

Ionization Potential of the Helium Atom

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(Received 5 July 2001; revised manuscript received 17 September 2001; published 23 October 2001)

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 α^4 , $\alpha^3 m_e/m_\alpha$, and $\alpha^5 \ln^2 \alpha$. 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.

DOI: 10.1103/PhysRevLett.87.193003

PACS numbers: 31.30.Jv, 12.20.Ds, 32.10.Fn

In contrast to the theoretical description of electromagnetically bound two-body systems such as hydrogen, positronium, or muonium, where considerable progress has been achieved (for the recent reviews, see, e.g., [1]), high-precision calculations in more complex atoms have been worked out to a lesser degree. The central problem with an extension of the methods developed for the two-body problem to few-electron atoms is that those methods usually strongly rely on the solution of the Schrödinger equation for a single particle in the Coulomb field. Having a simple analytic form, such a solution is a perfect reference point for the quantum-mechanical perturbation theory, and various observables can be calculated as a power series in the fine structure constant α . In higher orders of this perturbation theory, where ultraviolet divergences usually appear indicating a breakdown of the nonrelativistic approximation, the explicit form of the nonrelativistic solution facilitates the extraction of these divergences. They can then be canceled by matching with 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 forces, can be solved numerically with very high accuracy [2], the lack of an analytic solution makes the problem of the divergences cancellation more complicated than in 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 (NRQED) [4] in dimensional regularization, it was demonstrated in [3] how all divergences arising in the quantum-mechanical perturbation theory can be extracted and canceled at the *operator* level, i.e., without recourse to an explicit form of the helium wave function. The $\mathcal{O}(\alpha^4)$ correction to singlet S levels of the He^4 atom was represented as a sum of finite average values of the regularization-independent operators. Another approach, using an auxiliary parameter to separate hard- and soft-scale contributions, has been developed in [5].

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

$$\nu_{\text{th}}(1^1S) = 5\,945\,204\,223(42) \text{ MHz}. \quad (1)$$

Along with the nonrelativistic energy, this result includes all $\mathcal{O}(\alpha^2)$, $\mathcal{O}(\alpha^3)$, $\mathcal{O}(\alpha^4)$, and $\mathcal{O}(\alpha^5 \ln^2 \alpha)$ relativistic and radiative corrections. We take into account the finite nucleus-to-electron mass ratio $M \equiv m_\alpha/m_e = 7\,294.299\,508(16)$ [6] exactly in the nonrelativistic and $\mathcal{O}(\alpha^2)$ contributions, include the first ($\sim 1/M$) recoil correction into the $\mathcal{O}(\alpha^3)$ 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

$$\delta_{\text{chr}} E = \frac{2\pi Z\alpha}{3} R_N^2 \langle \delta(\vec{r}_1) + \delta(\vec{r}_2) \rangle. \quad (2)$$

Here $Z = 2$ is the charge of the nucleus (in units of the proton charge), while \vec{r}_1 and \vec{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 $\mathcal{O}(\alpha^5 \ln^2 \alpha)$ 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 [8] and including the $\mathcal{O}(\alpha^4)$ and $\mathcal{O}(\alpha^3/M)$ effects only partially. The uncertainty in (3) exceeds that in (1) because only part of the $\mathcal{O}(\alpha^4)$ 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 α . The leading (~ 1) contribution, the Schrödinger energy E , and the corresponding wave function ψ are found as a solution of the variational problem,

$$E = \min_{\psi} \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}, \quad (4)$$

for the helium atom Hamiltonian taken in the nonrelativistic approximation,

$$H = \frac{p_1^2 + p_2^2}{2} + \frac{P^2}{2M} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r}. \quad (5)$$

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 $e = \hbar = m_e = 1$ 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,

$$\psi_n = \exp(-k_1^n r_1 - k_2^n r_2 - k_3^n r), \quad (6)$$

$$n = 1, \dots, N.$$

The complex exponents k_a^n are chosen in a quasirandom manner from a rectangular area on the complex plane, for example,

$$\text{Re} k_a^n = K_a^{\min} + \left\lfloor \frac{n(n+1)}{2} \sqrt{p_a} \right\rfloor (K_a^{\max} - K_a^{\min}), \quad (7)$$

where $\lfloor x \rfloor$ denotes a fractional part of x , p_a is some prime number, while (K_a^{\min}, K_a^{\max}) is a variational interval. Imaginary parts of the exponents are generated in a similar way. We use both real and imaginary parts of ψ_n to form a set of real basis functions. In particular, the ground-state wave function ψ is a linear combination of $2N$ basis functions $\text{Re}\psi_n, \text{Im}\psi_n, n = 1, \dots, N$, symmetric over the interchange of the electrons 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,

$$\int d^3 r_1 \int d^3 r_2 \frac{\exp(-k_1 r_1 - k_2 r_2 - k_3 r)}{r_1 r_2 r} = \frac{16\pi^2}{(k_1 + k_2)(k_2 + k_3)(k_3 + k_1)}, \quad (8)$$

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,

$$E = -2.903\,304\,557\,727\,940\,23(1). \quad (9)$$

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 ψ :

$$\delta^{(2)} E = \alpha^2 \left\langle -\frac{p_1^4 + p_2^4}{8} - \frac{P^4}{8M^3} + \pi Z \frac{\delta(\vec{r}_1) + \delta(\vec{r}_2)}{2} + \pi \delta(\vec{r}) - \frac{1}{2} \left[\vec{p}_1 \frac{1}{r} \cdot \vec{p}_2 + (\vec{p}_1 \cdot \vec{n}) \frac{1}{r} (\vec{n} \cdot \vec{p}_2) \right] \right. \\ \left. + \frac{Z}{2M} \left[\vec{p}_1 \frac{1}{r_1} \cdot \vec{P} + (\vec{p}_1 \cdot \vec{n}_1) \frac{1}{r_1} (\vec{n}_1 \cdot \vec{P}) + (1 \rightarrow 2) \right] \right\rangle = -1.952\,050\,77(1)\alpha^2. \quad (10)$$

Here $\vec{n} = \vec{r}/r$ and $\vec{n}_{1,2} = \vec{r}_{1,2}/r_{1,2}$. 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 $\vec{s}_1 \vec{s}_2$ by its eigenvalue in the singlet state, $-3/4$.

Order α^3 and α^3/M corrections to the energy can be represented as follows (see [3] and references therein):

$$\delta^{(3)} E = \alpha^3 \left[\frac{4Z}{3} \left(-\ln \alpha^2 - \beta + \frac{19}{30} \right) \langle \delta(\vec{r}_1) + \delta(\vec{r}_2) \rangle + \left(\frac{14}{3} \ln \alpha + \frac{164}{15} \right) \langle \delta(\vec{r}) \rangle + \frac{7}{3\pi} \left\langle \frac{\ln r + \gamma}{r^2} i \vec{n} \cdot \vec{p} \right\rangle \right. \\ \left. + \frac{2Z^2}{3M} \left(-\ln \alpha - 4\beta + \frac{31}{3} \right) \langle \delta(\vec{r}_1) + \delta(\vec{r}_2) \rangle + \frac{7Z^2}{3\pi M} \left\langle \frac{\ln r_1 + \gamma}{r_1^2} i \vec{n}_1 \cdot \vec{p}_1 + (1 \rightarrow 2) \right\rangle \right] \\ = 57.270\,34(2)\alpha^3. \quad (11)$$

Here $\gamma = 0.5772\dots$ is the Euler constant and β is the helium Bethe logarithm [10] defined as

$$\beta = \frac{\langle (\vec{p}_1 + \vec{p}_2)(H - E) \ln[2(H - E)](\vec{p}_1 + \vec{p}_2) \rangle}{\langle (\vec{p}_1 + \vec{p}_2)(H - E)(\vec{p}_1 + \vec{p}_2) \rangle} = 4.370\,039(2). \quad (12)$$

The cited value of β was calculated for the finite mass of the nucleus. Details of the calculation in the limit of no recoil ($M \rightarrow \infty$) 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]:

$$Q = \lim_{\rho \rightarrow 0} \left\langle \frac{\Theta(r - \rho)}{4\pi r^3} + (\ln \rho + \gamma) \delta(\vec{r}) \right\rangle = -\frac{1}{2\pi} \left\langle \frac{\ln r + \gamma}{r^2} i\vec{n} \cdot \vec{p} \right\rangle. \quad (13)$$

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, $\mathcal{O}(\alpha^4)$ correction to the energy [3] is

$$\begin{aligned} \delta^{(4)}E = \alpha^4 & \left\{ -\frac{E^3}{2} + \frac{E^2 \langle c \rangle}{4} + \frac{E}{4} \left\langle 2C_N C + c^2 - \frac{p_1^2 p_2^2}{2} - \pi Z [\delta(\vec{r}_1) + \delta(\vec{r}_2)] \right\rangle \right. \\ & + \langle V_P G V_P \rangle + \langle V_S G V_S \rangle + \pi k_{eN} \langle \delta(\vec{r}_1) + \delta(\vec{r}_2) \rangle + \pi k_{ee} \langle \delta(\vec{r}) \rangle \\ & + \left\langle -\frac{3C_1 C_2 C_N}{4} - \frac{c C_N C}{2} - \frac{C_N c [\vec{p}_1 \cdot \vec{p}_2 + \vec{n}(\vec{n} \cdot \vec{p}_1) \vec{p}_2]}{4} + \frac{p_1^2 C_N p_2^2}{4} + \frac{\vec{p}_1 \cdot c^2 \vec{p}_1 + \vec{p}_2 \cdot c^2 \vec{p}_2}{8} \right. \\ & + \frac{(\vec{p}_1 \times \vec{p}_2) c (\vec{p}_1 \times \vec{p}_2)}{4} - \frac{p_1^2 c (\vec{n} \cdot \vec{p}_2)^2 + (\vec{p}_1 \cdot \vec{n})^2 c p_2^2 - 3(\vec{p}_1 \cdot \vec{n})^2 c (\vec{n} \cdot \vec{p}_2)^2}{8} \\ & - \frac{2(\vec{n} \cdot \vec{p}_2) (\vec{E}_1 \cdot \vec{p}_2) + (\vec{n} \cdot \vec{E}_1) [(\vec{n} \cdot \vec{p}_2)^2 - p_2^2]}{4} + r \frac{3\vec{E}_1 \cdot \vec{E}_2 - (\vec{n} \cdot \vec{E}_1) (\vec{n} \cdot \vec{E}_2) - 2(\vec{E}_1 - \vec{E}_2) \cdot \vec{e}}{8} \\ & - \frac{3}{32} \frac{P^2 - 3(\vec{n} \cdot \vec{P})^2}{r^3} + \frac{\pi \delta(\vec{r})}{2} \left(\frac{9P^2}{16} + C_N \right) + \frac{\pi Z}{4} \left[\delta(\vec{r}_1) \left(\frac{3p_2^2}{2} - \frac{2Z - 1}{r_2} \right) + (1 \leftrightarrow 2) \right] \\ & - \frac{(\vec{E}_1 - \vec{E}_2) \cdot \vec{e}}{32} + \frac{Z^2}{2} \left[\frac{1}{r_1^3} (i\vec{n}_1 \cdot \vec{p}_1 + Z) + (1 \leftrightarrow 2) \right] - \frac{\ln r + \gamma}{2r^2} i\vec{n} \cdot \vec{p} \\ & \left. + \frac{3}{2r^3} \left(i\vec{n} \cdot \vec{p} - \frac{1}{2} \right) \right\} + \frac{\alpha^2 \delta^{(2)} E \langle c \rangle}{2} = 139.60 (1) \alpha^4. \quad (14) \end{aligned}$$

Here we use the following notations: $C = C_N + c$, $C_N = C_1 + C_2$, $c = 1/r$, $C_{1,2} = -Z/r_{1,2}$, $\vec{e} = \vec{n}/r^2$, and $\vec{E}_{1,2} = -Z\vec{n}_{1,2}/r_{1,2}^2$. 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 $(H - E)G(\vec{r}_1, \vec{r}_2 | \vec{r}'_1, \vec{r}'_2) = \psi(\vec{r}_1, \vec{r}_2) \psi(\vec{r}'_1, \vec{r}'_2) - \delta(\vec{r}_1 - \vec{r}'_1) \delta(\vec{r}_2 - \vec{r}'_2)$, represent the effects of virtual transitions into triplet P and singlet S excited states, respectively (see [3] for details). Perturbations inducing those transitions are

$$V_P = \frac{\vec{s}_1 - \vec{s}_2}{4} \left(\frac{Z\vec{l}_1}{r_1^3} - \frac{Z\vec{l}_2}{r_2^3} + \frac{\vec{r} \times \vec{P}}{r^3} \right), \quad (15)$$

where $\vec{l}_{1,2} = \vec{r}_{1,2} \times \vec{p}_{1,2}$, and

$$\begin{aligned} V_S = E & \frac{C_N + 2c}{2} + \frac{\{p_1^2 + c, p_2^2 + c\}}{8} - \frac{C_N C}{2} - \frac{3c^2}{4} \\ & + \frac{\vec{p}_1 (C_N - c) \vec{p}_1 + (1 \leftrightarrow 2)}{4} \\ & - \frac{\vec{p}_1 c \vec{p}_2 + (\vec{p}_1 \cdot \vec{n}) c (\vec{n} \cdot \vec{p}_2)}{2}. \quad (16) \end{aligned}$$

TABLE I. Contributions to the total ionization potential of the helium ground state. Uncertainty in the nonrelativistic value is due to uncertainty in the nuclear mass.

	$\delta \nu_{\text{th}}(1^1S)$, MHz
Nonrelativistic approximation	5 945 262 288.62 (4)
α^2	-16 800.338 (4)
α^3	-40 483.984 (50)
α^4	-834.9 (2)
$\alpha^5 \ln^2 \alpha$ (and higher)	84 (42)
Finite charge radius	-29.55 (4)
Total	5 945 204 223 (42)

The contact terms enter into Eq. (14) with the coefficients

$$\begin{aligned} k_{eN} = & \frac{Z^3}{2} + \frac{427Z^2}{96} - \frac{10Z}{27} - \frac{9Z\zeta(3)}{4\pi^2} - \frac{2179Z}{648\pi^2} \\ & + \frac{3Z - 4Z^2}{2} \ln 2 = 16.3557, \quad (17) \end{aligned}$$

$$\begin{aligned} k_{ee} = & -\ln \alpha + \frac{3285}{216} - \frac{335}{54\pi^2} - \frac{29 \ln 2}{2} + \frac{15\zeta(3)}{4\pi^2} \\ & = 10.37657. \quad (18) \end{aligned}$$

Average values for a part of the operators entering into Eq. (14) can be found in the literature (see, e.g., [13]). For the average values of the new operators, we have obtained the following results:

$$\langle V_P G V_P \rangle = -0.392, \quad \langle V_S G V_S \rangle = -18.48,$$

$$\left\langle -\frac{C_N c [\vec{p}_1 \cdot \vec{p}_2 + \vec{n}(\vec{n} \cdot \vec{p}_1) \vec{p}_2]}{4} \right\rangle = 0.811,$$

$$\left\langle \frac{p_1^2 C_N p_2^2}{4} \right\rangle = -36.983,$$

$$\left\langle \frac{\vec{p}_1 \cdot c^2 \vec{p}_1 + \vec{p}_2 \cdot c^2 \vec{p}_2}{8} \right\rangle = 1.142,$$

$$\left\langle \frac{(\vec{p}_1 \times \vec{p}_2) c (\vec{p}_1 \times \vec{p}_2)}{4} \right\rangle = 1.078,$$

$$\left\langle \frac{p_1^2 c (\vec{n} \cdot \vec{p}_2)^2 + (\vec{p}_1 \cdot \vec{n})^2 c p_2^2 - 3(\vec{p}_1 \cdot \vec{n})^2 c (\vec{n} \cdot \vec{p}_2)^2}{8} \right\rangle = 0.03,$$

$$\begin{aligned} \left\langle \frac{2(\vec{n} \cdot \vec{p}_2)(\vec{E}_1 \cdot \vec{p}_2) + (\vec{n} \cdot \vec{E}_1)[(\vec{n} \cdot \vec{p}_2)^2 - p_2^2]}{4} \right\rangle &= 4.749, \\ \left\langle r \frac{3\vec{E}_1 \cdot \vec{E}_2 - (\vec{n} \cdot \vec{E}_1)(\vec{n} \cdot \vec{E}_2) - 2(\vec{E}_1 - \vec{E}_2) \cdot \vec{e}}{8} \right\rangle &= 1.434, \\ \left\langle -\frac{3}{32} \frac{P^2 - 3(\vec{n} \cdot \vec{P})^2}{r^3} \right\rangle &= -0.353, \quad \left\langle \frac{9\pi\delta(\vec{r})P^2}{32} \right\rangle = 1.325, \quad \left\langle \frac{\pi\delta(\vec{r})C_N}{2} \right\rangle = -2.508, \\ \left\langle \frac{3\pi\delta(\vec{r}_1)p_2^2}{2} + (1 \leftrightarrow 2) \right\rangle &= 18.421, \quad \left\langle \frac{3\pi\delta(\vec{r}_1)C_2}{2} + (1 \leftrightarrow 2) \right\rangle = -25.066, \quad \left\langle -\frac{(\vec{E}_1 - \vec{E}_2) \cdot \vec{e}}{32} \right\rangle = 0.409, \\ \left\langle \frac{3}{2r^3} \left(i\vec{n} \cdot \vec{p} - \frac{1}{2} \right) \right\rangle &= -0.958, \quad \left\langle \frac{1}{r_1^3} (i\vec{n}_1 \cdot \vec{p}_1 + Z) + (1 \rightarrow 2) \right\rangle = 4.706. \end{aligned}$$

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

$$\delta^{(5)}E = -4Z^3\alpha^5 \ln^2(Z\alpha) \langle \delta(\vec{r}_1) + \delta(\vec{r}_2) \rangle \approx 2070\alpha^5. \quad (19)$$

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

$$\begin{aligned} E_{\text{He}^+} &= -\frac{\mu Z^2}{2} + \frac{2\mu^3 Z^4 r_N^2}{3} \\ &- \mu Z^4 \alpha^2 \left[\frac{5}{8} \left(1 + \frac{\mu^3}{M^3} \right) - \frac{\mu^2}{2} + \frac{\mu^2}{M} \right] \\ &- \frac{4\mu^3 Z^4 \alpha^3}{3\pi} \left[\ln\mu(Z\alpha)^2 + \beta_H - \frac{19}{30} \right] \\ &- \frac{2Z^5 \alpha^3}{3\pi M} \left[\ln(Z\alpha) + 4\beta_H - 7\ln 2 - \frac{31}{3} \right] \\ &+ Z^3 \alpha^4 \left(k_{eN} - \frac{9Z^3}{16} \right) - \frac{4Z^6 \alpha^5}{\pi} \ln^2(Z\alpha). \quad (20) \end{aligned}$$

Here $\beta_H = 2.984\,128\,555\,765\,5\dots$ is the Bethe logarithm for the hydrogen ground state, $r_N = 3.162(2) \times 10^{-5}$ 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,

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

and

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

extracted from the measurements of 1^1S-2^1P [15] and 1^1S-2^1S [16] intervals, respectively, shows that the theoretical value (1) agrees well with the former (21) and is within 2σ 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.

V. K. thanks K. Pachucki for useful discussions. A. Y. is grateful to V.F. Dmitriev, L.F. Hailo, the late V.B.

Telitsyn, V. V. Vecheslavov, and O. V. Zhirov for advice concerning numerical calculations and to A. Czarnecki and K. Melnikov for careful reading of the manuscript. V. K. was supported by the NSF through a grant for the Institute for Theoretical Atomic and Molecular Physics at Harvard University and Smithsonian Astrophysical Observatory, which is gratefully acknowledged. A. Y. was partially supported by the Russian Ministry of Higher Education and by the Russian Foundation for Basic Research under Grant No. 00-02-17646.

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