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Fine structure of ^2P energy levels of singly ionized carbon (C II)

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Benchmark variational calculations of the lowest eight Rydberg $^2P^o$ states of the singly ionized carbon atom (stable isotopes ^{12}C$^+$, ^{13}C$^+$, ^{14}C$^+$, as well as the infinite nuclear mass ion $^\infty$C$^+$) are reported and the fine structure of the energy levels is determined. The nonrelativistic wave functions of this six-particle, five-electron system are approximated using an expansion in terms of up to 16 000 all-particle explicitly correlated Gaussians (ECGs), who's nonlinear variational parameters are extensively optimized using a procedure that employs the analytic energy gradient. These highly accurate wave functions are used to compute the fine structure splittings including the corrections due to the electron magnetic moment anomaly. The results obtained in this work are considerably more accurate than the data from the previous theoretical calculations and from the available experimental measurements. For some states the present data are the first ever reported and can be useful in guiding future accurate spectroscopic measurements of C II.

INTRODUCTION

Chemical composition of interstellar medium (ISM) has always been of considerable interest to researchers in various fields. Detection of atomic and molecular species and determining their abundance allows analysis of the ISM chemical and physical properties as well as their evolution [1]. Due to the crucial role of carbon in the evolution of stars and its abundance in ISM (it is the fourth most abundant element in the universe), it is one of a few most important elements in astrophysical studies. By considering the relatively low ionization potential of neutral C ($\approx$ 11.26 eV), a large part of carbon in the ISM is in the form of C$^+$ which is easily produced by the process of photo-ionization [2]. The transitions between the fine structure levels of singly-ionized carbon (C II) has long been considered as one of the principal means for cooling interstellar atomic clouds by radiating energy into space [3]. Thermal collisions of (C II) with lighter particles, such as e$^-$, H$^+$, H, and D, induce the (C II) $1s^2 2s^2 2p\ ^2P^o_J\quad J = 3/2 \to 1/2$ emission that gives rise to a spectral line at wavelength $\lambda \approx 158\mu$m. This emission provides an effective coolant for ISM [2]. Such cooling involves $^2P^o_{3/2} \to {}^2P^o_{1/2}$ radiative transitions within the dominant ground state electron configuration, $1s^2 2s^2 2p$, of the C$^+$ ion (for brevity we will drop the o superscript in the notation of the considered states). The emitted photon has wavelength $\lambda \approx 158\ \mu m$. Its emission may be induced by thermal collisions of the C$^+$ ion with electrons, as well as hydrogen species, H$^+$, H and D [2]. Also the use of the C$^+$ fine-structure line as a tracer of star formation in the Milky Way and other galaxies should be mentioned [4].

Despite the importance of the C$^+$ ion, accurate experimental and theoretical studies are lacking. Recently, Kramida and Haris [2] published a compilation of energy levels of singly ionized carbon. They evaluated all the available experimental and theoretical data for C II and compiled an improved list of the energy levels and Ritz wavelengths with well-defined uncertainties. Their analysis was mostly based on the experiments by Glad [5]. It should be noted that further experiments proved that the wavelengths of C II reported by Glad are significantly red-shifted [2, 6]. The light source in Glad's study had a significant Stark shift whose magnitude is not precisely known, but it is estimated to be larger than 0.5 cm^{-1}. Due to the inconsistency between the wavelengths reported by different groups, it is difficult to extract accurate values for the transition energies corresponding to some levels (see section 2.1 in Ref. [2]). It appears that the only accurate experimental measurement for P states of C$^+$ was performed by Cooksy *et al.* [7]. They also provided a rather accurate value for the fine structure splitting for the C$^+$ ion in the ground $2s^2 2p$ state.

There have also been some advanced quantum-mechanical calculations of the spectra of the C$^+$ ion. Most of the previous studies were performed with the Multi-Configuration Dirac–Hartree–Fock (MCDHF) [8], Configuration Interaction (CI) [9, 10], and Diffusion Monte Carlo (DMC) [11] methods. The present authors previously carried out some very accurate calculations of several low-lying S and P states of the C$^+$ ion using all-electron explicitly correlated Gaussian (ECG) basis function. [12–16] Those previous calculations still remain the most accurate in the literature to date. As ECGs explicitly depend on all inter-electron distances, they very accurately describe the electron-electron correlation effects, significantly more so than the methods based on orbital expansions, such as the MCDHF and CI approaches. It should also be noted that our calculations of C II were performed without assuming the Born-Oppenheimer approximation and, thus, the motion of the nucleus and motion of the electrons were treated on an equal footing. Not only this increased the accuracy of the results, but it also allowed for determining the isotopic shifts of the transition energies.

In this Letter, we report on the next important step in high precision computational studies of the spectra of the C^+ ion. It involves accurate determination of the fine structure splittings for all major isotopes of C II. The present work follows the approach we recently developed and tested for the case of ^2P states of a simpler, three-electron system – isotopes of the lithium atom [17].

METHOD

The C^+ ion is a six-particle system consisting of five electrons and a nucleus. After separating out the motion of the center of mass [18], the six-particle problem is reduced to an effective five-particle problem ($n = 5$). The resulting internal nonrelativistic Hamiltonian, H_{nr}, for the C^+ ion has the following form (atomic units are adopted throughout this work):

$$H_{\mathrm{nr}}^{\mathrm{int}} = -\frac{1}{2}\left(\sum_{i=1}^{n}\frac{1}{\mu_i}\nabla^2_{\mathbf{r}_i} + \sum_{\substack{i=1\\ j\neq i}}^{n}\frac{1}{m_0}\nabla'_{\mathbf{r}_i}\nabla_{\mathbf{r}_j}\right) + \sum_{i=1}^{n}\frac{q_0 q_i}{r_i} + \sum_{\substack{i=1\\ j<i}}^{n}\frac{q_i q_j}{r_{ij}}. \tag{1}$$

Here $q_0 = 6$ is charge of the carbon nucleus, $q_i = -1$ ($i = 1,\ldots,5$) are the electron charges, m_0 is the nuclear mass, $\mu_i = m_0 m_i/(m_0 + m_i)$ is the reduced mass of electron i ($m_i = m_e = 1$), and $\mathbf{r}_i$ ($i = 1,\ldots,5$) denotes the position of the i-th electron with respect to the nucleus, at which we place the origin of the internal reference frame. Further, the prime symbol, $'$, denotes the vector transpose and $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$ is the distance between electrons i and j. The following values for the nuclear masses of $^{12}C^+$, $^{13}C^+$, and $^{14}C^+$ are adopted, respectively: $21\,868.663\,850\,5 m_e$, $23\,697.667\,827 m_e$ and $25\,520.350\,606 m_e$. These nuclear masses were derived from the experimentally determined values of atomic masses reported in Ref. [19].

The calculations involving nonrelativistic Hamiltonian $H_{\mathrm{nr}}^{\mathrm{int}}$ can be carried out for either a finite or infinite mass of the carbon nucleus. They yield the nonrelativistic ground- and excited-state energies (E_{nr}) and the corresponding wave functions. Both the energy and the wave function of each state depend on the mass of the nucleus. In this work, we report the infinite nuclear mass results as well as the data obtained for specific isotopes.

Basis functions

The all-electron ECG functions employed for expanding the spatial part of the wave functions of P-states have the following form:

$$\phi_k(\mathbf{r}) = z_{i_k}\exp\left[-\mathbf{r}'\mathbf{A}_k\mathbf{r}\right], \tag{2}$$

where z_{i_k} is the z-coordinate of the i_k-th electron. Subscript i_k, which labels an electron, can vary in the range $(1,\ldots,n)$ and can be treated as an adjustable integer variational parameter in the calculation. Because of this the z_{i_k} factor is specific for each basis function, ϕ_k. The value of i_k is determined variationally when the gaussian is first added to the basis set. In expression (2), $\mathbf{r}$ is a $3n$-component column vector formed by stacking 3-component vectors $\mathbf{r}_i$ on top of each other and matrix $\mathbf{A}_k$ is a $3n \times 3n$ real symmetric matrix of the exponential parameters. $\mathbf{A}_k$ is constructed as $\mathbf{A}_k = A_k \otimes I_3$, where A_k is a $n \times n$ dense real symmetric matrix and I_3 is a 3×3 identity matrix, while symbol $\otimes$ denotes the Kronecker product. Such representation of matrix $\mathbf{A}_k$ ensures that the exponential part of the basis functions is invariant with respect to 3D rotations. For more information on the basis sets see Ref. [18, 20].

FINE STRUCTURE SPLITTING

At the lowest-order approximation, the spin–orbit interaction that gives rise to the fine structure splitting is obtained as a sum of two terms. The first term in the finite-nuclear-mass (FNM) approach is an expectation value of the following operator:

$$H_{\mathrm{SO}} = H_{\mathrm{SO}_1} + H_{\mathrm{SO}_2} = -\sum_{i=1}^{n}\frac{q_0 q_i}{2m_i}\left(\frac{1}{m_i} + \frac{2}{m_0}\right)\frac{\mathbf{s}'_i}{r_i^3}(\mathbf{r}_i \times \mathbf{p}_i) - \sum_{\substack{i,j=1\\ j\neq i}}^{n}\left\{\frac{q_0 q_i}{m_0 m_i}\frac{\mathbf{s}'_i}{r_i^3}(\mathbf{r}_i \times \mathbf{p}_j) + \frac{q_i q_j}{2m_i}\frac{\mathbf{s}'_i}{r_{ij}^3}\left[\mathbf{r}_{ij} \times \left(\frac{1}{m_i}\mathbf{p}_i - \frac{2}{m_j}\mathbf{p}_j\right)\right]\right\} \tag{3}$$

where H_{SO_1} and H_{SO_2} are the one- and two-electron parts of the H_{SO} operator, respectively. Note that the expectation value is computed with the nonrelativistic wave function corresponding to finite nuclear mass. To obtain the contribution of this term to the total spin–orbit correction, the expectation value of H_{SO} is multiplied by α^2, where α is the fine structure constant. The second term calculated as the expectation value of the following Hamiltonian representing the correction to fine structure splitting due to anomalous magnetic moment (AMM) of the electron:

$$H_{\mathrm{AMM}} = H_{\mathrm{AMM}_1} + H_{\mathrm{AMM}_2} = -\sum_{i=1}^{n}\frac{q_0 q_i}{2m_i^2}\frac{\mathbf{s}'_i}{r_i^3}(\mathbf{r}_i \times \mathbf{p}_i) - \sum_{\substack{i,j=1\\ j\neq i}}^{n}\frac{q_i q_j}{2m_i}\frac{\mathbf{s}'_i}{r_{ij}^3}\left[\mathbf{r}_{ij} \times \left(\frac{1}{m_i}\mathbf{p}_i - \frac{1}{m_j}\mathbf{p}_j\right)\right], \tag{4}$$

TABLE I. Convergence of the nonrelativistic (E_{nr}) energies with the number of basis functions for the lowest eight ^2P odd-parity states of ^{12}C$^+$, ^{13}C$^+$, ^{14}C$^+$, and $^{\infty}$C$^+$. The numbers shown in parentheses are estimated uncertainties due to the basis truncation. All values are given in atomic units.

Basis	^{12}C$^+$	^{13}C$^+$	^{14}C$^+$	$^{\infty}$C$^+$
	$(1s^2\,2s^2\,2p)\ ^2P$			
14000	-37.42917150	-37.42930355	-37.42941631	-37.43088245
15000	-37.42917158	-37.42930363	-37.42941639	-37.43088253
16000	-37.42917161	-37.42930365	-37.42941641	-37.43088255
∞	-37.42917181(27)	-37.42930385(27)	-37.42941660(27)	-37.43088274(27)
	$(1s^2\,2s^2\,3p)\ ^2P$			
14000	-36.82901767	-36.82914967	-36.82926239	-36.83072797
15000	-36.82901769	-36.82914968	-36.82926240	-36.83072799
16000	-36.82901773	-36.82914972	-36.82926244	-36.83072803
∞	-36.82901810(49)	-36.82915009(49)	-36.82926278(49)	-36.83072837(49)
	$(1s^2\,2s^2\,4p)\ ^2P$			
14000	-36.6887644	-36.6888959	-36.6890082	-36.6904684
15000	-36.6887646	-36.6888961	-36.6890084	-36.6904686
16000	-36.6887647	-36.6888962	-36.6890085	-36.6904687
∞	-36.6887655(11)	-36.6888970(11)	-36.6890093(11)	-36.6904695(11)
	$(1s^2\,2p^3)\ ^2P$			
14000	-36.6612383	-36.6613653	-36.6614737	-36.6628837
15000	-36.6612393	-36.6613663	-36.6614747	-36.6628847
16000	-36.6612402	-36.6613672	-36.6614756	-36.6628856
∞	-36.6612456(76)	-36.6613726(76)	-36.6614801(76)	-36.6628901(76)
	$(1s^2\,2s^2\,5p)\ ^2P$			
14000	-36.6308903	-36.6310197	-36.6311302	-36.6325665
15000	-36.6308914	-36.6310208	-36.6311313	-36.6325677
16000	-36.6308923	-36.6310216	-36.6311321	-36.6325685
∞	-36.6308978(77)	-36.6310272(77)	-36.6311371(77)	-36.6325735(77)
	$(1s^2\,2s\,2p\,3s)\ ^2P$			
14000	-36.6195465	-36.6196759	-36.6197863	-36.6212218
15000	-36.6195473	-36.6196766	-36.6197870	-36.6212225
16000	-36.6195484	-36.6196777	-36.6197881	-36.6212236
∞	-36.6195540(81)	-36.6196834(81)	-36.6197935(81)	-36.6212285(81)
	$(1s^2\,2s^2\,6p)\ ^2P$			
14000	-36.5954479	-36.5955794	-36.5956917	-36.5971521
15000	-36.5954483	-36.5955798	-36.5956922	-36.5971525
16000	-36.5954485	-36.5955801	-36.5956924	-36.5971528
∞	-36.5954514(37)	-36.5955829(37)	-36.5956952(37)	-36.5971556(37)
	$(1s^2\,2s^2\,7p)\ ^2P$			
14000	-36.5783286	-36.5784602	-36.5785725	-36.5800332
15000	-36.5783289	-36.5784605	-36.5785728	-36.5800335
16000	-36.5783292	-36.5784608	-36.5785731	-36.5800338
∞	-36.5783350(73)	-36.5784665(73)	-36.5785789(73)	-36.5800395(73)

where $\kappa = 1.15965218128(18) \times 10^{-3}$ [21] is the electron magnetic moment anomaly. The H_{AMM} term is multiplied by $2\kappa\alpha^2$, which is roughly proportional to α^3. It should be noted that the above operator H_{AMM} is obtained within infinite-nuclear-mass (INM) approximation and, thus, does not contain any finite mass corrections. For more information on the operators see Ref. [17, 22].

RESULTS

In the first step, nonrelativistic variational calculations are performed for the lowest eight Rydberg ^2P states of C II using ECG expansions of the wave functions of the states and internal Hamiltonian (1). This is the most computationally demanding part of this work that demanded almost three years of continuous calculations performed with our in-house parallel computer code which makes use of the MPI (Message Passing Interface) protocol. By far the largest fraction of the computer time is used to grow the basis set and to optimize the nonlinear parameters of the gaussians. The calculations use the standard Rayleigh–Ritz variational method and involve independent energy minimization of each state with respect to the nonlinear ECG parameters used in expanding the wave function of that state. The calculations for each state yield basis sets of a progressively larger size (upto 16000 ECGs), which provides data that can be used to estimate the convergence of the numerical results. The basis sets are generated for ^{12}C isotope and then reused in the calculations for ^{13}C, ^{14}C, and $^{\infty}$C, for which only the linear variational parameters are adjusted. The approach used in the optimization was described in our previous works (e.g. Ref. [12, 18]). Some calculations, particularly for higher excited states, are done using the extended precision (80-bit floating-point numbers that have approximately 19 significant decimal figure precision).

Table I shows nonrelativistic energies (E_{nr}) of the eight lowest ^2P states of C$^+$ using basis sets with increasingly larger number of functions. The most accurate to date nonrelativistic energies for the ^2P states of C II ion have been obtained in the current work. For instance, -37.430 882 55 hartree value has been obtained for the ground state of $^{\infty}$C$^+$ ion using 16000 ECGs and extrapolated to an infinite number of functions of -37.430 882 74(27) hartree which are much lower than the -37.424 054 [24], -37.410 275 481 [9] and -37.430 73(4) [11] hartree values calculated with the MCHF, CI(SD), and DMC methods, respectively. Furthermore, as one can see from the table, the present non-BO calculations are well converged at the nonrelativistic level for all eight ^2P states and for all isotopes. For example, at least six and five dignits after the decimal point are converged for the $(1s^22s^22p)\ ^2P$ and $(1s^22s^27p)\ ^2P$ states, respectively. Also, by comparing the energies obtained with 14000, 15000, and 16000 ECGs shown in Table I one can conclude that the nonrelativistic energies obtained with 14000 ECGs for each state are already very accurate. This is an important point, as, due to computatonal constraints, the 14000-ECG basis sets are the largest ones used to calculate the fine structure splittings.

In the next step, the fine structure splitting calculations are performed for the considered states using the following formula

$$E(n\,^2P_{3/2}) - E(n\,^2P_{1/2}) = \underbrace{\alpha^2 C^{\mathrm{SO}} \langle H_{\mathrm{SO}} \rangle}_{\sim\alpha^2} + \underbrace{2\kappa\alpha^2 C^{\mathrm{SO}} \langle H_{\mathrm{AMM}} \rangle}_{\delta_{\mathrm{AMM}}}, \tag{5}$$

where the expectation values $\langle H_{\mathrm{SO}} \rangle$ and $\langle H_{\mathrm{AMM}} \rangle$ are calculated between the states $|n\,^2P, M_S = 1/2, M_L = 1\rangle$ obtained within FNM and INM approaches, respectively. The factor $C^{\mathrm{SO}} = 3$ determines the energy difference of Eq. (5) and it is derived from the recoupling coefficients of the angular momenta (for more details see Ref. [22]).

Table II presents the calculated results along with the NIST ASD [23] values for the studied states. To the best of our knowledge, our reported values are the most accurate values to date for the fine structure splitting of the C$^+$ ion. The previous most accurate calculations are those of Jönsson *et al.* [8],

TABLE II. Fine structure splittings of low-lying $^2P^o_J$ states of C$^+$ in cm^{-1}, where $J = 1/2,\ 3/2$. The α^2 and δ_{AMM} contributions to the fine structure splitting are defined in Eq. (5). The numbers in the first pair of parentheses provide estimates of uncertainties due to the basis truncation. The uncertainties due to the absence of the off-diagonal contributions due to coupling with states with different S and/or L quantum numbers from the quantum numbers of the considered state are shown in the second pair of parentheses. The numbers in the second pair of parentheses also include rough estimates of the uncertainties due to other neglected higher-order corrections.

State		Basis	^{12}C$^+$	^{13}C$^+$	^{14}C$^+$	$^{\infty}$C$^+$
$(1s^2\,2s^2\,2p)$ ^2P	α^2	14000	63.209089	63.209402	63.209670	63.213150
		∞	63.209168(88)	63.209481(88)	63.209750(88)	63.213232(88)
	$\alpha^2 + \delta_{\rm AMM}$	14000	63.372299	63.372613	63.372880	63.376361
		∞	63.372379(88)(31800)	63.372692(88)(31800)	63.372961(88)(31800)	63.376442(88)(31800)
	NIST		63.395087(20)	63.395380(30)	63.395640(50)	
$(1s^2\,2s^2\,3p)$ ^2P	α^2	14000	11.120309	11.120312	11.120314	11.120345
		∞	11.120332(26)	11.120334(26)	11.120336(26)	11.120368(26)
	$\alpha^2 + \delta_{\rm AMM}$	14000	11.149067	11.149070	11.149072	11.149103
		∞	11.149090(26)(5900)	11.149092(26)(5900)	11.149094(26)(5900)	11.149126(26)(5900)
	NIST		11.146(27)	11.152(27)	11.158(28)	
$(1s^2\,2s^2\,4p)$ ^2P	α^2	14000	6.7418	6.7413	6.7409	6.7355
		∞	6.7424(20)	6.7419(20)	6.7415(20)	6.7361(20)
	$\alpha^2 + \delta_{\rm AMM}$	14000	6.7596	6.7591	6.7587	6.7534
		∞	6.7602(20)(39)	6.7597(20)(39)	6.7593(20)(39)	6.7539(20)(39)
	NIST		6.662(47)	6.662(48)	6.662(50)	
$(1s^2\,2p^3)$ ^2P	α^2	14000	17.961	17.964	17.967	18.000
		∞	17.959(10)	17.962(10)	17.964(10)	17.997(10)
	$\alpha^2 + \delta_{\rm AMM}$	14000	18.011	18.014	18.017	18.050
		∞	18.009(10)(137)	18.012(10)(137)	18.014(10)(137)	18.047(10)(137)
	NIST		18.755(46)	18.756(49)	18.756(54)	
$(1s^2\,2s^2\,5p)$ ^2P	α^2	14000	8.248	8.243	8.238	8.176
		∞	8.256(23)	8.250(23)	8.245(23)	8.184(23)
	$\alpha^2 + \delta_{\rm AMM}$	14000	8.271	8.265	8.260	8.199
		∞	8.278(23)(19)	8.273(23)(19)	8.268(23)(19)	8.206(23)(19)
	NIST		7.380(57)	7.380(59)	7.380(65)	
$(1s^2\,2s\,2p\,3s)$ ^2P	α^2	14000	18.414	18.418	18.421	18.459
		∞	18.411(16)	18.414(16)	18.417(16)	18.454(16)
	$\alpha^2 + \delta_{\rm AMM}$	14000	18.463	18.467	18.470	18.508
		∞	18.460(16)(67)	18.463(16)(67)	18.466(16)(67)	18.503(16)(67)
	NIST		18.970(78)	18.970(83)	18.970(94)	
$(1s^2\,2s^2\,6p)$ ^2P	α^2	14000	2.4134	2.4137	2.4139	2.4171
		∞	2.4117(52)	2.4119(52)	2.4122(52)	2.4155(52)
	$\alpha^2 + \delta_{\rm AMM}$	14000	2.4197	2.4200	2.4202	2.4234
		∞	2.4179(52)(16)	2.4182(52)(16)	2.4184(52)(16)	2.4217(52)(16)
	NIST *		2.17(17)	2.17(17)	2.170(17)	
$(1s^2\,2s^2\,7p)$ ^2P	α^2	14000	1.0970	1.0971	1.0972	1.0979
		∞	1.0962(33)	1.0963(33)	1.0964(33)	1.0969(33)
	$\alpha^2 + \delta_{\rm AMM}$	14000	1.0999	1.0999	1.1000	1.1007
		∞	1.0991(33)(5)	1.0991(33)(5)	1.0992(33)(5)	1.0997(33)(5)
	NIST		0.970(524)	0.970(524)	0.970(524)	

* The authors of Ref. [23] confirmed to us that there was a problem in the fitting procedure and the correct values are presented for this state in this table.

in which the MCDHF method was employed. Jönsson *et al.* investigated the first four ^2P states of C$^+$. The agreement between their calculated and the experimental values are fairly good, but they are not at the same level of accuracy as the ones reported in the present work. For example, 63.01 cm^{-1} value has been obtained for the fine structure splitting of the lowest ^2P state while an experimental value of 63.395 087(20) cm^{-1} was reported by Cooksy *et al.* [7] for ^{12}C$^+$. In the present work, 63.372 299 cm^{-1} is obtained at the $\alpha^2 + \delta_{\rm AMM}$ order which is in much better agreement with the experiment. It should be noted that the major source of the total uncertainty in our spin–orbit calculations is different for lower and higher states. As it can be deduced from Table II, the dominant part of the uncertainty for lower states comes from the missing higher orders and hyperfine-mixing corrections. In the case of highly excited states, however, basis set truncation error becomes the dominant source of uncertainty (for more information about the procedure used to estimate the uncertainties in the present calculations see Ref. [25], as well as Table 5 and the explanations in Ref. [17]). At this development stage, higher order corrections have not been implemented in our code; however, a rough estimation of the two latter corrections are included in Table II (for more information, see Refs. [26]).

At first glance, it seems that the agreement between the calculated fine structure splitting and experimental data for higher states is not as good as for the lowest state. As discussed previously, the available experimental data for the energy levels of the C$^+$ ion, except the first one, are not accurate enough to be used to verify the accuracy of the present calculations. As mentioned, in the experiments of Glad, the light source had a significant Stark shift whose magnitude was not precisely known. Thus, the expected uncertainty of the experimental data can be as high as 0.5 cm^{-1} or higher (see section 2.1 in Ref. [2]). In view of that, the main goal of the present work is to perform the most accurate theoretical calculation to date of the fine splitting of the low lying ^2P levels of the C$^+$ ion and to probe the accuracy of the available experimental values of the splitting, as well as the accuracy of the previous theoretical studies. We hope that this work will provide motivation to experimentally remeasure the fine structure splitting of this important atomic system at much higher accuracy.

SUMMARY

To summarize, high-precision calculations are performed for the lowest eight $^2P^o$ Rydberg states of the ^{12}C$^+$, ^{13}C$^+$, ^{14}C$^+$, and $^\infty$C$^+$ ions. The nonrelativistic calculations do not assume the Born-Oppenheimer approximation (i.e. they use the finite nuclear mass approach) and employ the Rayleigh-Ritz variational method complemented with the use of all-particle explicitly correlated Gaussian basis functions. Very accurate nonrelativistic energies and the corresponding wave functions are generated. The wave functions are used to compute the fine structure splitting of the considered levels using the algorithms recently developed and implemented in our group. Even though the calculated splittings are in very good agreement with the available accurate experimental data for the lowest state, they also reveal that more accurate measurements are highly desirable for higher states. For some of the considered Rydberg states, these are the first high precision calculations performed to date.

The future extension of the present work will include implementation of the algorithm to calculate the hyperfine structure of the C$^+$ spectra. The calculated fine and hyperfine transitions and the corresponding oscillator strengths will be used to analyze the collisional excitations of ionized carbon in terms of line intensities produced by simple cloud models. As mentioned in the introduction, the fine-structure transitions of C$^+$ can be excited via collisions with small molecules (e.g. hydrogen molecules), light atoms, and electrons resulting in cooling for ISM. Thus, the interplay between these species in the interstellar clouds is very important to understand the dynamics of the interstellar chemical and physical processes, In modeling this dynamics, the spectra due to the fine transitions of C$^+$ calculated in the present work will be used.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article. Additional data can be requested from the corresponding author.

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