Ionization Potential of the Helium Atom

Vladimir Korobov*
Joint Institute for Nuclear Research, Dubna, 141980, Russia

Alexander Yelkhovsky†
Budker Institute of Nuclear Physics, Novosibirsk, 630090, Russia

Ground state ionization potential of the He$^4$ atom is evaluated to be 5 945 204 221 (42) MHz. Along with lower order contributions, this result includes all effects of the relative orders $\alpha^4$, $\alpha^3 m_e/m_\alpha$ and $\alpha^5 \ln^2 \alpha$.

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In contrast to the theoretical description of electromagnetically bound two-body systems like hydrogen, positronium or muonium, where considerable progress is achieved (for the recent reviews see, e.g., [1]), high precision calculations in more complex atoms are elaborated to a lesser degree. The central problem with an extension of the methods developed for the two-body problem to a few-electron atoms is that those methods are usually strongly rely on the solution of the Schrödinger equation for a single particle in the Coulomb field. Having a simple analytic form, this solution is a perfect reference point for the calculation of various observables as power series in the fine structure constant $\alpha$ using the quantum-mechanical perturbation theory. In higher orders of this perturbation theory, where the nonrelativistic approximation usually breaks down, the explicit form of the nonrelativistic solution facilitates the extraction of the ultraviolet divergences. These divergences are canceled by matching to their finite counterparts calculated in the fully relativistic framework of the quantum electrodynamics.

Although the Schrödinger equation for, e.g., three particles bound by the Coulomb potentials can be solved numerically with very high accuracy [2], the lack of an analytic solution makes the problem of the divergences cancellation more involved as compared to the two-body case. This problem was recently analyzed in Ref. [3] using singlet states of the helium atom as an example. Employing the nonrelativistic quantum electrodynamics of regularized dimensionally, it is demonstrated in [3] how all the divergences arising in the quantum-mechanical perturbation theory can be extracted and canceled at the operator level, without recourse to an explicit form of the helium wave function. For the first time the $O(\alpha^4)$ correction to singlet $S$ levels of the He$^4$ atom is represented as a sum of apparently finite average values of the regularization-independent operators.

In this Letter we present the most precise evaluation of the helium ground state energy. Expressed in terms of the ionization potential (the difference between ground state energies of the singly charged ion and of the atom), our result reads:

$$\nu_{\text{th}}(1^1S) = 5 945 204 221 (42) \, \text{MHz}. \quad (1)$$

Along with the nonrelativistic energy, this result includes all $O(\alpha^2)$, $O(\alpha^3)$, $O(\alpha^4)$ and $O(\alpha^5 \ln^2 \alpha)$ relativistic and radiative corrections. We take into account the finite nucleus-to-electron mass ratio $M \equiv m_\alpha/m_e = 7 294.299 508(16)$ exactly in the nonrelativistic and $O(\alpha^2)$ contributions, include the first ($\sim 1/M$) recoil correction into the $O(\alpha^3)$ contribution and neglect the nucleus recoil in higher orders. The effect of a finite nucleus charge radius $R_N = 1.673(1) \, \text{fm}$ [6] is included into the helium ground state energy as

$$\delta_{\text{cha}} E = \frac{2\pi Z\alpha}{3} r_N^2\langle \delta(r_1) + \delta(r_2) \rangle. \quad (2)$$

Here $Z = 2$ is the nucleus charge (in units of the proton one), while $r_1$ and $r_2$ denote the positions of the electrons with respect to the nucleus. The angle brackets in (2) and below denote the average value over the nonrelativistic ground state. In [3] we take one half of the $O(\alpha^5 \ln^2 \alpha)$ correction as an estimate of the uncertainty due to higher orders. Our result agrees with the previous theoretical estimate

$$\nu_{\text{th}}^\text{DM}(1^1S) = 5 945 204 226 (91) \, \text{MHz}, \quad (3)$$

obtained in [6] and including the $O(\alpha^4)$ and $O(\alpha^3/M)$ effects only partially.

In the remaining part of this Letter we briefly describe details of our calculation. Ground state energy of the helium atom is calculated as power series in the fine structure constant $\alpha$. Leading ($\sim 1$) contribution the Schrödinger energy $E$, and the corresponding wave function $\psi$ are found as a solution of the variational problem

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* e-mail: korobov@thsun1.jinr.su
† e-mail: yelkhovsky@inp.nsk.su
\[ E = \min_{\psi} \langle \psi | H | \psi \rangle , \]  
for the helium atom Hamiltonian taken in the nonrelativistic approximation,
\[ H = \frac{p_1^2 + p_2^2}{2} + \frac{p^2}{2M} \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r}. \]  
Here \( r_{1,2} = |r_{1,2}| \) and \( r = |r_1 - r_2| \); \( p_{1,2} \) are the momenta of the electrons and \( \mathbf{P} = -p_1 - p_2 \) is the momentum of the nucleus.

To construct the variational wave function we use the simplest form of the basis,
\[ \psi_n = \exp(-k_1^n r_1 - k_2^n r_2 - k_3^n r), \quad n = 1, \ldots, N. \]  
The complex exponents \( k_a^n \) are chosen in a quasi-random manner from a rectangular area on the complex plane, for example,
\[ \text{Re } k_a^n = K_a^{\text{min}} + \frac{n(n+1)}{2} \sqrt{p_a} \left( K_a^{\text{max}} - K_a^{\text{min}} \right), \]  
where \( \lfloor x \rfloor \) denotes a fractional part of \( x \), \( p_a \) is some prime number, while \( (K_a^{\text{min}}, K_a^{\text{max}}) \) is a variational interval. Imaginary parts of the parameters are generated in a similar way. We use both real and imaginary parts of \( \psi_n \) to form a set of real basis functions. In particular, the ground state wave function \( \psi \), \( \text{Im } \psi_n, n = 1, \ldots, N \), symmetric over the interchange of the electrons positions, \( r_1 \leftrightarrow r_2 \).

Variational expansion in the basis (1) was shown in [3] to be very effective. It yields the best available nonrelativistic energies for many atomic and molecular systems and in particular for the ground state of the helium atom. Simplicity of the basis (1) allows us to evaluate analytically matrix elements of all the operators that appear in the calculation. By a proper differentiation and/or integration of the basic integral,
\[ \int d^3r_1 \int d^3r_2 \exp(-k_1 r_1 - k_2 r_2 - k_3 r) \]  

\[ = \frac{\pi^{3/2}}{(k_1 + k_2)(k_2 + k_3)(k_3 + k_1)} , \]  
with respect to \( k_1, k_2 \) and \( k_3 \) we express the matrix element of any operator involved in our calculation in terms of rational functions of \( k \)'s, their logarithms and dilogarithms.

For the zeroth order approximation a wave function built within a set of \( 2N = 1200 \) basis functions has been used that yields the nonrelativistic energy
\[ E = -2.903 \, 304 \, 557 \, 727 \, 940 \, 23(1) \]  
Here and below we cite the uncertainty of the numerical results due to finiteness of the basis set. The uncertainties due to incomplete knowledge of the physical constants are included into the final result for the ionization potential (see Table). High accuracy of (1) is not redundant since the calculation of rather singular matrix elements of higher order corrections requires very accurate variational wave function.

First relativistic correction to the nonrelativistic value (1) is the average of the Breit Hamiltonian (see, e.g., [8]),
\[ \delta^{(2)} E = \alpha^2 \left\langle -\frac{p_1^2 + p_2^2}{8} - \frac{P^4}{8M^3} + \pi Z \delta(r_1) + \delta(r_2) \right\rangle \]  
\[ + \frac{Z}{2M} \left( \frac{1}{r_1} P + (p_1 n_1) (1 \rightarrow 2) \right) \]  
\[ = -1.952 \, 050 \, 77(1) \alpha^2. \]  
Here \( \mathbf{n} = r/r \) and \( n_{1,2} = r_{1,2}/r_{1,2} \). To simplify the presentation, we explicitly take into consideration that the spin of the nucleus and the total spin of electrons are both equal to zero. In particular, we replace the product of the electron spin operators \( s_1 s_2 \) by its eigenvalue in the singlet state, \(-3/4\).

Order \( \alpha^3 \) and \( \alpha^3/M \) corrections to the energy can be represented as follows (see [3] and references therein):
\[ \delta^{(3)} E = \alpha^3 \left\{ \frac{4Z}{3} \left( -2 \ln \alpha - \beta + \frac{19}{30} \right) \langle \delta(r_1) + \delta(r_2) \rangle \right. \]  
\[ + \left. \left( \frac{14}{3} \ln \alpha + \frac{164}{15} \right) \langle \delta(r) \rangle + \frac{7}{3\pi} \left\langle \frac{\ln r + \gamma}{r^2} \right\rangle \right\} \]  
\[ + \frac{2Z^2}{3M} \left( \frac{\ln \alpha - 4\beta + \frac{31}{3} \delta(r_1) + \delta(r_2)}{3\pi} \right) + \frac{7Z^2}{3\pi M} \left\langle \frac{\ln r_1 + \gamma}{r_1^2} \right\rangle \]  
\[ = 57.270 \, 34(2) \alpha^3. \]  
Here \( \gamma = 0.5772 \ldots \) is the Euler constant and \( \beta \) is the helium Bethe logarithm [3] defined as
\[ \beta = \frac{\langle (p_1 + p_2)(H-E) \rangle \ln[2(H-E)/(p_1 + p_2)]}{\langle (p_1 + p_2)(H-E)(p_1 + p_2) \rangle} \]  
\[ = 4.370 \, 039(2). \]  
The cited value of \( \beta \) has been calculated for the finite mass of the nucleus. Details of calculations in the limit of no recoil \( (M \to \infty) \) can be found in [3]. For convenience of comparison with earlier results it is worth to write explicitly the relation to the \( Q \)-term introduced by Araki and Sucher [3],
\[ Q = \lim_{\rho \to 0} \left\langle \frac{\Theta(r - \rho)}{4\pi \rho^3} + (\ln \rho + \gamma) \delta(r) \right\rangle \]  
\[ = -\frac{1}{2\pi} \left\langle \frac{\ln r + \gamma}{r^2} \right\rangle. \]  
The next, \( O(\alpha^4) \) correction to the energy is [3]:

\[ \cdot \cdot \cdot \]
\[
\delta^{(4)} E = \frac{\alpha^2 \delta^{(2)} E \langle \phi \rangle}{2} + \alpha^4 \left\{ -\frac{E^3}{2} + \frac{E^2 \langle \phi \rangle}{4} \right\} \\
+ \frac{E}{4} \left\langle 2C_N C + c^2 - \frac{p_1^2 p_2^2}{2} - \pi Z [\delta (r_1) + \delta (r_2)] \right\rangle \\
+ \langle V_p G V_p \rangle + \langle V_S G V_S \rangle \\
+ \pi k_{NC} \delta (r_1) + \delta (r_2)] + \pi k_{ec} \delta (r) \\
+ \left\langle -\frac{3C_1 C_2 C_N}{4} - \frac{c C_N C}{4} - \frac{C_N C [p_1 p_2 + n (n p_1) p_2]}{4} \right\rangle \\
+ \frac{p_1^2 C N p_2^2}{4} + \frac{p_1 c^2 p_1 + p_2 c^2 p_2 + (p_1 \times p_2) c (p_1 \times p_2)}{4} \\
\frac{p_2^2 c (n p_2)^2}{8} + \frac{(p_1 n) c (n p_2)^2}{8} - 3 (p_1 n)^2 c (n p_2)^2 \\
\frac{2 (n p_2) (E_1 p_2) + (n E_1) \left[(n p_2)^2 - p_2^2\right]}{4} \\
+ \frac{3 E_1 E_2 - (n E_1) (n E_2) - 2 (E_1 - E_2) e}{8} \\
\frac{-3 P^2 - 3(n P)^2}{32} + \frac{\pi \delta (r)}{r^3} \left[ \frac{9 P^2}{16} + C_N \right] \\
+ \frac{\pi Z}{4} \left[ \delta (r_1) \left( \frac{3 p_2^2}{2r_2} - \frac{2Z - 1}{r_2} \right) (1 \leftrightarrow 2) \right] \\
(\frac{E_1 - E_2}{2} + (p_1 n) \left[\frac{1}{r_1} (n p_1 + Z) + (1 \rightarrow 2) \right] \\
\frac{-\ln r + \gamma}{2r^3} \left[\frac{1}{r_1} (n p_1 - 1/2) \right] \right\rangle \\
= 139.60(1) \alpha^4. \tag{14}
\]

Here we use the following notations: \( C = C_N + c, \)
\( C_N = C_1 + C_2, \)
\( C_1, C_2 = -Z/r_{1,2}, \)
\( c = n/r^2 \) and \( E_{1,2} = -Z n_{1,2}/r_{1,2} \). The terms \( \langle V_p G V_p \rangle \) and \( \langle V_S G V_S \rangle \) in \((14)\), where \( G \) is the reduced Green function of the Schrödinger equation, \((H - E) G (r_1, r_2) = \psi (r_1, r_2) \psi^* (r_1', r_2') - \delta (r_1 - r_1') \delta (r_2 - r_2'), \) represent the effects of virtual transitions into triplet \( P \) and singlet \( S \) excited states, respectively (see \( 3 \) for details). Perturbations which induce those transitions are
\[
V_P = \frac{s_1 - s_2}{4} \left( \frac{Z_1}{r_1^2} - \frac{Z_2}{r_2^2} + \frac{r \times P}{r^3} \right), \tag{15}
\]
where \( l_{1,2} = r_{1,2} \times p_{1,2}, \) and
\[
V_S = \frac{E}{2} \left( C_N + c \right) + \left\{ \frac{p_1^2 + c, p_2^2 + c}{2} - \frac{c c}{4} - \frac{3 c^2}{2} \right\} \\
+ \frac{p_1 (C_N - c) p_1 + (1 \rightarrow 2)}{4} - \frac{p_1 c p_2 + (p_1 n) c (n p_2)}{2}. \tag{16}
\]

The contact terms enter into Eq.\((14)\) with the coefficients
\[
k_{eC} = \frac{Z^3}{2} + \frac{427 Z^2}{96} - \frac{10Z}{27} - \frac{9 Z \zeta (3)}{4 \pi^2} - \frac{2179 Z}{648 \pi^2} \\
+ \frac{3 Z - 4 Z^2}{2} \ln 2 \rightarrow 16.3557, \tag{17}
\]
\[
k_{eC} = -\ln \alpha + \frac{3285}{216} - \frac{335}{54 \pi^2} - \frac{29 \ln 2}{2} + \frac{15 \zeta (3)}{4 \pi^2} \rightarrow 10.37657. \tag{18}
\]
In \((14)\), all momentum operators standing to the right (left) of position-dependent operators are assumed to act on the right (left) wave function.

Average values for a part of the operators entering into Eq.\((14)\) can be found in the literature. For the average values of the new operators we have obtained the following results:
\[
\langle V_P G V_P \rangle = -0.392; \quad \langle V_S G V_S \rangle = -18.48; \\
\left\langle -\frac{C_N [p_1 p_2 + n (n p_1) p_2]}{4} \right\rangle = 0.811; \\
\left\langle \frac{p_1^2 C N p_2^2}{4} \right\rangle = -36.938; \quad \left\langle \frac{p_1^2 c p_1 + p_2 c^2 p_2}{8} \right\rangle = 1.142; \\
\left\langle \frac{(p_1 \times p_2) c (p_1 \times p_2)}{4} \right\rangle = 1.078; \\
\left\langle -\frac{p_1^2 c (n p_2)^2}{8} - (p_1 n)^2 c (n p_2)^2 \right\rangle = -0.03; \\
\left\langle -\frac{2 (n p_2) (E_1 p_2) + (n E_1) \left[(n p_2)^2 - p_2^2\right]}{4} \right\rangle = -4.749; \\
\left\langle \frac{3 E_1 E_2 - (n E_1) (n E_2) - 2 (E_1 - E_2) e}{8} \right\rangle = 1.434; \\
\left\langle -\frac{3 P^2 - 3(n P)^2}{32} + \frac{9 \pi \delta (r) P^2}{32} \right\rangle = 1.325; \\
\left\langle \frac{\pi \delta (r) C_N}{2} \right\rangle = -2.508; \quad \left\langle \frac{E_1 - E_2}{2} \right\rangle = 0.409; \\
\left\langle \frac{3 \pi \delta (r_1) p_1^2}{2} + (1 \leftrightarrow 2) \right\rangle = 18.421; \\
\left\langle \frac{3 \pi \delta (r_1) C_2}{2} + (1 \leftrightarrow 2) \right\rangle = -25.066; \\
\left\langle \frac{3}{2 r^3} \left[\frac{1}{r_1} (n p_1 - 1/2) \right] \right\rangle = -0.958; \\
\left\langle \frac{1}{r_1} (n p_1 + Z) + (1 \rightarrow 2) \right\rangle = 4.706.
Finally, the enhanced by $\ln^{2} \alpha$ (and hence presumably the leading) part of the $O(\alpha^{5})$ correction is [12]:

$$\delta^{(5)} E = -4Z^{3}\alpha^{5} \ln^{2}(Z \alpha)(\delta(r_{1}) + \delta(r_{2})) \approx 2\,070\,\alpha^{3}. \quad (19)$$

Numerical results for all the contributions to the helium ionization potential are collected in the Table. Appropriate expression for the ground state energy of the helium ground state is

$$E_{\text{He}^{+}} = -\frac{Z^{2}}{2} \frac{M}{M+1} - \frac{Z^{4}\alpha^{2}}{8} \frac{M(M^{2}+3M+5)}{(M+1)^{3}}$$

$$-\frac{4Z^{4}\alpha^{3}}{3\pi} \left( \frac{1}{3} - \frac{\beta_{H}}{M} \right) \left[ \ln(Z \alpha) + \beta_{H} - \frac{19}{30} \right]$$

$$-\frac{2Z^{5}\alpha^{3}}{3\pi M} \left( \ln(Z \alpha) + 4\beta_{H} - 7\ln 2 - \frac{31}{3} \right)$$

$$+ Z^{3}\alpha^{4} \left( k_{eN} - \frac{9Z^{3}}{16} \right) - \frac{4Z^{6}\alpha^{5}}{\pi} \ln^{2}(Z \alpha) + \frac{2Z^{4}\alpha^{2}}{3}. \quad (20)$$

Here $\beta_{H} = 2.984128557655\ldots$ is the Bethe logarithm for the hydrogen ground state and $r_{N} = 3.162(2) \cdot 10^{-5}$ is the nucleus charge radius $R_{N}$ expressed in the atomic units.

A comparison of our result [1] and the most recent experimental values,

$$\nu_{\exp}^{1S-2P} (1^{1}S) = 5\,945\,204\,238\,45\,(45)\,\text{MHz}, \quad (21)$$

and

$$\nu_{\exp}^{1S-2S} (1^{1}S) = 5\,945\,204\,356\,48\,(48)\,\text{MHz}, \quad (22)$$

extracted from the measurements of $1^{1}S - 2^{1}P$ [13] and $1^{1}S - 2^{1}S$ [14] intervals, respectively, shows that the theoretical value [1] agrees well with the former [21] and is within $2\sigma$ from the latter [22] if the theoretical and experimental uncertainties are added linearly. Efforts in both theoretical and experimental directions are desirable in order to further clarify the situation.

| TABLE I. Contributions to the total ionization potential of the helium ground state. Uncertainty in the nonrelativistic value is due to uncertainty in the nucleus mass. |
|---------------------------------|-----------------|
|                                  | $\delta\nu_{\exp}(1^{1}S)$, MHz |
| Nonrelativistic approximation    | 5\,945\,262\,288.62(4) |
| $\alpha^{2}$                    | $-16\,800.338(4)$ |
| $\alpha^{3}$                    | $-40\,486.375(50)$ |
| $\alpha^{4}$                    | $-834.9(2)$ |
| $\alpha^{5} \ln^{2} \alpha$ (and higher) | 84 (42) |
| Finite charge radius            | $-29.55(4)$ |
| total                           | 5\,945\,204\,221 (42) |

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[1] Hydrogen Atom: Precision Physics of Simple Atomic System, ed. S. G. Karshenboim et al., Springer-Verlag, 2001.
[2] V. I. Korobov, Phys. Rev. A61, 064503 (2000).
[3] A. Yelkhovsky, hep-ph/0103241.
[4] W. E. Caswell and G. P. Lepage, Phys. Lett. 167B, 437 (1986).
[5] For $M$, $\alpha$ and the Rydberg constant $R_{y}$ we use the values recommended by the National Institute of Standards and Technology (see http://physics.nist.gov/cuu).
[6] E. Borie and G. Rinker, Phys. Rev. A18, 324 (1978).
[7] G. W. F. Drake and P. C. Martin, Can. J. Phys. 76, 679 (1998).
[8] H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One and Two Electron Atoms (Springer-Verlag, New York, 1977).
[9] P. K. Kabir and E. E. Salpeter, Phys. Rev. 108, 1256 (1957).
[10] V. I. Korobov and S. V. Korobov, Phys. Rev. A59, 3394 (1999).
[11] H. Araki, Prog. Theor. Phys. 17, 619 (1957); J. Sucher, Phys. Rev. 109, 1010 (1958).
[12] A. J. Layzer, Phys. Rev. Lett. 4, 580 (1960); H. M. Fried and D. R. Yennie, Phys. Rev. Lett. 4, 583 (1960).
[13] K. S. E. Eikema, W. Ubachs, W. Vassen, and W. Hogervorst, Phys. Rev. A55, 1866 (1997).
[14] S. D. Bergeson, A. Balakrishnan, K. J. H. Baldwin, T. B. Lucatorto, J. P. Marangos, T. J. McIlrath, T. R. O’Brien, S. L. Rolston, C. J. Sansonetti, J. Wen, N. Westbrook, C. H. Cheng, and E. E. Eyler, Phys. Rev. Lett. 80, 3475 (1998).