Ionization Potential of the Helium Atom

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The ground-state ionization potential of the He\(^4\) atom is found to be 5 945 204 223 (42) MHz. Along with lower-order contributions, this result includes all effects of relative order \(\alpha^4\), \(\alpha^3m_e/m_n\), and \(\alpha^3\ln^2\alpha\). Effective operators derived in dimensionally regularized nonrelativistic quantum electrodynamics are employed. The average values of these operators are evaluated using a high-accuracy variational wave function constructed in an exponential basis.

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In this Letter we report on 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

\[ \nu_{\text{th}}(1^1S) = 5 945 204 223 (42) \text{ MHz} \]

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

\[ \delta_{\text{ch}}E = \frac{2\pi Z\alpha}{3} R_N^2 (\delta(r_1) + \delta(r_2)) \]

Here \(Z = 2\) is the charge of the nucleus (in units of the proton charge), 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 (1) we take one half of the \(O(\alpha^3\ln^2\alpha)\) correction as an estimate of the uncertainty due to higher orders. Our result agrees with the previous theoretical estimate,

\[ \nu_{\text{th}}(1^1S) = 5 945 204 226 (91) \text{ MHz} \]

obtained in [8] and including the \(O(\alpha^4)\) and \(O(\alpha^3/M)\) effects only partially. The uncertainty in (3) exceeds that in (1) because only part of the \(O(\alpha^4)\) corrections has been included into the calculation that leads to Eq. (3).

In the remaining part of this Letter, we briefly describe the details of our calculation. The ground-state energy of the helium atom is calculated as a power series in the fine structure constant \(\alpha\). The leading \((\sim 1)\) contribution, the Schrödinger energy \(E\), and the corresponding wave function \(\psi\) are found as a solution of the variational problem,
\[ E = \min_{\psi} \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}, \]  

(4)

for the helium atom Hamiltonian taken in the nonrelativistic approximation,

\[ H = \frac{p_1^2 + p_2^2}{2} + \frac{Z^2}{r_1} - \frac{Z}{r_2} + \frac{1}{r}. \]  

(5)

Here \( r_{1,2} = |\vec{r}_{1,2}| \) and \( r = |\vec{r}_1 - \vec{r}_2|; \) \( \vec{p}_{1,2} \) are momenta of the electrons and \( \vec{P} = -\vec{p}_1 - \vec{p}_2 \) is the momentum of the nucleus. Unless otherwise specified, we use the atomic units \( \hbar = m_e = 1 \) and \( c = 1/\alpha \) throughout this paper. In particular, the unit of energy is \( m_e c^2 \alpha^2 \).

To construct the variational wave function, we use the simplest form of the basis,

\[
\psi_n = \exp(-k_n^1 r_1 - k_n^2 r_2 - k_n^3 r), \\
n = 1, \ldots, N.
\]  

(6)

The complex exponents \( k_n^1 \) are chosen in a quasirandom manner from a rectangular area on the complex plane, for example,

\[ \Re k_n^1 = K_{n}^{\text{min}} + \left[ \frac{n(n + 1)}{2} \sqrt{\rho_{n}} \right] (K_{n}^{\text{max}} - K_{n}^{\text{min}}), \]  

(7)

where \([x]\) denotes a fractional part of \( x \), \( \rho_n \) is some prime number, while \( (K_{n}^{\text{min}}, K_{n}^{\text{max}}) \) is a variational interval. Imaginary parts of the exponents 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 \( \psi \) is a linear combination of \( 2N \) basis functions \( \Re \psi_n, \Im \psi_n, n = 1, \ldots, N \), symmetric over the interchange of the electron positions, \( r_1 \leftrightarrow r_2 \).

Variational expansion in the basis (6) was shown in [2] 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 (6) 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,

\[
\int d^3r_1 \int d^3r_2 \frac{\exp(-k_1 r_1 - k_2 r_2 - k_3 r)}{r_1 r_2 r} = \frac{16\pi^2}{(k_1 + k_2)(k_2 + k_3)(k_3 + k_1)},
\]  

(8)

with respect to \( k_1, k_2, \) and \( k_3 \), we express the matrix element of any operator involved in the calculation in terms of rational functions of \( k \), their logarithms, and dilogarithms.

For the zeroth order approximation, a wave function built within a set of \( 2N = 1200 \) basis functions has been used. It yields the nonrelativistic energy,

\[
E = -2.90330455772794023(1).
\]  

(9)

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 I). The high accuracy of (9) is not redundant since the calculation of rather singular matrix elements of higher order corrections requires a very accurate wave function.

The first relativistic correction to the nonrelativistic energy (9) is the average value of the Breit Hamiltonian (see, e.g., [9]) over \( \psi \):

\[
\delta^{(2)}E = \alpha^2 \left[ -\frac{p_1^4 + p_2^4}{8} - \frac{P_1^4}{8M^3} + \frac{\pi Z}{2M} \left[ \frac{\delta(\vec{r}_1) + \delta(\vec{r}_2)}{2} + \pi \delta(\vec{r}) - \frac{1}{2} \left[ \frac{\hat{\vec{p}}_1}{r_1} \cdot \hat{\vec{p}}_2 + (\hat{\vec{p}}_1 \cdot \hat{n}_1) \frac{1}{r_1} (\hat{n}_1 \cdot \hat{\vec{p}}) + (1 \rightarrow 2) \right] \right] \right] \]  

(10)

Here \( \hat{n} = \vec{n}/r \) and \( \hat{n}_{1,2} = \vec{n}_{1,2}/r_{1,2} \). To simplify the presentation, we explicitly take into account 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 \( \hat{s}_1 \hat{s}_2 \) 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):

\[
\delta^{(3)}E = \alpha^3 \left[ \frac{4Z}{3} \left( -\ln \alpha - \beta + \frac{19}{30} \right) \langle \delta(\vec{r}_1) + \delta(\vec{r}_2) \rangle + \left( \frac{14}{3} \ln \alpha + \frac{164}{15} \right) \langle \delta(\vec{r}) \rangle + \frac{7}{3\pi} \ln \gamma \frac{i\hat{n} \cdot \hat{\vec{p}}}{r^2} \right] 
\]  

(11)

Here \( \gamma = 0.5772 \ldots \) is the Euler constant and \( \beta \) is the helium Bethe logarithm [10] defined as

\[
\beta = \frac{\langle (\hat{\vec{p}}_1 + \hat{\vec{p}}_2)(H - E) \ln[2(H - E)](\hat{\vec{p}}_1 + \hat{\vec{p}}_2) \rangle}{\langle (\hat{\vec{p}}_1 + \hat{\vec{p}}_2)(H - E)(\hat{\vec{p}}_1 + \hat{\vec{p}}_2) \rangle} = 4.370039(2).
\]  

(12)

The cited value of \( \beta \) was calculated for the finite mass of the nucleus. Details of the calculation in the limit of no recoil \( (M \to \infty) \) can be found in [11]. For convenience of comparison with earlier results, it is worth writing explicitly the relation to the \( Q \) term introduced by Araki and Sucher [12]:

\[ VOLUME 87, NUMBER 19 PHYSICAL REVIEW LETTERS 5 NOVEMBER 2001 \]

193003-2
\[
Q = \lim_{\rho \to 0} \left\langle \Theta(r - \rho) + (\ln \rho + \gamma)\delta(\vec{r}) \right\rangle = -\frac{1}{2\pi} \left\langle \frac{\ln r + \gamma}{r^2} \right\rangle \cdot \vec{p} \cdot \vec{p} 
\]

In Eqs. (11), (13), and below, all momentum operators standing to the right (left) of position-dependent operators are assumed to act on the right (left) wave function.

The next, \( \Theta(\alpha^4) \) correction to the energy [3] is
\[
\delta^{(4)}E = \alpha^4 \left[ -\frac{E^3}{2} + \frac{E^2(c)}{4} + \frac{E}{2} \left\{ 2CNC + c^2 - \frac{p^2}{2} + \pi Z[\delta(\vec{r}_1) + \delta(\vec{r}_2)] \right\} 
+ (V_{PGV_P} + V_{S\delta GSV_S}) + \pi k_{ee}(\delta(\vec{r}_1) + \delta(\vec{r}_2)) + \pi k_{ee}(\delta(\vec{e})) \right.
+ \left\langle \left\{ \frac{-3C_2(C_2 - C_N)^2}{4} - \frac{cC_2}{2} - \frac{C_N[c(\vec{p}_1 \cdot \vec{p}_2 + \vec{n}(\vec{n} \cdot \vec{p}_1)\vec{p}_2)]}{4} + \frac{p^2C_Np^2}{4} + \frac{1}{8} (\vec{p}_1 \cdot c^2\vec{p}_1 + \vec{p}_2 \cdot c^2\vec{p}_2 \right. 
\frac{1}{4} (\vec{p}_1 \times \vec{p}_2)\vec{p}_1 \times \vec{p}_2) + \frac{p^2}{4} \vec{n}\vec{p}_2 - \frac{3p^2}{8} \vec{n}\vec{p}_2 \right\} + \left( \vec{E}_1 \cdot \vec{E}_2 - (\vec{n} \cdot \vec{E}_1) \vec{n} \cdot \vec{E}_2 - 2(\vec{E}_1 - \vec{E}_2) \cdot \vec{e} \right)
+ \left[ \frac{3}{32} \left( \frac{p^2 - 3(\vec{n} \cdot \vec{p})^2}{r^2} + \frac{\pi \delta(\vec{r})}{2} \left( \frac{9p^2}{16} + C_N \right) + \pi Z \left[ \frac{3p^2}{2} - \frac{2Z - 1}{r^2} \right] + (1 \leftrightarrow 2) \right) 
- \frac{Z^2}{2} \left( \frac{1}{r} \right) (i\vec{n} \cdot \vec{p}_1 + Z) + (1 \leftrightarrow 2) \right] - \frac{\ln r + \gamma}{r^2} i\vec{n} \cdot \vec{p}
\right\} + \alpha^2 \delta^{(2)}E \left( \frac{E^2}{2} \right) = 139.60(1)\alpha^4. \quad (14)
\]

Here we use the following notations: \( C = C_N + c \), \( C_N = C_1 + C_2 \), \( c = 1/r \), \( C_1 = 2D(\vec{r}_1) \), \( C_2 = -Z/r^2 \), \( \vec{e} = \vec{n}/r^2 \), and \( \vec{E}_1, \vec{E}_2 = -Z\vec{n}_1/\vec{r}_1, Z\vec{n}_2/\vec{r}_2 \). The terms \( \langle V_{PGV_P} \rangle \) and \( \langle V_{S\delta GSV_S} \rangle \) in (14), where \( G \) is the reduced Green function of the Schrödinger equation \((H - E)G(\vec{r}_1, \vec{r}_1'; \vec{r}_2, \vec{r}_2') = \psi(\vec{r}_1, \vec{r}_2)\psi(\vec{r}_1', \vec{r}_2') - \delta(\vec{r}_1 - \vec{r}_1')\delta(\vec{r}_2 - \vec{r}_2') \), represent the effects of virtual transitions into triplet \( P \) and singlet \( S \) excited states, respectively (see [3] for details). Perturbations inducing those transitions are
\[
V_P = \frac{\bar{s}_1 - \bar{s}_2}{4} \left( \frac{\bar{Z}_1}{\bar{r}_1} - \frac{\bar{Z}_2}{\bar{r}_2} + \vec{\tilde{p}} \times \vec{\tilde{p}} \right), \quad (15)
\]
where \( \bar{1}, \bar{2} = \bar{r}_1, \bar{2} \times \bar{p}_1, \bar{2} \), and \( V_S = E \frac{C_N + 2c}{2} + \frac{\{p^2 + c, p^2 + c\}}{8} - \frac{C_Nc}{2} - \frac{3c^2}{4}
\]
\[
+ \frac{1}{4} (\vec{p}_1 \cdot c\vec{p}_1 + (\vec{p}_1 \cdot \vec{n})c(\vec{n} \cdot \vec{p}_2 \right\} + \left( \vec{p}_1 \times \vec{p}_2 \right)c(\vec{p}_1 \times \vec{p}_2) \right) \right. 
+ \left\langle \left( \vec{p}_1 \cdot c^2\vec{p}_1 + \vec{p}_2 \cdot c^2\vec{p}_2 \right) \right\rangle = 0.811,
\]
\[
\left\langle \frac{p^2C_Np^2}{4} \right\rangle = -36.983,
\]
\[
\left\langle \frac{\vec{p}_1 \cdot c^2\vec{p}_1 + \vec{p}_2 \cdot c^2\vec{p}_2}{8} \right\rangle = 1.142,
\]
\[
\left\langle \frac{\vec{p}_1 \times \vec{p}_2 c(\vec{p}_1 \times \vec{p}_2)}{4} \right\rangle = 1.078,
\]
\[
\left\langle \frac{p^2c(\vec{n} \cdot \vec{p}_2)^2 + (\vec{p}_1 \cdot \vec{n})^2c(\vec{n} \cdot \vec{p}_2)^2}{8} \right\rangle = 0.03,
\]

Here we use the following notations: \( C = C_N + c \), \( C_N = C_1 + C_2 \), \( c = 1/r \), \( C_1 = 2D(\vec{r}_1) \), \( C_2 = -Z/r^2 \), \( \vec{e} = \vec{n}/r^2 \), and \( \vec{E}_1, \vec{E}_2 = -Z\vec{n}_1/\vec{r}_1, Z\vec{n}_2/\vec{r}_2 \). The terms \( \langle V_{PGV_P} \rangle \) and \( \langle V_{S\delta GSV_S} \rangle \) in (14), where \( G \) is the reduced Green function of the Schrödinger equation \((H - E)G(\vec{r}_1, \vec{r}_1'; \vec{r}_2, \vec{r}_2') = \psi(\vec{r}_1, \vec{r}_2)\psi(\vec{r}_1', \vec{r}_2') - \delta(\vec{r}_1 - \vec{r}_1')\delta(\vec{r}_2 - \vec{r}_2') \), represent the effects of virtual transitions into triplet \( P \) and singlet \( S \) excited states, respectively (see [3] for details). Perturbations inducing those transitions are
\[
V_P = \frac{\bar{s}_1 - \bar{s}_2}{4} \left( \frac{\bar{Z}_1}{\bar{r}_1} - \frac{\bar{Z}_2}{\bar{r}_2} + \vec{\tilde{p}} \times \vec{\tilde{p}} \right), \quad (15)
\]
where \( \bar{1}, \bar{2} = \bar{r}_1, \bar{2} \times \bar{p}_1, \bar{2} \), and \( V_S = E \frac{C_N + 2c}{2} + \frac{\{p^2 + c, p^2 + c\}}{8} - \frac{C_Nc}{2} - \frac{3c^2}{4}
\]
\[
+ \frac{1}{4} (\vec{p}_1 \cdot c\vec{p}_1 + (\vec{p}_1 \cdot \vec{n})c(\vec{n} \cdot \vec{p}_2 \right\} + \left( \vec{p}_1 \times \vec{p}_2 \right)c(\vec{p}_1 \times \vec{p}_2) \right) \right. 
+ \left\langle \left( \vec{p}_1 \cdot c^2\vec{p}_1 + \vec{p}_2 \cdot c^2\vec{p}_2 \right) \right\rangle = 0.811,
\]
\[
\left\langle \frac{p^2C_Np^2}{4} \right\rangle = -36.983,
\]
\[
\left\langle \frac{\vec{p}_1 \cdot c^2\vec{p}_1 + \vec{p}_2 \cdot c^2\vec{p}_2}{8} \right\rangle = 1.142,
\]
\[
\left\langle \frac{\vec{p}_1 \times \vec{p}_2 c(\vec{p}_1 \times \vec{p}_2)}{4} \right\rangle = 1.078,
\]
\[
\left\langle \frac{p^2c(\vec{n} \cdot \vec{p}_2)^2 + (\vec{p}_1 \cdot \vec{n})^2c(\vec{n} \cdot \vec{p}_2)^2}{8} \right\rangle = 0.03,
\]
\[
\langle 2(\hat{n} \cdot \hat{p}_2)(\hat{E}_1 \cdot \hat{p}_2) + (\hat{n} \cdot \hat{E}_1)[(\hat{n} \cdot \hat{p}_2)^2 - p_2^2]\rangle = 4.749,
\]
\[
\langle r \frac{3\hat{E}_1 \cdot \hat{E}_2 - (\hat{n} \cdot \hat{E}_1)(\hat{n} \cdot \hat{E}_2) - 2(\hat{E}_1 - \hat{E}_2) \cdot \hat{e}}{8} \rangle = 1.434,
\]
\[
\langle -\frac{3}{32} \frac{p_2^2 - 3(\hat{n} \cdot \hat{p})^2}{r^3} \rangle = -0.353,
\]
\[
\langle \frac{9\pi \delta(\hat{r})p_2^2}{32} \rangle = 1.325,
\]
\[
\langle \frac{\pi \delta(\hat{r})C_N}{2} \rangle = -2.508,
\]
\[
\langle \frac{3\pi \delta(\hat{r}_1)p_2^2}{2} + (1 \leftrightarrow 2) \rangle = 18.421,
\]
\[
\langle \frac{3\pi \delta(\hat{r}_1)C_2}{2} + (1 \leftrightarrow 2) \rangle = -25.066,
\]
\[
\langle \frac{3}{2\pi^3} \left( i\hat{n} \cdot \hat{p} - \frac{1}{2} \right) \rangle = -0.958,
\]
\[
\langle \frac{1}{\hat{r}_1^3} (i\hat{n}_1 \cdot \hat{p}_1 + Z) + (1 \leftrightarrow 2) \rangle = 4.706.
\]

Finally, the part of the \( O(\alpha^5) \) correction enhanced by \( \ln^2 \alpha \) (and, hence, presumably the leading one) [14] is

\[
\delta^{(5)} E = -4Z^3\alpha^5 \ln^2(Z\alpha) \langle \delta(\hat{r}_1) + \delta(\hat{r}_2) \rangle = 2070\alpha^5.
\]

(19)

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

\[
E_{\text{He}^+} = -\frac{\mu Z^2}{2} + \frac{2\mu^3 Z^4 R_N^2}{3}
\]
\[
- \mu Z^4 \alpha^2 \left[ \frac{5}{8} \left( 1 + \frac{\mu^3}{M^3} \right) - \frac{\mu^2}{2} + \frac{\mu^2}{M} \right]
\]
\[
- \frac{4\mu^3 Z^4 \alpha^3}{3\pi} \left[ \ln(\mu Z\alpha)^2 + \beta_H - \frac{19}{30} \right]
\]
\[
- \frac{2Z^5 \alpha^3}{3\pi M} \left[ \ln(Z\alpha) + 4\beta_H - 7\ln2 - \frac{31}{3} \right]
\]
\[
+ Z^3 \alpha^4 \left( k_eN - \frac{9Z^3}{16} \right) - 4Z^6 \alpha^5 \ln^2(Z\alpha).
\]

(20)

Here \( \beta_H = 2.984 \times 10^{-5} \) is the nuclear charge radius \( R_N \) expressed in the atomic units, and \( \mu = M/(M+1) \) is the reduced mass of the ion in units of the electron mass.

Comparison of our result (1) with the most recent experimental values,\n\[
\nu_{\text{expt}}^{1S-2P}(1S) = 5945204238(45) \text{ MHz},
\]
and\n\[
\nu_{\text{expt}}^{2S-2S}(1S) = 5945204356(48) \text{ MHz},
\]
extracted from the measurements of \( 1S-2P \) [15] and \( 1S-2S \) [16] 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. Further theoretical and experimental efforts are desirable in order to further clarify the situation.

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[6] For \( M, \alpha, \) and the Rydberg constant \( \text{Ry} \), we use the values recommended by the National Institute of Standards and Technology (see http://physics.nist.gov/cuu).