Transition frequencies between the 2*S* and 2*P* states of the lithiumlike ion O^{5+}

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The Schrödinger equation for the 2*S* state and 2*P* state of the lithiumlike ion O^{5+} is solved by using the Rayleigh-Ritz variational method in Hylleraas coordinates. The leading-order relativistic and QED corrections are calculated perturbatively and higher-order corrections are estimated approximately. The transition frequencies between the $2S_{1/2}$ and $2P_J$ ($J = 1/2, 3/2$) states, as well as the fine-structure splitting between the $2P_{1/2}$ and $2P_{3/2}$ states, are determined and compared with experimental results.

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I. INTRODUCTION

For light atomic systems, such as $Z \leqslant 5$ with Z the nuclear charge number, the energy levels can be calculated to very high precision in the framework of the nonrelativistic quantum electrodynamics (NRQED) [1]. In this method, the energy level of an atomic system can be formally expressed as (in atomic units throughout, unless otherwise stated)

$$E = E_0 + \alpha^2 E_2 + \alpha^3 E_3 + \alpha^4 E_4 + \alpha^5 E_5 + \cdots , \qquad (1)$$

where E_0 denotes the nonrelativistic energy, $\alpha^2 E_2$ the leading-order relativistic correction, $\alpha^3 E_3$ the leading-order QED correction, and so on. For two- and three-electron atomic systems [1–3], E_0 can be calculated to sufficiently high accuracy by solving the Schrödinger equation using the variational method in Hylleraas coordinates. For four- and five-electron atomic systems, the most accurate nonrelativistic energies are determined variationally using explicitly correlated Gaussian (ECG) functions [4–7]. The leading-order relativistic and QED corrections of orders α^2 and α^3 can be evaluated perturbatively based on the nonrelativistic solutions.

For heavy atoms or ions, say $Z \geqslant 30$, due to large relativistic effects, the NRQED method is no longer adequate. The relativistic effects have to be taken into consideration from the beginning. Many theoretical methods have been developed for treating these systems, such as the relativistic many-body perturbation (RMBP) theory [8,9] and its variant the coupled cluster (CC) method [10,11], the relativistic configuration interaction (RCI) method [12], and the multiconfiguration Dirac-Fock (MCDF) method [13]. From now on, we will call all these methods the relativistic many-body (RMB) theory for convenience. At present, the accuracy of the RMB theory is mainly limited by the slow convergence of electron correlation effect and by the inadequate treatment of QED effect.

For the case of intermediate Z, for example $Z \sim 14$, the two above-mentioned kinds of approaches are feasible but with relatively lower accuracy. For the NRQED theory, the magnitude of high-order relativistic and QED corrections will increase fast as Z increases. These high-order corrections are very difficult to evaluate for a general state of an atomic system with more than one electron. Take the lithium atom as an example. The order α^4 corrections have only been calculated rigorously for the fine-structure splitting of the 2*P* state up to now [14,15]. For the RMB theory, the relatively strong electron correlation effect with $Z \sim 14$ is one of the main factors limiting the accuracy of the theory. Drake has developed a unified computational scheme that is valid over the whole range of nuclear charge [16], but this method has so far only been applied to two-electron atomic systems.

In this work, we will study the lithiumlike ion O^{5+} ($Z = 8$) using NRQED and compare our results with other theoretical and experimental values. The main motivation of this work is to supply reliable theoretical transition frequencies between the $2S_{1/2}$ and $2P_J$ ($J = 1/2, 3/2$) states of O^{5+} for the ongoing experiment on the precision measurement of O^{5+} at the Institute of Modern Physics, Chinese Academy of Sciences [17].

The lithiumlike ion O^{5+} ($Z = 8$) is an interesting system to which the high precision calculation of energy levels is challenging for both the NRQED theory and the RMB theory. Some nonrelativistic properties of a few low-lying states of this system were calculated by King [18,19] and by Godefroid and co-workers [20]. The transition frequencies between the $2S_{1/2}$ and $2P_{1/2}$ states were calculated by Cheng and co-workers using the MCDF theory [21] and by Johnson and co-workers using the RMBP theory [9]. The QED corrections to the 2*S* and 2*P* states were calculated approximately by McKenzie and Drake [22]. Recently, this frequency was recalculated by Yerokhin and co-workers using the RCI method [23]. In addition to O^{5+}, the 2*S* and 2*P* states of many other lithiumlike ions with middle or higher Z have also been explored by many authors under the framework of QED, such as Yerokhin *et al.* [24], Kozhedub *et al.* [25], and Sapirstein and Cheng [26]. In the present work, we will calculate the energies of the 2*S* and $2P_J$ states using the NRQED method. The nonrelativistic energies and leading-order relativistic and

TABLE I. Convergence study of the nonrelativistic energies for the $1s^2 2s\ ^2S$ and $1s^2 2p\ ^2P$ states of O^{5+} with infinite nuclear mass. The last row is the energy for $^{16}O^{5+}$ with finite nuclear mass. In atomic units.

Ω	No. of terms ($2S/2P$)	$2S$	$2P$
7	910/670	−64.228 542 043 971 34	−63.790 739 211 831 34
8	1 580/1 016	−64.228 542 078 742 87	−63.790 739 509 987 01
9	2 620/1 870	−64.228 542 082 324 97	−63.790 739 573 598 86
10	3 910/3 300	−64.228 542 082 951 26	−63.790 739 579 454 65
11	6 039/5 600	−64.228 542 083 010 45	−63.790 739 580 419 39
12	9 056/9 170	−64.228 542 083 019 19	−63.790 739 580 538 34
13	13 248/14 532	−64.228 542 083 020 50	−63.790 739 580 555 76
Extrap.	∞	−64.228 542 083 020 7(2)	−63.790 739 580 558(3)
King [18]	561	−64.228 540	
$^{16}O^{5+}$	∞	−64.226 302 024 344 4(2)	−63.788 612 585 607(3)

QED corrections will be calculated precisely, and the α^4- and α^5-order corrections will be estimated. We will see that our transition frequencies between the $2S_{1/2}$ and $2P_J$ ($J = 1/2, 3/2$) states are consistent with the experimental results [27]. We will also see that the fine-structure splitting between the $2P_{1/2}$ and $2P_{3/2}$ states also agrees with the experimental result [27].

The physical constants used here are as follows. The fine-structure constant is $\alpha = 1/137.035\,999\,139(31)$ [28], the Rydberg constant is $R_\infty = 10\,973\,731.568\,508(65)\ \mathrm{m}^{-1}$ [28], and the atomic mass of ^{16}O is $15\,994\,914.619\,566\ \mu u$ [29].

II. NONRELATIVISTIC WAVE FUNCTIONS AND ENERGIES

After separating out the center-of-mass motion, the nonrelativistic energy eigenvalue problem for a three-electron atomic system is [30]

$$H_0 \Psi_0 = E_0 \Psi_0, \tag{2}$$

where

$$H_0 = -\frac{1}{2}\sum_{i=1}^{3}\nabla_i^2 - Z\sum_{i=1}^{3}\frac{1}{r_i} + \sum_{i<j}^{3}\frac{1}{r_{ij}} - \frac{\mu}{M}\sum_{i<j}^{3}\nabla_i\cdot\nabla_j, \tag{3}$$

in units of $2R_M$ with $R_M = (1 - \frac{\mu}{M})R_\infty$, μ is the reduced mass of electron, and M is the nuclear mass.

We use the Rayleigh-Ritz variational method to solve Eq. (2). The variational wave function is expanded in terms of the following Hylleraas-type basis functions:

$$\{\mathcal{A}\phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\}, \tag{4}$$

where

$$\phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} e^{-\alpha r_1 - \beta r_2 - \gamma r_3} \times \mathcal{Y}^{LM}_{(\ell_1\ell_2)\ell_{12},\ell_3}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\chi_1, \tag{5}$$

and

$$\mathcal{Y}^{LM}_{(\ell_1\ell_2)\ell_{12},\ell_3}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = r_1^{\ell_1} r_2^{\ell_2} r_3^{\ell_3} \sum_{m_i} \langle \ell_1 m_1; \ell_2 m_2 | \ell_1 \ell_2; \ell_{12} m_{12}\rangle \times \langle \ell_{12} m_{12}; \ell_3 m_3 | \ell_{12}\ell_3; LM\rangle Y_{\ell_1 m_1}(\mathbf{r}_1) \times Y_{\ell_2 m_2}(\mathbf{r}_2) Y_{\ell_3 m_3}(\mathbf{r}_3) \tag{6}$$

is the vector-coupled product of spherical harmonics for the three electrons to form a state of total angular momentum L and z component M. Also in the above, χ_1 is the spin-wave function and $\mathcal{A}$ is the three-particle antisymmetrizer. With some truncations to avoid near linear dependence, all the terms in Eq. (4) are included in the basis set such that

$$j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \leqslant \Omega, \tag{7}$$

where Ω is an integer. For more details about the construction of variational wave functions, see Ref. [31].

Table I lists the nonrelativistic energies of the $2S$ and $2P$ states of O^{5+} for different sizes of basis sets. Comparing to the case of lithium [3], we see that the nonrelativistic energies converge very fast due to relatively weak Coulomb interaction between electrons. We stop our calculation at the basis size of 13 248 for the $2S$ state and 14 532 for the $2P$ state. The nonrelativistic energies of the $2S$ and $2P$ states reach, respectively, a relative accuracy of 10^{-15} and of 10^{-14}, which is sufficient for comparison with the available experimental values.

III. LEADING-ORDER RELATIVISTIC CORRECTIONS

The leading relativistic correction of order α^2, including the relativistic recoil corrections of order $(\mu/M)\alpha^2$, is calculated according to

$$\Delta E_{\mathrm{rel}} = \langle \Psi_0 | H_{\mathrm{rel}} | \Psi_0 \rangle, \tag{8}$$

where Ψ_0 is the nonrelativistic wave function for the state of interest and H_{rel} is the total leading-order relativistic correction operator, which can be written in the form [32]

$$H_{\mathrm{rel}} = B_1 + B_2 + B_{3z} + B_{3e} + B_5 - \pi\alpha^2 \sum_{i<j}^{3}\left(1 + \frac{8}{3}\mathbf{s}_i\cdot\mathbf{s}_j\right)\delta(\mathbf{r}_{ij}) + \frac{1}{2}Z\pi\alpha^2\sum_{i=1}^{3}\delta(\mathbf{r}_i) + \frac{m_e}{M}(\tilde{\Delta}_2 + \tilde{\Delta}_{3z}) + \gamma\left(2B_{3z} + \frac{4}{3}B_{3e} + \frac{2}{3}B_{3e}^{(1)} + 2B_5\right) + \gamma\frac{m_e}{M}\tilde{\Delta}_{3z}, \tag{9}$$

TABLE II. Expectation values of the relativistic correction operators for the $1s^2 2s\ ^2S$ and $1s^2 2p\ ^2P$ states of O^{5+} with infinite nuclear mass. In atomic units.

Ω	B_1	$10^4 B_2$	$\sum_i \delta(\mathbf{r}_i)$	$\sum_{i<j} \delta(\mathbf{r}_{ij})$	$\tilde{\Delta}_2$
			$1s^2 2s\ ^2S$		
7	−0.258 743 899 15	−2.442 270 991	311.668 973 1	16.947 183 090	−0.425 084 144 9
8	−0.258 743 863 71	−2.442 243 248	311.669 016 9	16.947 173 632	−0.425 084 246 0
9	−0.258 743 847 15	−2.442 237 916	311.669 025 6	16.947 171 571	−0.425 084 266 6
10	−0.258 743 844 67	−2.442 236 848	311.669 031 7	16.947 171 476	−0.425 084 282 0
11	−0.258 743 841 74	−2.442 236 690	311.669 031 5	16.947 171 412	−0.425 084 281 5
12	−0.258 743 841 74	−2.442 236 664	311.669 031 6	16.947 171 413	−0.425 084 281 8
13	−0.258 743 841 61	−2.442 236 655	311.669 031 7	16.947 171 414	−0.425 084 282 0
Extrap.	−0.258 743 841 7(1)	−2.442 236 651(2)	311.669 031 9(2)	16.947 171 417(3)	−0.425 084 282 4(4)
			$1s^2 2p\ ^2P$		
7	−0.246 680 517 91	1.034 763 016	298.199 722 7	16.012 948 15	−0.397 038 287 8
8	−0.246 680 322 29	1.034 874 751	298.199 771 4	16.012 909 68	−0.397 038 321 0
9	−0.246 680 320 58	1.034 894 269	298.199 800 2	16.012 893 00	−0.397 038 385 9
10	−0.246 680 287 94	1.034 901 327	298.199 811 2	16.012 890 27	−0.397 038 412 3
11	−0.246 680 290 75	1.034 901 704	298.199 812 7	16.012 889 48	−0.397 038 416 2
12	−0.246 680 287 18	1.034 901 991	298.199 812 8	16.012 889 44	−0.397 038 420 0
13	−0.246 680 287 40	1.034 902 015	298.199 813 2	16.012 889 48	−0.397 038 421 1
Extrap.	−0.246 680 287 4(1)	1.034 902 018(2)	298.199 814(1)	16.012 889 46(2)	−0.397 038 421 5(4)

where

$$B_1 = -\frac{\alpha^2}{8}\left(\nabla_1^4 + \nabla_2^4 + \nabla_3^4\right), \tag{10}$$

$$B_2 = \frac{\alpha^2}{2}\sum_{i<j}^{3}\left[\frac{1}{r_{ij}}\nabla_i\cdot\nabla_j + \frac{1}{r_{ij}^3}\mathbf{r}_{ij}\cdot(\mathbf{r}_{ij}\cdot\nabla_i)\nabla_j\right], \tag{11}$$

$$B_{3z} = \frac{Z\alpha^2}{2}\sum_{i=1}^{3}\frac{1}{r_i^3}\mathbf{r}_i\times\mathbf{p}_i\cdot\mathbf{s}_i, \tag{12}$$

$$B_{3e} = \frac{\alpha^2}{2}\sum_{i\neq j}^{3}\frac{1}{r_{ij}^3}\mathbf{r}_{ji}\times\mathbf{p}_i\cdot(\mathbf{s}_i + 2\mathbf{s}_j), \tag{13}$$

$$B_5 = \alpha^2\sum_{i>j}^{3}\left[\frac{1}{r_{ij}^3}(\mathbf{s}_i\cdot\mathbf{s}_j) - \frac{3}{r_{ij}^5}(\mathbf{r}_{ij}\cdot\mathbf{s}_i)(\mathbf{r}_{ij}\cdot\mathbf{s}_j)\right], \tag{14}$$

$$\tilde{\Delta}_2 = \frac{iZ\alpha^2}{2}\sum_{j=1}^{3}\left[\frac{1}{r_j}\mathbf{p}\cdot\nabla_j + \frac{1}{r_j^3}\mathbf{r}_j\cdot(\mathbf{r}_j\cdot\mathbf{p})\nabla_j\right], \tag{15}$$

$$\tilde{\Delta}_{3z} = Z\alpha^2\sum_{i=1}^{3}\frac{1}{r_i^3}\mathbf{r}_i\times\mathbf{p}\cdot\mathbf{s}_i, \tag{16}$$

$$B_{3e}^{(1)} = \frac{\alpha^2}{2}\sum_{i\neq j}^{3}\frac{1}{r_{ij}^3}\mathbf{r}_{ji}\times\mathbf{p}_i\cdot(\mathbf{s}_i - \mathbf{s}_j), \tag{17}$$

and

$$\mathbf{p} = \mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3, \tag{18}$$

$$\gamma \approx \frac{\alpha}{2\pi} + (-0.32847)\left(\frac{\alpha}{\pi}\right)^2. \tag{19}$$

For a spin doublet state, the operator $-\pi\alpha^2\sum_{i<j}^{3}(1+\frac{8}{3}\mathbf{s}_i\cdot\mathbf{s}_j)\delta(\mathbf{r}_{ij})$ can be simplified into $\pi\alpha^2\sum_{i<j}^{3}\delta(\mathbf{r}_{ij})$ and the expectation value of the spin-spin term B_5 vanishes. The terms proportional to m_e/M are the nuclear relativistic recoil corrections and the terms proportional to γ are the spin-dependent part of the electron anomalous magnetic-moment corrections. The spin-independent part of the electron anomalous magnetic-moment corrections is included in the QED corrections discussed in the next section. For more details about the relativistic corrections, see Ref. [33]. Some special numerical methods have been developed by Yan and Drake [34] to deal with the singular integrals encountered in the calculations of the relativistic correction operators. Tables II and III list the expectation values of the relativistic operators. From their convergence patterns against the size of basis set, one can see that a relative accuracies of 10^{-10} and 10^{-9} for the spin-independent and the spin-dependent operators have been obtained.

IV. LEADING-ORDER QED CORRECTIONS

For few-electron atomic systems, the leading-order QED corrections to the energy levels can be expressed in the form [35,36]

$$E_{\rm QED} = E_{\rm L,1} + E_{\rm M,1} + E_{\rm R,1} + E_{\rm L,2}, \tag{20}$$

where $E_{\rm L,1}$ denotes the mass-independent part of the QED corrections to the electron-nucleus interaction, the so-called Kabir-Salpeter term [37], $E_{\rm M,1}$ contains the QED corrections due to the mass scaling and the mass polarization, $E_{\rm R,1}$ is the recoil correction, and $E_{\rm L,2}$ is the QED correction due to the interaction between two electrons [38,39]. Using the notation $\langle\sum_i \delta(\mathbf{r}_i)\rangle = \langle\sum_i \delta(\mathbf{r}_i)\rangle^{(0)} + (\mu/M)\langle\sum_i \delta(\mathbf{r}_i)\rangle^{(1)} + \cdots$, these QED terms can be written as

$$E_{\rm L,1} = \frac{4Z\alpha^3\langle\sum_i \delta(\mathbf{r}_i)\rangle^{(0)}}{3}\left\{\ln(Z\alpha)^{-2} - \beta(1s^2 nL\ ^2L) + \frac{19}{30} + (3\pi\alpha Z)\,0.765\,405\,577\right.$$

TABLE III. Expectation values of the spin-dependent relativistic correction operators for the $2P_{1/2}$ state of O^{5+} with infinite nuclear mass. In atomic units.

Ω	$B_{3z}\times 10^3$	$B_{3e}\times 10^4$	$B^{(1)}_{3e}\times 10^4$	$\tilde{\Delta}_{3z}\times 10^3$
7	−2.333 838 378	7.258 929 00	3.600 787 49	1.920 696 88
8	−2.333 839 450	7.259 022 68	3.600 776 63	1.920 759 03
9	−2.333 841 649	7.259 135 42	3.600 776 87	1.920 832 86
10	−2.333 841 652	7.259 152 62	3.600 775 99	1.920 821 13
11	−2.333 841 812	7.259 158 42	3.600 775 83	1.920 816 81
12	−2.333 841 798	7.259 158 98	3.600 775 44	1.920 817 35
13	−2.333 841 792	7.259 158 89	3.600 775 34	1.920 817 61
Extrap.	−2.333 841 78(2)	7.259 158 90(5)	3.600 775 31(3)	1.920 817 8(2)

$$+\frac{\alpha}{\pi}[0.404\,206-(3\alpha Z/4)21.556\,85]+(Z\alpha)^2\left[-\frac{3}{4}\ln^2(Z\alpha)^{-2}+C_{61}(1s^2nL^2L)\ln(Z\alpha)^{-2}+C_{60}(1s^2nL^2L)\right]\Bigg\}, \tag{21}$$

$$E_{\mathrm{M},1}=\frac{\mu\langle\sum_i\delta(\mathbf{r}_i)\rangle^{(1)}}{M\langle\sum_i\delta(\mathbf{r}_i)\rangle^{(0)}}E_{\mathrm{L},1}+\frac{4Z\alpha^3\mu\langle\sum_i\delta(\mathbf{r}_i)\rangle^{(0)}}{3M}[1-\Delta\beta_{\mathrm{MP}}(1s^2nL^2L)], \tag{22}$$

and

$$E_{\mathrm{R},1}=\frac{4Z^2\alpha^3\mu\langle\sum_i\delta(\mathbf{r}_i)\rangle^{(0)}}{3M}\left[\frac{1}{4}\ln(Z\alpha)^{-2}-2\beta(1s^2nL^2L)-\frac{1}{12}-\frac{7}{4}a(1s^2nL^2L)-\frac{3}{4}(\pi\alpha)1.364\,49+\frac{3}{4}\pi Z\alpha D_{50}(1s^2nL^2L)+\frac{1}{2}\alpha^2Z\ln^2(Z\alpha)^{-2}\right], \tag{23}$$

and they are the three-electron generalization of the hydrogenic Lamb shift [40]. The quantity $\beta(1s^2nL^2L)\equiv\ln(k_0/Z^2R_\infty)$ is the three-electron Bethe logarithm with k_0 measured in Z^2R_∞, and the two terms in $1-\Delta\beta_{\mathrm{MP}}(1s^2nL^2L)$ are due, respectively, to the mass scaling and mass polarization corrections to $\beta(1s^2nL^2L)$. The term $a(1s^2nL^2L)$, first derived by Pachucki [41], is defined by

$$a(1s^2nL^2L)=\frac{2Q_1^{(0)}}{\langle\sum_i\delta(\mathbf{r}_i)\rangle^{(0)}}+2\ln Z-3, \tag{24}$$

where

$$Q_1^{(0)}=\frac{1}{4\pi}\lim_{\epsilon\to0}\sum_i\langle r_i^{-3}(\epsilon)+4\pi(\gamma_{\mathrm{eu}}+\ln\epsilon)\delta(\mathbf{r}_i)\rangle, \tag{25}$$

with γ_{eu} being Euler's constant and ϵ the radius of a sphere about $r_i=0$ that is excluded from the integration. The state-dependent coefficients $C_{61}(1s^2nL^2L)$, $C_{60}(1s^2nL^2L)$, and $D_{50}(1s^2nL^2L)$ are all estimated from the generic formula [42]

$$X(1s^2nL^2L)=\frac{2X(1s)+X(nL)/n^3}{2+\delta_{L,0}/n^3}. \tag{26}$$

The electron-electron QED shift $E_{\mathrm{L},2}$ can similarly be separated into the mass-independent and the mass-dependent parts according to

$$E_{\mathrm{L},2}=E^{(0)}_{\mathrm{L},2}+\frac{\mu}{M}E^{(1)}_{\mathrm{L},2}+\cdots, \tag{27}$$

where [38,39]

$$E^{(0)}_{\mathrm{L},2}=\alpha^3\left(\frac{14}{3}\ln\alpha+\frac{164}{15}\right)\sum_{i>j}\langle\delta(\mathbf{r}_{ij})\rangle^{(0)}-\frac{14}{3}\alpha^3Q^{(0)}, \tag{28}$$

and

$$E^{(1)}_{\mathrm{L},2}=\alpha^3\left(\frac{14}{3}\ln\alpha+\frac{164}{15}\right)\sum_{i>j}\langle\delta(\mathbf{r}_{ij})\rangle^{(1)}-\frac{14}{3}\alpha^3\left(Q^{(1)}+\sum_{i>j}\langle\delta(\mathbf{r}_{ij})\rangle^{(0)}\right). \tag{29}$$

Following our notation, the $Q^{(0)}$ term for infinite mass is given by

$$Q^{(0)}=\frac{1}{4\pi}\lim_{\epsilon\to0}\sum_{i>j}\langle r_{ij}^{-3}(\epsilon)+4\pi(\gamma+\ln\epsilon)\delta(\mathbf{r}_{ij})\rangle, \tag{30}$$

and the $Q^{(1)}$ term is the correction due to the effects of mass polarization and mass scaling.

The QED formulas discussed above completely account for the $O(\alpha^3)$ corrections. However they only take the dominate parts of the $O(\alpha^4)$ and $O(\alpha^5)$ corrections into consideration [1]. A complete calculation of $O(\alpha^4)$ corrections for a general state of a few-electron system is very difficult and so far it has only been done for two-electron atomic systems [43,44]. For a three-electron atomic system, the $O(\alpha^4)$ corrections have only been calculated for the fine-structure splitting of the $2P$ state [14,15]. We do not intend to calculate the $O(\alpha^4)$ corrections rigorously in this work; however, we will give an estimation for them and also an estimation for the $O(\alpha^5)$ corrections based on the above formulas. Following Puchalski and co-workers [1], the uncertainty due to the omission of some relatively small corrections is taken to be 10% for the $O(\alpha^4)$ corrections and 25% for the $O(\alpha^5)$ corrections.

For the evaluation of the QED corrections, besides the $\delta(\mathbf{r}_i)$ and $\delta(\mathbf{r}_{ij})$ terms already calculated in the leading-order relativistic corrections, we have to calculate the expectation values of the operators $Q_1^{(0)}$, $Q^{(0)}$, and $Q^{(1)}$, as well as the

TABLE IV. Expectation values of the QED correction operators $Q_1^{(0)}$, $Q^{(0)}$, and $Q^{(1)}$ for the $1s^2 2s\ ^2S$ and $1s^2 2p\ ^2P$ states of O^{5+}. In atomic units.

Ω	$Q_1^{(0)}$	$Q^{(0)}$	$Q^{(1)}$
		$1s^2 2s\ ^2S$	
7	−214.103 485	−2.912 83	6.404 959
8	−214.105 740	−2.910 86	6.410 108
9	−214.106 024	−2.910 22	6.410 680
10	−214.106 610	−2.909 95	6.410 805
11	−214.106 593	−2.909 88	6.410 695
12	−214.106 623	−2.909 88	6.410 779
13	−214.106 632	−2.909 87	6.410 771
Extrap.	−214.106 637(5)	−2.909 89(2)	6.410 77(7)
		$1s^2 2p\ ^2P$	
7	−203.408 24	−1.881 581	6.497 3
8	−203.409 38	−1.876 619	6.503 6
9	−203.410 72	−1.875 741	6.515 6
10	−203.411 53	−1.874 616	6.511 1
11	−203.411 57	−1.874 639	6.511 4
12	−203.411 66	−1.874 540	6.511 2
13	−203.411 70	−1.874 532	6.511 1
Extrap.	−203.411 76(6)	−1.874 53(1)	6.511 0(3)

three-electron Bethe logarithm defined by

$$\beta(1s^2 nL\ ^2L) = \frac{\sum_m |\langle 0|\mathbf{p}_1+\mathbf{p}_2+\mathbf{p}_3|m\rangle|^2 (E_m-E_0)\ln|2Z^{-2}(E_m-E_0)|}{\sum_m |\langle 0|\mathbf{p}_1+\mathbf{p}_2+\mathbf{p}_3|m\rangle|^2 (E_m-E_0)}. \tag{31}$$

The numerical techniques to deal with the singular integrals encountered in the calculations of expectation values of $Q_1^{(0)}$ and $Q^{(0)}$ have been developed by Yan [45]. The Bethe logarithm is calculated by using the Drake-Goldman method [46]. The problem of slow convergence of some integrals involved in the Drake-Goldman method was solved by Li *et al.* [47]. The expectation values of $Q_1^{(0)}$, $Q^{(0)}$, and $Q^{(1)}$ for the $2S$ and $2P$ states of O^{5+} are listed in Table IV, and the Bethe logarithms are listed in Table V.

The corrections to energy levels due to the finite distribution of nuclear charge is also considered, which can be written as

$$\Delta E_{\rm nuc} = \frac{2\pi Z (r_c/a_0)^2}{3}\left\langle \sum_i \delta(\mathbf{r}_i)\right\rangle, \tag{32}$$

where r_c is the root-mean-square radius of the nuclear charge distribution and a_0 is the Bohr radius. For ^{16}O, we use r_c = 2.7013(55) fm [48].

V. RESULTS AND DISCUSSION

Combining the nonrelativistic energies with the leading-order relativistic and QED corrections, we finally obtain the frequencies for the transitions $2S_{1/2} - 2P_{1/2}$ and $2S_{1/2} - 2P_{3/2}$, as well as the fine-structure splitting between the $2P_{1/2}$ and $2P_{3/2}$ states, as presented in Tables VI and VII. From Table VI, one can see that the contributions due to the nonrelativistic energies, the leading-order relativistic corrections, the leading-order QED corrections, and the finite nuclear mass corrections are all calculated to an accuracy better than 10^{-6} eV. The dominant contributions to the uncertainties of the transition frequencies come from the $O(\alpha^4)$ and $O(\alpha^5)$ relativistic and QED effects. The final transition frequencies determined in this work are 11.948 77(10) eV for $2S_{1/2} - 2P_{1/2}$ and 12.014 56(10) eV for $2S_{1/2} - 2P_{3/2}$, which are in good accord with the experimental results [27] 11.948 98(12) eV and 12.014 69(12) eV, and are also consistent with the theoretical results 11.948 2(16) eV and 12.013 8(16) eV calculated recently by Yerokhin *et al.* [23] using the RCI method.

TABLE V. Bethe logarithms for the $1s^2 2s\ ^2S$ and $1s^2 2p\ ^2P$ states of O^{5+}, expressed in the form $\beta = \beta^{(0)} + (\mu/M)\Delta\beta_{\rm MP} + \ln(\mu/m_e)$. N_1 denotes the number of basis functions for the state of interest, and N_2 the number of basis functions for the intermediate states. For the $1s^2 2p\ ^2P$ state, there are three types of intermediate states with different symmetries [46].

N_1	N_2	$\beta^{(0)}$	$\Delta\beta_{\rm MP}$
		$1s^2 2s\ ^2S$	
6039	347	2.888 889 9	0.143 640
6039	682	2.967 753 1	0.145 384
6039	1013	2.975 368 3	0.145 089
6039	1590	2.976 225 7	0.144 923
6039	2583	2.976 339 1	0.144 873
6039	4247	2.976 357 6	0.144 854
6039	6947	2.976 362 2	0.144 866
∞		2.976 364(2)	0.144 86(1)
		$1s^2 2p\ ^2P$	
5600	337+220+238	2.727 783	0.152 812
5600	457+294+357	2.929 135	0.143 748
5600	713+470+612	2.973 221	0.140 973
5600	1215+842+1113	2.980 567	0.139 852
5600	2133+1560+2030	2.981 808	0.139 737
5600	3722+2854+3618	2.981 994	0.140 645
5600	6347+5059+6242	2.982 024	0.139 799
∞		2.982 030(6)	0.140 2(5)

For the fine-structure splitting between the $2P_{1/2}$ and $2P_{3/2}$ states, the dominant contribution comes from the $O(\alpha^2)$ spin-dependent relativistic corrections. The α^3 contribution is due to the electron anomalous magnetic moment. The final value of the fine-structure splitting is 530.646 48(1) cm^{-1}, which is consistent with the experimental result [27] 531(1) cm^{-1} and also consistent with the theoretical value 531(4) cm^{-1} calculated by Johnson *et al.* [9] using the RMBP theory and the theoretical value 529(10) cm^{-1} calculated by Yerokhin *et al.* [23] using the RCI method. However, the uncertainty of our result is just the uncertainty of the leading-order relativistic corrections that is not the final uncertainty of the fine-structure splitting. For assigning a more realistic uncertainty, we use the quantum-defect method to estimate the $O(\alpha^4)$ contribution to the fine-structure splitting. We consider the O^{5+} ion in the $1s^2 2p^2 P$ state as a heliumlike O^{6+} core in the $1s^2\ ^1S$ state plus an outer electron in the hydrogenic $2p$ orbit. The nonrelativistic energy of the system is separated into two parts,

$$E_0 = E_{\rm core} + E_{2p}, \tag{33}$$

where $E_0 = -63.790\,739$ a.u. is the nonrelativistic energy of the O^{5+} ion, $E_{\rm core} = -59.156\,596$ a.u. is the nonrelativistic

TABLE VI. Contributions to the transition frequencies of $2S_{1/2} - 2P_{1/2}$ and $2S_{1/2} - 2P_{3/2}$ in $^{16}O^{5+}$, in eV.

Term	$2S_{1/2} - 2P_{1/2}$	$2S_{1/2} - 2P_{3/2}$
E_{NR}	11.913 212 895 015(25)	11.913 212 895 015(25)
μ/M	−0.003 076 610 370(2)	−0.003 076 610 370(2)
$(\mu/M)^2$	−0.000 000 010 367(1)	−0.000 000 010 367(1)
α^2	0.044 456 904(4)	0.110 087 74(4)
$(\mu/M)\alpha^2$	0.000 004 259 62(3)	0.000 001 191 43(4)
α^3	−0.005 304 2(2)	−0.005 140 2(2)
$(\mu/M)\alpha^3$	0.000 001 870(2)	0.000 001 866(4)
α^4	−0.000 64(6)	−0.000 64(6)
α^5	0.000 13(4)	0.000 13(4)
$(\mu/M)(\alpha^4 + \alpha^5)$	0.000 000 10(2)	0.000 000 10(2)
Nuclear size	−0.000 016 00(7)	−0.000 016 00(7)
Total (theory)	11.948 77(10)	12.014 56(10)
Johnson *et al.* (theory) [9]	11.955 05(27)[a] 11.948 98[b]	12.021 01(35)[a]
Yerokhin *et al.* (theory) [23]	11.948 2(16)	12.013 8(16)
Edlen (experiment) [27]	11.948 98(12)	12.014 69(12)

[a]Results calculated using the RMBP method without QED corrections.
[b]RMBP results from Ref. [9] supplemented by the QED corrections calculated by McKenzie and Drake [22].

energy of the core [44], and E_{2p} is the energy of the outer electron. From Eq. (33) we can obtain $E_{2p} = -4.634\,143$ a.u.. In our model, the energy of the outer electron is also determined by the Bohr formula with an effective principal quantum number n^*

$$E_{2p} = -\frac{Z^2}{2n^{*2}}, \tag{34}$$

where $Z = 6$. From Eq. (34) and the value of E_{2p}, we determine the value of the effective principal quantum number $n^* = 1.9708$. Substituting this effective principal quantum number into the Dirac formula (in natural units)

$$\begin{aligned} E_{nj} &= m\left[1 + \frac{(Z\alpha)^2}{(\sqrt{(j+1/2)^2 - (Z\alpha)^2} + n - (j+1/2))^2}\right]^{-1/2} \\ &= m\left\{1 - \frac{(Z\alpha)^2}{2n^2} - \frac{(Z\alpha)^4}{2n^3}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right)\right. \\ &\quad - \frac{(Z\alpha)^6}{8n^3}\left[\frac{1}{(j+1/2)^3} + \frac{3}{n(j+1/2)^2}\right. \\ &\quad \left.\left. - \frac{6}{n^2(j+1/2)} + \frac{5}{2n^3}\right] + \cdots\right\}, \end{aligned} \tag{35}$$

we obtain the leading-order α^2 a.u. relativistic contribution to the fine-structure splitting of the $2P$ state of O^{5+} to be $\Delta E^{(2)} = 494$ cm^{-1}, which is close to the accurate value 529.348 42(1) cm^{-1} in Table VII. This demonstrates that the quantum-defect method used by us is meaningful in estimating the magnitude of the relativistic corrections to the fine-structure splitting, at least for the leading-order relativistic contribution. The $O(\alpha^4)$ contribution, estimated by using Eq. (35) and the effective quantum number n^*, is $\Delta E^{(4)} \approx 0.6$ cm^{-1}. We add this value to the subtotal contribution and take it to be the total uncertainty of the final fine-structure splitting. The fine-structure splitting now becomes 531.2(6) cm^{-1}, which agrees with the experimental value 531(1) cm^{-1} [27] very well.

VI. SUMMARY

The transition frequencies between the $2S_{1/2}$ and $2P_J$ ($J = 1/2, 3/2$) states of the lithiumlike $^{16}O^{5+}$ ion have been determined in the NRQED framework. The nonrelativistic contribution and the leading-order relativistic and QED corrections have been calculated to an accuracy of better than 10^{-6} eV. The higher-order relativistic and QED contributions of $O(\alpha^4)$ and $O(\alpha^5)$ have been estimated approximately. Our final theoretical values for the transition frequencies are consistent with the experimental results [27]. In order to improve the accuracy of our theoretical results, it is necessary to perform the $O(\alpha^4)$ and even $O(\alpha^5)$ corrections rigorously, which is a very challenging task. The fine-structure splitting between the $2P_{1/2}$ and $2P_{3/2}$ states has also been calculated and our result agrees with the experimental value [27].

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TABLE VII. Contributions to the fine-structure splitting of the $2P$ state of $^{16}O^{5+}$, in cm^{-1}.

Term	$2P_{3/2} - 2P_{1/2}$
α^2	529.348 42(1)
$(\mu/M)\alpha^2$	−0.024 745 12(4)
α^3	1.322 833 0(1)
$(\mu/M)\alpha^3$	−0.000 031 256(1)
Subtotal	530.646 48(1)
α^4	0.6(6)
Total (theory)	531.2(6)
Johnson *et al.* (theory) [9]	531(4)
Yerokhin *et al.* (theory) [23]	529(10)
Edlen (experiment) [27]	531(1)

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[1] M. Puchalski, D. Kedziera, and K. Pachucki, Phys. Rev. A **82**, 062509 (2010).
[2] G. W. F. Drake, M. M. Cassar, and R. A. Nistor, Phys. Rev. A **65**, 054501 (2002).
[3] L. M. Wang, Z.-C. Yan, H. X. Qiao, and G. W. F. Drake, Phys. Rev. A **85**, 052513 (2012).
[4] M. Puchalski, J. Komasa, and K. Pachucki, Phys. Rev. A **87**, 030502(R) (2013).
[5] S. Bubin and L. Adamowicz, J. Chem. Phys. **140**, 024301 (2014).
[6] M. Puchalski, J. Komasa, and K. Pachucki, Phys. Rev. A **92**, 062501 (2015).
[7] S. Bubin and L. Adamowicz, Phys. Rev. Lett. **118**, 043001 (2017).
[8] I. Lindgren, Rep. Prog. Phys. **47**, 345 (1984).
[9] W. R. Johnson, S. A. Blundell, and J. Sapirstein, Phys. Rev. A **37**, 2764 (1988).
[10] I. Lindgren, Phys. Rev. A **31**, 1273 (1985).
[11] S. A. Blundell, W. R. Johnson, Z. W. Liu, and J. Sapirstein, Phys. Rev. A **40**, 2233 (1989).
[12] M. H. Chen, K. T. Cheng, W. R. Johnson, and J. Sapirstein, Phys. Rev. A **52**, 266 (1995).
[13] P. Indelicato and J. P. Desclaux, Phys. Rev. A **42**, 5139 (1990).
[14] M. Puchalski and K. Pachucki, Phys. Rev. Lett. **113**, 073004 (2014).
[15] M. Puchalski and K. Pachucki, Phys. Rev. A **92**, 012513 (2015).
[16] G. W. F. Drake, Phys. Rev. A **19**, 1387 (1979).
[17] W. Q. Wen *et al.*, Hyperfine Interact. **240**, 45 (2019).
[18] F. W. King, Phys. Rev. A **40**, 1735 (1989).
[19] F. W. King, Phys. Rev. A **43**, 3285 (1991).
[20] M. Godefroid, C. F. Fischer, and P. Jönsson, J. Phys. B **34**, 1079 (2001).
[21] K. T. Cheng, Y.-K. Kim, and J. P. Desclaux, At. Data Nucl. Data Tables **24**, 111 (1979).
[22] D. K. McKenzie and G. W. F. Drake, Phys. Rev. A **44**, R6973 (1991); **48**, 4803(E) (1993).
[23] V. A. Yerokhin, A. Surzhykov, and A. Müller, Phys. Rev. A **96**, 042505 (2017).
[24] V. A. Yerokhin, A. N. Artemyev, and V. M. Shabaev, Phys. Rev. A **75**, 062501 (2007).
[25] Y. S. Kozhedub, A. V. Volotka, A. N. Artemyev, D. A. Glazov, G. Plunien, V. M. Shabaev, I. I. Tupitsyn, and Th. Stöhlker, Phys. Rev. A **81**, 042513 (2010).
[26] J. Sapirstein and K. T. Cheng, Phys. Rev. A **83**, 012504 (2011).
[27] B. Edlén, Phys. Scr. **28**, 51 (1983).
[28] P. J. Mohr, D. B. Newell, and B. N. Taylor, Rev. Mod. Phys. **88**, 035009 (2016).
[29] M. Wang, G. Audi, A. H. Wapstra, F. G. Kondev, M. MacCormick, X. Xu, and B. Pfeiffer, Chin. Phys. C **36**, 1603 (2012).
[30] G. W. F. Drake, W. Nörtershäuser, and Z.-C. Yan, Can. J. Phys. **83**, 311 (2005).
[31] L. M. Wang, Z.-C. Yan, H. X. Qiao, and G. W. F. Drake, Phys. Rev. A **83**, 034503 (2011).
[32] A. P. Stone, Proc. Phys. Soc. **77**, 786 (1961); **81**, 868 (1963).
[33] G. F. W. Drake, in *Long-Range Casimir Forces: Theory and Recent Experiments on Atomic Systems*, edited by F. S. Levin and D. A. Micha (Plenum, New York, 1993), p. 142.
[34] Z.-C. Yan and G. W. F. Drake, J. Phys. B **30**, 4723 (1997).
[35] W. Nörtershäuser, R. Sánchez, G. Ewald, A. Dax,, J. Behr, P. Bricault, B. A. Bushaw, J. Dilling, M. Dombsky, G. W. F. Drake, S. Götte, H.-J. Kluge, Th. Kühl, J. Lassen, C. D. P. Levy, K. Pachucki, M. Pearson, M. Puchalski, A. Wojtaszek, Z.-C. Yan, and C. Zimmermann, Phys. Rev. A **83**, 012516 (2011).
[36] L. M. Wang, Chun Li, Z.-C. Yan, and G. W. F. Drake, Phys. Rev. A **95**, 032504 (2017).
[37] P. K. Kabir and E. E. Salpeter, Phys. Rev. **108**, 1256 (1957).
[38] H. Araki, Prog. Theor. Phys. **17**, 619 (1957).
[39] J. Sucher, Phys. Rev. **109**, 1010 (1958).
[40] M. I. Eides, H. Grotch, and V. A. Shelyuto, Phys. Rep. **342**, 63 (2001).
[41] K. Pachucki, J. Phys. B **31**, 5123 (1998).
[42] Z.-C. Yan and G. W. F. Drake, Phys. Rev. A **66**, 042504 (2002).
[43] K. Pachucki, Phys. Rev. A **74**, 022512 (2006); **74**, 062510 (2006); **76**, 059906(E) (2007).
[44] V. A. Yerokhin and K. Pachucki, Phys. Rev. A **81**, 022507 (2010).
[45] Z.-C. Yan, J. Phys. B **33**, 2437 (1997).
[46] G. W. F. Drake and S. P. Goldman, Can. J. Phys. **77**, 835 (1999).
[47] C. Li, L. Wang, and Z.-C. Yan, Int. J. Quantum Chem. **113**, 1307 (2013).
[48] I. Angeli, At. Data Nucl. Data Tables **87**, 185 (2004).