Precision Spectroscopy of the Pionic Helium-4

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(Received 27 January 2022; revised 16 February 2022; accepted 9 March 2022; published 3 May 2022)

The transition frequency of $(n,\ell)=(17,16)\to(16,15)$ in pionic helium-4 is calculated to an accuracy of 4 ppb (parts per billion), including relativistic and quantum electrodynamic corrections up to $O(R_\infty\alpha^5)$. Our calculations significantly improve the recent theoretical values [Hori *et al.*, Phys. Rev. A **89**, 042515 (2014)]. In addition, collisional effects between pionic helium and target helium on transition frequencies are estimated. Once measurements reach the ppb level, our Letter will improve the value of the π^- mass by 2–3 orders of magnitude.

DOI: 10.1103/PhysRevLett.128.183001

Pionic helium $\pi\mathrm{He}^+$ is an exotic three-body atomic system that consists of a helium nucleus, an electron, and a negatively charged π^- meson. This system can be formed by a negative pion that is stopped and then replaces one of the electrons in a helium atom. If it occupies a nearly circular orbit $n\sim\ell+1$ with $n\sim 16$, it forms a long-lived state that can be studied by methods of precision laser spectroscopy. The principal motivation of studying this three-body pionic helium is to determine the pion mass at the ppb level. The basic idea is that, since the sensitivity coefficient η of a transition frequency ν to the π^- mass m_π can be expressed as $\eta\sim(\delta\nu/\nu)/(\delta m_\pi/m_\pi)$, which is 1.88 for the transition $(n,\ell)=(17,16)\to(16,15)$, if this frequency can be both measured and calculated to an accuracy of ppb level, one can derive a value of m_π at a similar ppb level. Such a high precision value of m_π can impose direct experimental constraints on the mass of the antineutrino of muon flavor [1]. Currently, the most precise value of π^- mass is $m_\pi=273.13244(35)m_e$ at 1.3 ppm determined by x-ray wavelength measurements for transitions in π^--mesonic atoms [2–4], where the precision is mainly limited by large line widths [5].

Recently, significant progress has been made in experiments confirming the existence of $\pi\mathrm{He}^+$ by detecting the $(17,16)\to(17,15)$ transition at the frequency of 183760 GHz at Paul Scherrer Institute (PSI) [6]. However, for this transition the line broadening about 100 GHz due to atomic collisions prevents experiments from achieving higher precision. Therefore, the PSI team plans to search for a narrower transition $(17,16)\to(16,15)$, which may potentially improve the accuracy by at least three orders of magnitude at ppb level [6–8].

The purpose of this Letter is to present the quantum electrodynamic (QED) calculations of some important transition frequencies in $\pi^4\mathrm{He}^+$. Special attention will be paid to the ppb-level experiments planned by PSI on the $(17,16)\to(16,15)$ transition. This level of accuracy requires not only the leading-order relativistic and QED corrections of $R_\infty\alpha^2$ and $R_\infty\alpha^3$ (R_∞ is the Rydberg constant and α is the fine structure constant) that have been previously evaluated [1], but also the higher-order terms of $R_\infty\alpha^4$ and $R_\infty\alpha^5$ that have never been calculated for $\pi^4\mathrm{He}^+$. In addition, the collisional frequency shifts for some transitions, including $(17,16)\to(16,15)$, are estimated for the first time, providing useful information for future high-precision experiments. Atomic units (a.u.) are used throughout unless otherwise stated. In order to facilitate a comparison with the previous calculations in Ref. [1], the same masses of π^- and ^{4}He nucleus are used: $m_\pi=273.1320m_e$ [9,10] and $m_\alpha=7294.2995361m_e$ [10] without considering their uncertainties.

According to the theory of nonrelativistic QED (NRQED) [11–13], an energy level of pionic helium can be expanded in powers of the fine structure constant α

$$E=E^{(0)}+E^{(2)}+E^{(3)}+E^{(4)}+E^{(5)}+O(\alpha^6),\quad (1)$$

where $E^{(n)}$ is the contribution of order $R_\infty\alpha^n$ that may include powers of $\ln\alpha$. Each term of $E^{(n)}$ can be written as an expectation value of some effective Hamiltonian.

$E^{(0)}$ in Eq. (1) is the eigenvalue of the nonrelativistic Hamiltonian $H^{(0)}=T+V$, where the kinetic and potential energy operators, in the center of mass frame, are respectively [14]

$$T = \frac{1}{2\mu_1}\mathbf{p}_1^2 + \frac{1}{2\mu_2}\mathbf{p}_2^2 + \frac{1}{m_0}\mathbf{p}_1\cdot\mathbf{p}_2, \tag{2}$$

$$V = \frac{z_0 z_1}{r_1} + \frac{z_0 z_2}{r_2} + \frac{z_1 z_2}{r_{12}}, \tag{3}$$

where the helium nucleus is taken as the zeroth particle sitting at the origin of the reference frame, indices 1 and 2 are designated, respectively, for the electron and pion, μ_1 and μ_2 are their reduced masses with respect to the helium nuclear mass m_0, z_0, z_1, and z_2 are the charges of the three particles, and $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$.

Since pion-excited states in $\pi\mathrm{He}^+$ are embedded in the electron continuum, these states are quasi-bound ones against Auger decay. Here we use the method of complex coordinate rotation (CCR) [15] to determine the complex eigenvalues of the rotated Hamiltonian

$$H^{(0)} \to H^{(0)}(\theta) = T\exp(-2i\theta) + V\exp(-i\theta), \tag{4}$$

under $r \to r\exp(i\theta)$, where the rotational angle θ is real and positive. Computational details can be found in Ref. [16] and see Supplemental Material [17].

$E^{(2)}$ is the expectation value of the spin-independent Breit-Pauli Hamiltonian [21]

$$\begin{aligned} H^{(2)} = \alpha^2\Bigg\{ &-\frac{\mathbf{p}_0^4}{8m_0^3} - \frac{\mathbf{p}_1^4}{8m_1^3} - \frac{\mathbf{p}_2^4}{8m_2^3} - \frac{\pi}{2}z_0 z_1\delta(\mathbf{r}_1) - \frac{\pi}{2}z_1 z_2\delta(\mathbf{r}_{12}) - \frac{z_0 z_1}{2m_0 m_1}\left[\frac{\mathbf{p}_0\cdot\mathbf{p}_1}{r_1} + \frac{\mathbf{r}_1\cdot(\mathbf{r}_1\cdot\mathbf{p}_0)\mathbf{p}_1}{r_1^3}\right] \\ &- \frac{z_0 z_2}{2m_0 m_2}\left[\frac{\mathbf{p}_0\cdot\mathbf{p}_2}{r_2} + \frac{\mathbf{r}_2\cdot(\mathbf{r}_2\cdot\mathbf{p}_0)\mathbf{p}_2}{r_2^3}\right] - \frac{z_1 z_2}{2m_1 m_2}\left[\frac{\mathbf{p}_1\cdot\mathbf{p}_2}{r_{12}} + \frac{\mathbf{r}_{12}\cdot(\mathbf{r}_{12}\cdot\mathbf{p}_1)\mathbf{p}_2}{r_{12}^3}\right]\Bigg\}, \end{aligned} \tag{5}$$

where $\mathbf{p}_0 = -\mathbf{p}_1 - \mathbf{p}_2$. For the nonrecoil part of $H^{(2)}$, in order to obtain enough significant digits, we not only apply the complex rotated wave functions but also apply the global operator method [22] to deal with more singular operators such as $\mathbf{p}_1^4$, $\delta(\mathbf{r}_1)$, and $\delta(\mathbf{r}_2)$. For the recoil part, it is sufficient to only use the closed-channel method [23]. It should be mentioned that in the work of Hori *et al.* [1], only the nonrecoil part of $H^{(2)}$ is considered by treating the electron in the field of two massive particles. This adiabatic approximation to the leading relativistic correction can cause an error of hundreds of ppb in the final transition frequency.

Moreover, the finite size correction of He^{2+} and π^- should be considered [24]:

$$E^{(2)}_{\mathrm{nuc}} = \frac{2\pi z_0 (R_0/a_0)^2}{3}\langle\delta(\mathbf{r}_1)\rangle + \frac{2\pi z_2 (R_2/a_0)^2}{3}\langle\delta(\mathbf{r}_{12})\rangle, \tag{6}$$

where R_0 is the root-mean-square (rms) radius of the nuclear charge distribution of He^{2+} and R_2 is for π^-, which are $R_0 = 1.6757(26)$ [25] and $R_2 = 0.659(4)$ fm [3]. This correction is included in $E^{(2)}$:

$$E^{(2)} = \langle H^{(2)}\rangle + E^{(2)}_{\mathrm{nuc}}. \tag{7}$$

$E^{(3)}$ is the leading radiative contribution of $R_\infty\alpha^3$, which can be expressed as [26–29]

$$\begin{aligned} E^{(3)} = &\frac{4\alpha^3}{3m_1^2}\left(-\ln\alpha^2 - \beta(n,\ell) + \frac{19}{30}\right)[z_0\langle\delta(\mathbf{r}_1)\rangle + z_2\langle\delta(\mathbf{r}_{12})\rangle] + \frac{2\alpha^3}{3m_1}\left(-\ln\alpha - 4\beta(n,\ell) + \frac{31}{3}\right)\left[\frac{z_0^2}{m_0}\langle\delta(\mathbf{r}_1)\rangle + \frac{z_2^2}{m_2}\langle\delta(\mathbf{r}_{12})\rangle\right] \\ &- \frac{14\alpha^3}{3m_1}\left[\frac{z_0^2}{m_0}Q_1 + \frac{z_2^2}{m_2}Q_{12}\right], \end{aligned} \tag{8}$$

where Q_1 and Q_{12} are the Araki-Sucher terms [30,31] for $\mathrm{He}^{2+} - e$ and $\pi^- - e$ pairs, respectively. Equation (8) should, in principle, also include the terms involving $\langle\delta(\boldsymbol{r}_2)\rangle$ and the Araki-Sucher term Q_{02} between the helium nucleus and pion. However, since the pionic helium is a quasiadiabatic system [32], and also the pion is in a circular orbital (n,ℓ) with high $\ell \sim 14$–16, $\langle\delta(\boldsymbol{r}_2)\rangle$ can be effectively assumed to be zero. In fact, the pion in $\pi\mathrm{He}^+$ is about 20 times slower than the electron for the states under consideration. The contribution from Q_{02} is also negligible due to the prefactor $1/(m_0 m_2)$ of two heavy particles. Finally, Eq. (8) contains the Bethe logarithm defined by

$$\beta(n,\ell) = \frac{\langle\mathbf{J}(H^{(0)} - E^{(0)})\ln[(H^{(0)} - E^{(0)})/R_\infty]\mathbf{J}\rangle}{\langle[\mathbf{J},[H^{(0)},\mathbf{J}]]/2\rangle}, \tag{9}$$

where $\mathbf{J}$ is the electric current density operator of the system [28]. Here $\beta(n,\ell)$ is evaluated for states of $\pi^4\mathrm{He}^+$ using the advanced Schwartz approach [33,34] to improve the previous calculations of Ref. [1] that use the adiabatic effective potential. For the $(17,16) \to (16,15)$ transition, our results are $\beta(17,16) = 4.428\,69(3)$ and $\beta(16,15) = 4.457\,87(3)$, which reduce the uncertainty of the $E^{(3)}$ contribution to 0.5 MHz.

The $R_\infty\alpha^4$-order contribution contains relativistic and radiative corrections

$$E^{(4)} = E^{(4)}_{\rm rel} + E^{(4)}_{\rm rad}. \tag{10}$$

In the above,

$$E^{(4)}_{\rm rel} = \langle H^{(4)}\rangle + \langle H^{(2)}\mathcal{Q}(E^{(0)} - H^{(0)})^{-1}\mathcal{Q}H^{(2)}\rangle, \tag{11}$$

where $\mathcal{Q}$ is the projection operator, $H^{(4)}$ is the $R_\infty\alpha^4$-order effective Hamiltonian for one-electron system

$$H^{(4)} = \alpha^4\left[\frac{\mathbf{p}_1^6}{16m_1^5} + \frac{(\nabla_1 V)^2}{8m_1^3} - \frac{3\pi}{16m_1^4}(\mathbf{p}_1^2\rho + \rho\mathbf{p}_1^2) + \frac{5}{128m_1^4}(\mathbf{p}_1^4 V + V\mathbf{p}_1^4) - \frac{5}{64m_1^4}(\mathbf{p}_1^2 V\mathbf{p}_1^2)\right], \tag{12}$$

and $\rho = \nabla_1^2 V/(4\pi)$. The calculation of $E^{(4)}_{\rm rel}$ has been performed in the two-center adiabatic approximation [35]. The obtained effective potential is averaged over the radial wave function of a particular state to obtain a final result.The correction due to the vibration is obtained using adiabatic approximation as Eq. (8b) of Ref. [36]. The $R_\infty\alpha^4$-order radiative correction can be taken in the external field approximation [24]. Following Ref. [37], one has

$$E^{(4)}_{\rm rad} = \alpha^4\frac{4\pi}{m_1^2}\left\{\left(\frac{139}{128} - \frac{\ln 2}{2} + \frac{5}{192}\right)[z_0^2\delta(\mathbf{r}_1) + z_2^2\delta(\mathbf{r}_{12})] - \frac{1}{4\pi^2}\left[\frac{2179}{648} + \frac{10}{27}\pi^2 - \frac{3}{2}\pi^2\ln 2 + \frac{9}{4}\zeta(3)\right] \times [z_0\delta(\mathbf{r}_1) + z_2\delta(\mathbf{r}_{12})]\right\}. \tag{13}$$

The dominant part of order $R_\infty\alpha^5$ contribution for the electron bounded by the $\mathrm{He}^{2+} - \pi^-$ two-center electrostatic field is [24,38]

$$E^{(5)} = E^{(5)}_{\rm se} + E^{(5)}_{\rm 2loop}, \tag{14}$$

where

$$E^{(5)}_{\rm se} = \alpha^5\left\{\left[A_{61}\ln\frac{1}{(z_0\alpha)^2} + A_{60} - \ln^2\frac{1}{(z_0\alpha)^2}\right]z_0^3\langle\delta(\mathbf{r}_1)\rangle + \left[A_{61}\ln\frac{1}{(z_2\alpha)^2} + A_{60} - \ln^2\frac{1}{(z_2\alpha)^2}\right]z_2^3\langle\delta(\mathbf{r}_{12})\rangle\right\}, \tag{15}$$

and

$$E^{(5)}_{\rm 2\,loop} = \frac{\alpha^5}{\pi}B_{50}z_0^2\langle\delta(\mathbf{r}_1)\rangle. \tag{16}$$

Here state independent coefficients $A_{61} = 5.419$ [39], $A_{60} = -30.924$ [40], and $B_{50} = -21.556$ [41,42] are taken from the atomic hydrogen ground state calculations. Although the contribution of this order can be evaluated using the Schwartz approach for the relativistic Bethe logarithm [43,44], the above approximation is sufficient to achieve a precision of ppb level.

Table I presents nonrelativistic energies and their associated widths, as well as the expectation values of operators of $\mathbf{p}_1^4$, $\delta(\mathbf{r}_1)$, and $\delta(\mathbf{r}_{12})$ for some metastable states with possible large populations in experiments (though the distribution of occupancy numbers of mesons captured by atoms in experiments is not clear). Our results are in agreement with the previous ones [1]. As can be seen from the table, the resulting accuracy for narrower-width states is generally higher than for wider-width states, and the calculations also favor those with smaller vibrational quantum numbers $\nu = n - \ell - 1$. Nonetheless, for the particular states of (17,16) and (16,15), the nonrelativistic energies are accurate to few parts in 10^{15} and 10^{13}, respectively, which far exceeds our target accuracy of the ppb level.

Table II lists our theoretical transition frequencies for some transitions in $\pi^4\mathrm{He}^+$, and comparison with available data. Table II also lists theoretical collisional shifts of frequencies due to the long-range interaction between $\pi^4\mathrm{He}^+$ and He. For $(17,16) \to (16,15)$ in particular, we also display all the nonrelativistic and QED contributions up to $R_\infty\alpha^5$. Compared to the values of Hori *et al.* [1], our calculations not only have significantly improved their leading-order relativistic and radiative corrections, but also have included, for the first time, the higher-order corrections of the $R_\infty\alpha^4$ term, obtained within the adiabatic approximation, and the $R_\infty\alpha^5$ term, which contributes to the final transition frequency at 140 and 14 ppb, respectively, with their uncertainty being 2.8 ppb. For the experimentally confirmed transition $(17,16) \to (17,15)$ [6], there is a 78(8) GHz difference from our value, which is roughly in agreement with the estimation based on the binary collision theory of spectral line shape [45]. In fact, at the density of helium target 2.18×10^{22} cm^{-3} used in the PSI experiment [6], the blueshift estimated by the theory is between 96 and 142 GHz. A rigorous calculation of collisional effects may be done by treating $\pi^4\mathrm{He}^+$-He as a six-body system using Gaussian basis sets [46,47] so that both short- and long-range interactions can be taken into consideration, which is very difficult and requires large computational efforts. As shown in Table II, when the target helium density is as low as 2×10^{18} cm^{-3}, where the short-range interaction may be neglected, the collisional shifts can be estimated using our long-range dispersion

TABLE I. Comparison of present nonrelativistic energies $E^{(0)}$, half Auger widths $\Gamma/2$, and the expectation values of operators $\mathbf{p}_1^4$, $\delta(\mathbf{r}_1)$, and $\delta(\mathbf{r}_2)$ (first row) with those of Ref. [1] (second row) for the $\pi^4\mathrm{He}^+$ system. In atomic units.

(n,ℓ)	$E^{(0)}$	$\Gamma/2$	$\mathbf{p}_1^4$	$\delta(\mathbf{r}_1)$	$\delta(\mathbf{r}_{12})$
(15,14)	−3.056 948 141(5)	$5.14(1)\times10^{-6}$	37.587(1)	1.271 445 7(1)	0.080 743 5(1)
	−3.056 948 141 7(4)	5.1380×10^{-6}	37.586951	1.271 444	0.080 743 4
(16,15)	−2.828 549 393 729(1)	$2.04(3)\times10^{-10}$	45.004 23(2)	1.495 184 39(1)	0.060 627 193(1)
	−2.828 549 393 73(4)	2.1×10^{-10}	45.004 106	1.495 182	0.060 6279
(17,15)	−2.685 427 191(5)	$2.502(2)\times10^{-6}$	53.949 5(3)	1.762 600(3)	0.040 246 3(3)
	−2.685 427 22(2)	2.50×10^{-6}	53.948 888	1.762 586	0.040 250 0
(17,16)	−2.657 512 438 501 60(1)	$1.1(1)\times10^{-13}$	52.830 545 9(3)	1.730 040 988 8(3)	0.041 122 564 48(3)
	−2.657 512 438 501 71	1.0×10^{-13}	52.830 517	1.730 041	0.041 122 6
(18,15)	−2.580 025 5(1)	$6.50(1)\times10^{-6}$	60.777(8)	1.966 93(4)	0.026 982(3)
	−2.580 025 54(1)	6.53×10^{-6}	60.776 506	1.966 939	0.026 981 8
(18,16)	−2.556 984 919 572(3)	$1.4(3)\times10^{-11}$	60.537 962(3)	1.960 760 468(1)	0.026 721 711 5(3)
	−2.556 984 919 572(2)	1.3×10^{-11}	60.537 978	1.960 761	0.026 721 7
(19,15)	−2.500 498 2(5)	$2.54(1)\times10^{-5}$	64.94(2)	2.090 28(5)	0.018 440(5)
	−2.500 498 02(7)	2.533×10^{-5}	64.946 166	2.090 275	0.018 439 8
(19,16)	−2.481 540 552 383(5)	$1.87(5)\times10^{-10}$	65.816 458(1)	2.119 201 966(3)	0.018 427 738 0(1)
	−2.481 540 552 39(1)	2.0×10^{-10}	65.817 187	2.119 201	0.018 427 7

TABLE II. Transition frequencies in $\pi^4\mathrm{He}^+$, as well as the collisional shifts at target He density of 2×10^{18} cm^{-3}, in GHz.

	Frequency	Collisional shift
	$(16,15)\to(15,14)$	
This Letter	1 502 734.38(42)	-6.28×10^{-8}
[1]	1 502 734.2	
	$(17,16)\to(17,15)$	
This Letter	183 681.654(41)	-8.71×10^{-8}
[1]	183 681.8(5)	
Experiment [6]	$183\,760(6)_{\mathrm{stat}}(6)_{\mathrm{syst}}$	
	$(17,16)\to(16,15)$	
$\Delta E^{(0)}$	1 125 369.104 121(7)	
$\Delta E^{(2)}$	−73.281 2(9)	
$\Delta E^{(3)}$	10.376 5(5)	
$\Delta E^{(4)}$	0.155 5(32)	
$\Delta E^{(5)}$	−0.015 5(31)	
Total (This Letter)	1 125 306.339 4(45)	1.14×10^{-8}
[1]	1 125 306.1	
	$(17,16)\to(18,15)$	
This Letter	509 770.3(10)	-3.40×10^{-7}
[1]	509 769.9	
	$(18,16)\to(17,15)$	
This Letter	845 055.577(41)	1.41×10^{-7}
[1]	845 055.5	
	$(18,16)\to(19,15)$	
This Letter	371 624.4(37)	-6.68×10^{-7}
[1]	371 625.8	

coefficients C_6 [48] of $\pi^4\mathrm{He}^+$-He, which are well below the ppb level.

In summary, we have greatly improved the accuracy of the transition frequency of $(17,16)\to(16,15)$ in $\pi^4\mathrm{He}^+$ by including the relativistic and QED corrections up to $R_\infty\alpha^5$, at the ppb level. Combined with future measurements of a similar level of precision, our result can be used to derive an atomic physics value of the π^- mass that is more accurate than the current value by 2–3 orders of magnitude.

This research was supported by the National Natural Science Foundation of China (Grants No. 11974382, No. 12121004 and No. 91636216) and the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB21020200). V. I. K. acknowledges the support from Chinese Academy of Science President's International Fellowship Initiative (Grant No. 2016VMA077). Z. C. Y. acknowledges the support from NSERC and SHARCnet of Canada.

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