0;p_2^j] + \frac{1}{32}\,p_1^i\left[p_2^2;\left[\frac{r^i r^j}{r} - 3\delta^{ij}r;p_1^2\right]\right]p_2^j\right\}, \end{aligned} \tag{12}$$

$$H_{\mathrm{RC}1} = \pi Z^2\left(\frac{139}{32} - 2\ln(2) + \frac{5}{48}\right)[\delta^3(r_1) + \delta^3(r_2)], \tag{13}$$

$$H_{\mathrm{RC}2} = \frac{Z}{\pi}\left(-\frac{4358}{1296} - \frac{10}{27}\,\pi^2 + \frac{3}{2}\,\pi^2\ln(2) - \frac{9}{4}\,\zeta(3)\right)[\delta^3(r_1) + \delta^3(r_2)]. \tag{14}$$

These effective operators have been derived in [8]. Here we put $\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2 = 1$, which holds for triplet states. Moreover, they were transformed here to a form which is more suited for numerical calculations of matrix elements. Namely, we expressed them in terms of a few basic operators containing fewer derivatives. A further transformation is required for E_A and $H_{e\text{-}n}$ since both of these terms are divergent, but in such a way that this divergence cancels out in the sum. This cancellation of properly regularized singularities was demonstrated in [8]. Here, we slightly simplify that method and remove divergences as follows. Let us define new Hamiltonians H'_A and $H'_{e\text{-}n}$ with $\delta V = (\frac{Z}{r_1} + \frac{Z}{r_2})/4$:

$$H'_A = H_A - \delta V(H_0 - E_0) - (H_0 - E_0)\delta V\,, \tag{15}$$

$$\begin{aligned} H'_{e\text{-}n} = {} & H_{e\text{-}n}(1) + H_{e\text{-}n}(2) - \delta V(E_0 - H_0)\delta V \\ & + \delta V H_A + H_A\delta V - 2\delta V\langle H_A\rangle\,. \end{aligned} \tag{16}$$

The correction to the energy,

$$E'_A = \left\langle H'_A\,\frac{1}{(E - H)'}\,H'_A\right\rangle + \langle H'_{e\text{-}n}\rangle\,, \tag{17}$$

is finite for separate terms and equal to the original expression $E_A + \langle H_{e\text{-}n}(1) + H_{e\text{-}n}(2)\rangle$.

An analogous numerical calculation for helium fine structure has already been performed by several groups, the most recent one by Yan and Drake [10]. We used here a completely different basis set, similar to the one used by Frolov [11] and Korobov *et al.* [5]. In this approach the helium wave function is expanded in a basis set of exponential functions of the form

$$\phi(r_1, r_2, r) = \sum_i v_i[e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i r} \pm (r_1 \leftrightarrow r_2)], \tag{18}$$

where α_i, β_i, and γ_i are real and chosen in a uniform and random way with the following conditions:

$$A_1 < \alpha_i < A_2, \qquad \beta_i + \gamma_i > \epsilon\,, \tag{19}$$

$$B_1 < \beta_i < B_2, \qquad \alpha_i + \gamma_i > \epsilon\,, \tag{20}$$

$$C_1 < \gamma_i < C_2, \qquad \alpha_i + \beta_i > \epsilon\,. \tag{21}$$

The parameters A_i, B_i, C_i, and ϵ are determined by minimization of the energy of the state of interest. The condition $\epsilon > 0$ is necessary for the normalizability of the wave function. In order to obtain a more precise wave function, we subdivided these sections, for example, $\langle A_1 \cdots A_2\rangle$, into two subsections $\langle A_1 \cdots A_2 \cdots A_3\rangle$ with an equal number of randomly chosen α_i terms. The coefficients v_i in Eq. (18) form a vector v which is a solution of the generalized eigenvalue problem,

$$Hv = ENv\,, \tag{22}$$

where H is a matrix of the Hamiltonian in this basic set, N is a normalization matrix, and E is an eigenvalue, the energy of the state corresponding to v. For the solution of the eigenvalue problem with a typical value of $N = 600$, we use Lapack libraries in the quadruple precision. As a result for the nonrelativistic energy of the helium 2^3S_1 state, we got

$$E(2^3S_1) = -2.175\,229\,378\,236\,791\,2\,. \tag{23}$$

This value agrees up to all digits with the still more accurate result of Drake and Yan [12]. The calculation of all matrix elements can be performed with the use of one formula:

$$\frac{1}{16\pi^2}\int d^3r_1\int d^3r_2\,\frac{e^{-\alpha r_1-\beta r_2-\gamma r}}{r_1 r_2 r}=\frac{1}{(\alpha+\beta)(\beta+\gamma)(\gamma+\alpha)}\,. \tag{24}$$

The result with any additional r_i in the numerator can be obtained by differentiation with respect to the corresponding parameter α, β, or γ. Any additional r_i in the denominator can be obtained by integration with respect to its associated parameter. This leads to the appearance of logarithmic and dilogarithmic functions:

$$\frac{1}{16\pi^2}\int d^3r_1\int d^3r_2\,\frac{e^{-\alpha r_1-\beta r_2-\gamma r}}{r_1 r_2 r^2}=\frac{1}{(\beta+\alpha)(\alpha+\beta)}\ln\!\left(\frac{\beta+\gamma}{\alpha+\gamma}\right), \tag{25}$$

$$\frac{1}{16\pi^2}\int d^3r_1\int d^3r_2\,\frac{e^{-\alpha r_1-\beta r_2-\gamma r}}{r_1^2 r_2 r^2}=\frac{1}{2\beta}\left[\frac{\pi^2}{6}+\frac{1}{2}\ln^2\!\left(\frac{\alpha+\beta}{\beta+\gamma}\right)+\mathrm{Li}_2\!\left(1-\frac{\alpha+\gamma}{\alpha+\beta}\right)+\mathrm{Li}_2\!\left(1-\frac{\alpha+\gamma}{\beta+\gamma}\right)\right]. \tag{26}$$

All matrix elements involved in the $m\alpha^6$ correction can be expressed in terms of rational, logarithmic, and dilogarithmic functions, as above. It is the power of this basis set that matrix elements could be easily calculated algebraically. Although the binding energy is highly accurate, the precision of matrix elements is not so. One reason is due to the variational method, another one being associated to high singularity of operators in $H^{(6)}$. With the exception of V_{4A}, the term in braces in Eq. (12), all matrix elements in H_V were calculated as described above. V_{4A} was too complicated for the analytic calculation of matrix element. In fact, the analytic expression was so large and singular that we were worried about its numerical stability. Instead, we calculated the r_i integrals numerically using the Gaussian method. Even more numerically involved is the calculation of second order corrections. The spin algebra in the calculation of the matrix element in E_I in Eq. (9) is simplified with the help of

$$\frac{1}{3}\sum_{m=-1}^{1}|2^3S_1,m\rangle\langle m,2^3S_1|=\frac{1}{6}\left(\frac{\boldsymbol{\sigma}_1+\boldsymbol{\sigma}_2}{2}\right)^2\times|2^3S\rangle\langle 2^3S|\,. \tag{27}$$

The inversion of the operator E_0-H_0 in the expression for E_B and E_C is performed in a basis set of even functions with $l=1$ of the form

$$\phi(r_1,r_2,r)=\sum_i v_i[\boldsymbol{r}_1\times\boldsymbol{r}_2 e^{-\alpha_i r_1-\beta_i r_2-\gamma_i r}\mp(r_1\leftrightarrow r_2)], \tag{28}$$

and for E_D in the subspace of states with $l=2$,

$$\phi^{ab}(r_1,r_2,r)=\sum_i v_i\left[\left(r_1^a r_1^b-\frac{\delta^{ab}}{3}r_1^2\right)e^{-\alpha_i r_1-\beta_i r_2-\gamma_i r}-(r_1\leftrightarrow r_2)\right]+\sum_j w_j\left(r^a r^b-\frac{\delta^{ab}}{3}r^2\right)[e^{-\alpha_j r_1-\beta_j r_2-\gamma_j r}-(r_1\leftrightarrow r_2]. \tag{29}$$

To find the optimized values of parameters A_i, B_i, and C_i necessary for generation of ϕ, we minimize with respect to them the corresponding correction to energy E_I. Results of these calculations [13] are presented in Table I. The most intensive numerical calculation was required for E_A' for the following two reasons. It is not a simple inversion of E_0-H_0, but an inversion with the exclusion of the 2^3S state, where it is equal to 0. Therefore, such an inversion requires full diagonalization of E_0-H_0, which is a time consuming process. The next reason was the large magnitude of second order correction and $H_{e\text{-}n}'$. However, the sum with the subtracted value of the Dirac energy of He$^+$ is fairly small, as given in Table I. The estimated numerical error of E_A' is the dominant theoretical uncertainty of this calculation. The numerical result for the matrix element of $H_{e\text{-}n}'$, although equally large, was obtained with much higher precision than this second order term.

The summary of numerical results for $m\alpha^6$ contributions is presented in Table I. The new term calculated here, beyond the previously known radiative corrections, is

$$\Sigma=-m\alpha^6\,0.160\,80(50)=-3.00(1)\ \mathrm{MHz}\,. \tag{30}$$

This result is surprisingly small, but brings theoretical predictions closer to the experimental value. Other contributions to helium ionization energy have already been calculated and are presented in Table II. Therefore, we are now at the position to give an improved value for the helium 2^3S_1 ionization energy. We base our analysis on a recent work of Drake and Martin [1]. The nonrelativistic

TABLE I. Numerical results for $m\alpha^6$ contributions to 2^3S_1 ionization energy.

Contribution	$m\alpha^6$
E_V	0.16754(5)
$E_A'-Z^6/16$	−0.30480(50)
E_B	−0.01860(2)
E_C	−0.00111
E_D	−0.00383
Σ	−0.16080(50)
$E_{\mathrm{RC}}-E_{\mathrm{RC}}(\mathrm{He}^+)$	3.65773
Σ_{tot}	3.49693(50)

TABLE II. Summary of contributions to 2^3S_1 ionization energy.

Contribution	Value in MHz
E_N	$-1\,152\,846\,800.14$
$E^{(5)}$	3998.65
$E^{(6)}$	65.24(0.01)
$E^{(7)}$	$-5.31(1.00)$
$-E_{\text{theor}}$	$-1\,152\,842\,741.56(1.00)$
$-E_{\text{expt}}$	$-1\,152\,842\,742.87(0.06)$

energies of helium low lying states are known with precision highly exceeding any other contribution. The relativistic correction of relative order α^2, which involves the calculation of the matrix element of the Breit Hamiltonian, is also known very accurately. The complete non-QED value for ionization energy, including the effect of the finite size of the nucleus, is denoted by E_N in Table II. The leading QED contribution of order α^3 includes the so-called Bethe logarithms, the average excitation energy. This term has been recently calculated with very high precision by Korobov [5] for singlet S states, and Baker *et al.* [6] for the triplet S state, as well as singlet S states. The value of $E^{(5)}$ in Table II includes also very recently calculated small recoil corrections [14]. 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 also include higher order QED effects, which are known to be large in hydrogenic atoms. We promote the hydrogenic value for the $m\alpha^7$ contribution to helium assuming that it is proportional to $\delta^3(r_1) + \delta^3(r_2)$, as was done in [1]. Although this correction is certainly not given by the Dirac delta function, based on the behavior of lower order results one hopes to incorporate in this way the largest contribution. We estimate the remaining unknown contribution to be of the order of 1 MHz, and this is now the dominant source of theoretical uncertainty provided the calculation presented in this paper is correct. The numerical uncertainties are much smaller, of the order of 10 kHz, mainly due to E'_A.

From the most precise measurement $2^3S_1 - 3^3D_1$ by the Paris group [4], one gets 2^3S_1 ionization energy by subtraction of the theoretically well-known value for the 3^3D_1 state, E_{expt} in Table II. It agrees with the theoretical value, a difference is 1.3(1.0) MHz: 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 [8], 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 in QED tests on the helium 2^3S_1 state would require the complete calculation of the $m\alpha^7$ term, which, if not impossible, is a quite difficult task. A similar set of $m\alpha^6$ operators has already been derived for singlet S states [15]: it therefore should be possible in the near future to obtain an improved ground state Lamb shift and compare with the known experimental value. Another project is the helium fine structure splitting. Here the target is the $m\alpha^7$ contribution. The author has unsuccessfully attempted to derive a complete set of operators. However, an approximate approach, in which a selection of the most numerically important but algebraically simple operators is made, may allow the calculation of the bulk of the fine structure at this order. This would lead to an uncertainty in the fine structure splitting below 1 kHz, i.e., below the experimental error.

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