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Isotope shifts of the $1s^22s^2(^1S_0) \rightarrow 1s^22p^2(^1S_0)$ transition in the doubly ionized carbon ion C^{2+}

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Highly accurate quantum mechanical calculations are performed for the $1s^22s^2\ (^1S_0) \rightarrow 1s^22p^2\ (^1S_0)$ transition energy in the isotopomers of C^{2+} ion to determine the isotope shifts. Explicitly correlated Gaussian functions and a variational approach that explicitly includes the nuclear motion are employed in the calculations. The leading relativistic and quantum electrodynamics corrections to the transition energy are also calculated using the perturbation theory with the nonrelativistic wave function as the zero-order approximation. It is determined that the $^{12}C^{2+}$ transitions energy, which is obtained from the calculations to be 182 519.031 cm^{-1} (vs the experimental value of 182 519.88 cm^{-1}, an excellent sub-wave-number agreement) up-shifts by 1.755 cm^{-1} for $^{13}C^{2+}$ and by additional 1.498 cm^{-1} for $^{14}C^{2+}$. Those shifts are sufficiently large to be measured experimentally.

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I. INTRODUCTION

Understanding the physical state of the interstellar medium (ISM) is a fundamental area of research in astrophysics [1–8]. The classical theoretical models predict the stable coexistence in pressure ISM equilibrium of various phases of interstellar matter: the cold neutral medium (CNM), the warm neutral medium (WNM), the warm ionized medium (WIM), and the hot ionized medium (HIM). The HIM, which was identified by the presence of soft x-ray emission by Snowden *et al.* [9], has been the focus of the study with the Cosmic Hot Interstellar Plasma Spectrometer (CHIPS) instrument launched on January 12, 2003 [10]. As ultraviolet (uv) spectra of absorption lines of atomic ions can be used to make accurate temperature and turbulent-velocity measurements of gas in the WIM by comparing the observed linewidths of ions with different atomic masses, the spectra of ions of the carbon isotopes at various ionization stages can be particularly useful. These ions include the doubly charged carbon ion, C^{2+}, which is the target of the quantum mechanical calculations performed in this work.

Isotope shifts of atomic spectral transition energies are among the properties that are also used to test the agreement between the experimental results and high-level theoretical calculations. Since those shifts result from the different nuclear masses of the isotopes, the nuclear mass has to be explicitly included in the calculations of the energy levels of the atom (or atomic ion). This can be done either directly by using a nuclear-mass-dependent Hamiltonian in the energy calculations or by employing the perturbation theory and treating the mass effect as a correction to the infinite-nuclear-mass energy. In this work we use the former approach. As the isotope shifts of the atomic energy levels are very small, their calculations have to be performed with very high accuracy. Such accuracy is achieved in the present calculations with the use of all-electron explicitly correlated Gaussian functions (ECGFs). We have used these types of functions to calculate transitions energies in other three-, four-, and five-electron atomic systems [11–13] and we showed that sub-wave-number accuracy is achievable with those functions provided that several thousands of them are used and their nonlinear parameters are extensively optimized. Also, the calculations have to include the leading relativistic (REL) and quantum electrodynamics (QED) corrections. In this work the calculations of both corrections are carried out using the perturbation theory. A brief description of the method used here is presented in what follows.

The focus of the present calculation is two lowest $^1S_0$ states of three isotopomers of the C^{2+} ion: $^{12}C^{2+}$, $^{13}C^{2+}$, and $^{14}C^{2+}$. We have also performed calculations for the infinite-nuclear-mass case, $^{\infty}C^{2+}$. The quantity, which is compared with experiment, is the transition energy between these two states for the $^{12}C^{2+}$ isotope. The experimental value for this transition energy is 182 519.88 cm^{-1} [14]. The finite-mass calculations allows us to determine how much this transition frequency shifts in $^{13}C^{2+}$ and $^{14}C^{2+}$.

The other purpose for performing high-accuracy calculations on the doubly ionized carbon atom is to determine how well the perturbation-theory calculations of the REL and QED corrections work in this case. Our previous calculation of some lowest ^1S states of the beryllium atom [15] showed that the approach works very well for that system. However, in C^{2+} the REL and QED effects are expected to be about two orders of magnitude larger than for Be and a question arises as to whether the perturbation-theory approach based on the nonrelativistic Schrödinger equation as the zeroth-order approximation is equally good in this case.

II. THE METHOD

In the nonrelativistic variational calculations we use the following Hamiltonian (in a.u.) [16,17]:

$$\hat{H}_{\rm int} = -\frac{1}{2}\left(\sum_{i=1}^{4}\frac{1}{\mu_i}\nabla^2_{\mathbf{r}_i} + \sum_{i=1}^{4}\sum_{j\neq i}^{4}\frac{1}{m_0}\nabla_{\mathbf{r}_i}\cdot\nabla_{\mathbf{r}_j}\right) + \sum_{i=1}^{4}\frac{q_0q_i}{r_i} + \sum_{i=1}^{4}\sum_{i<j}^{4}\frac{q_iq_j}{r_{ij}}, \tag{1}$$

where m_0 is the mass of the nucleus ($m_0 = 21\,868.663\,82$ for ^{12}C, $m_0 = 23\,697.667\,79$ for ^{13}C, and $m_0 = 25\,520.350\,57$ for ^{14}C), μ_i are the reduced electron masses, $\mu_i = m_0 m_i/(m_0 + m_i)$, $m_1 = m_2 = m_3 = m_4 = 1$, $q_0 = 6$ (the charge of the nucleus), $q_1 = q_2 = q_3 = q_4 = -1$ (the charges of the electrons), $\mathbf{r}_i$, $i = 1,2,3,4$, are the position vectors of the electrons with respect to the nucleus, r_i are their lengths, and $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$ are the distances between the electrons. The Hamiltonian (1) is obtained by rigorously separating the center-of-mass motion from the nonrelativistic laboratory frame Hamiltonian [16–19]. This separation reduces the five-particle problem of the C^{2+} ion to a four-"pseudoparticle" problem. The calculations have been carried out for finite masses of the carbon nucleus, as well as for infinite nuclear mass. They yielded the nonrelativistic energies, E_{nonrel}, and the corresponding wave functions. The infinite-nuclear-mass results were generated to serve as a reference for calculations performed by others in the framework of the Born-Oppenheimer approximation.

Denoting by $\mathbf{r}$ the 12×1 vector of the internal Cartesian electron coordinates, $\mathbf{r} = (\mathbf{r}'_1,\mathbf{r}'_2,\mathbf{r}'_3,\mathbf{r}'_4)'$ (the prime symbol denotes the vector or matrix transposition) and by σ the spin coordinates of the electrons and the nucleus, we can write the complete wave function of C^{2+} as

$$\Psi(\mathbf{r},\sigma) = \hat{\mathcal{A}}[\Phi(\mathbf{r})\Omega_{S,M_S}(\sigma)]. \tag{2}$$

In (2) $\hat{\mathcal{A}}$ antisymmetrizes the electron labels and $\Omega_{S,M_S}(\sigma)$ is a product of the spin functions of the electrons and the nucleus, $\Omega_{S,M_S} = \Omega^e\Omega^N$. For the states considered in this work Ω^e represents a four-electron singlet spin function. In practical calculations it is more convenient to use the spin-free formalism [20,21]. In that formalism only the spatial wave function, $\Phi(\mathbf{r})$, enters the calculation. However, before it is used, $\Phi(\mathbf{r})$ has to be acted on by the appropriate Young operator that represents the permutational symmetry properties of the state under consideration [20,21].

The following s Gaussians are used in this work to expand the spatial wave functions, $\Phi(\mathbf{r})$, for the two considered $^1S_0$ states of C^{2+}:

$$\phi_k = \exp[-\mathbf{r}'(L_k L'_k \otimes I_3)\mathbf{r}], \tag{3}$$

where $\otimes$ is the Kronecker product symbol, L_k is a 4×4 lower triangular matrix of nonlinear variational parameters, and I_3 is the 3×3 identity matrix. The Cholesky factored form representation, $L_k L'_k$, of the matrix of the Gaussian exponential parameters automatically makes the ϕ_k function square integrable for any values of the L_k matrix elements. This is important in optimizing these parameters because such an optimization can be carried out without any restrictions (i.e., the L_k matrix elements can be varied in the range of $[-\infty,+\infty]$), which makes it much more efficient.

The optimization of elements L_k is performed by minimizing the total energy, which in the present calculations has been done separately for each state. In the minimization we employed the analytic gradient of the energy determined with respect to the L_k matrix elements [18,19], which significantly accelerates the optimization process and reduces its computational cost. Without the use of the analytic gradient, the present calculations could not be performed at the accuracy level achieved in this work.

The relativistic effects have been computed as the expectation value of the Dirac-Breit Hamiltonian in the Pauli approximation ($\hat{H}_{\text{rel}}$) [22,23] transformed to the internal coordinate system. For the states with the S symmetry considered in this work, $\hat{H}_{\text{rel}}$ includes the mass-velocity (MV), Darwin (D), orbit-orbit (OO), and spin-spin (SS) terms:

$$\hat{H}_{\text{rel}} = \hat{H}_{\text{MV}} + \hat{H}_{\text{D}} + \hat{H}_{\text{OO}} + \hat{H}_{\text{SS}}. \tag{4}$$

In the internal coordinates these operators have the following form:

$$\hat{H}_{\text{MV}} = -\frac{1}{8}\left[\frac{1}{m_0^3}\left(\sum_{i=1}^{4}\nabla_{\mathbf{r}_i}\right)^4 + \sum_{i=1}^{4}\frac{1}{m_i^3}\nabla^4_{\mathbf{r}_i}\right], \tag{5}$$

$$\hat{H}_{\text{D}} = -\frac{1}{2}\pi\left[\sum_{i=1}^{4}\frac{q_0 q_i}{m_i^2}\,\delta^3(\mathbf{r}_i) + \sum_{i=1}^{4}\sum_{j\neq i}^{4}\frac{q_i q_j}{m_i^2}\,\delta^3(\mathbf{r}_{ij})\right], \tag{6}$$

$$\begin{aligned}\hat{H}_{\text{OO}} = &-\frac{1}{2}\sum_{i=1}^{4}\sum_{j=1}^{4}\frac{q_0 q_i}{m_0 m_i}\left[\frac{1}{r_i}\boldsymbol{\nabla}_{\mathbf{r}_i}\cdot\boldsymbol{\nabla}_{\mathbf{r}_j}\right.\\ &\left.+\frac{1}{r_i^3}\,\mathbf{r}_i\cdot(\mathbf{r}_i\cdot\boldsymbol{\nabla}_{\mathbf{r}_i})\boldsymbol{\nabla}_{\mathbf{r}_j}\right] + \frac{1}{2}\sum_{i=1}^{2}\sum_{j>i}^{4}\frac{q_i q_j}{m_i m_j}\\ &\times\left[\frac{1}{r_{ij}}\,\boldsymbol{\nabla}_{\mathbf{r}_i}\cdot\boldsymbol{\nabla}_{\mathbf{r}_j} + \frac{1}{r_{ij}^3}\,\mathbf{r}_{ij}\cdot(\mathbf{r}_{ij}\cdot\boldsymbol{\nabla}_{\mathbf{r}_i})\boldsymbol{\nabla}_{\mathbf{r}_j}\right],\end{aligned} \tag{7}$$

$$\hat{H}_{\text{SS}} = -\frac{2}{3}\pi\sum_{i=1}^{4}\sum_{j>i}^{4}\frac{q_i q_j}{m_i m_j}\,\delta^3(\mathbf{r}_{ij})(\mathbf{s}_i\cdot\mathbf{s}_j), \tag{8}$$

where $\delta^3(\mathbf{r}_i)$ denotes the three-dimensional Dirac δ function. We should note that in the present calculations we have not included the magnetic anomaly factors for the electrons and the nucleus in the Darwin and spin-spin corrections. The relativistic correction calculations have been performed for the finite and infinite masses of the carbon nucleus. Thus, the value of the correction varies with the nuclear mass.

In calculating the leading QED corrections of the order α^3 and α^4 (called here E_{QED} and E_{HQED}, respectively), in this work we used the approach described by Pachucki *et al.* [24–27]. The approach is based on the perturbation theory employed in the framework of the the nonrelativistic QED (NRQED) [28–30]. The zeroth-order level in this approach is the nonrelativistic Schrödiger equation. The algorithm used here was also employed in our recent work on the ground and excited states of the Be atom [15]. The α^3 and α^4 QED corrections represent the two-photon exchange, the vacuum polarization, and the electron self-energy effects. The algorithm for calculating the α^3 QED correction includes the magnetic anomaly factors for the electrons. As the procedure used in this work for calculating the α^3 and α^4 QED corrections was only developed for the infinite-mass case, only this type of calculation has been performed.

We note that, while the complete α^3 QED correction (denoted as $\alpha^3 E_{\text{QED}}$) is determined in the present calculations, only the dominant contribution of the α^4 QED (denoted as

TABLE I. The convergence of the nonrelativistic energies and the leading relativistic corrections (all values are in a.u.) for different isotopes of C^{2+} with the number of basis functions. The rightmost column contains the total energy calculated as the sum of the nonrelativistic energy plus the relativistic corrections multiplied by α^2: $E_{\rm tot} = E_{\rm nonrel} + \alpha^2(\langle H_{\rm MV}\rangle + \langle H_{\rm D}\rangle + \langle H_{\rm SS}\rangle + \langle H_{\rm OO}\rangle)$. The values in parentheses are estimates of the remaining theoretical uncertainty.

System	State	Basis size	$E_{\rm nonrel}$	$\langle H_{\rm MV}\rangle$	$\langle H_{\rm D}\rangle$	$\langle H_{\rm SS}\rangle$	$\langle H_{\rm OO}\rangle$	$E_{\rm nonrel} + \alpha^2 E_{\rm rel}$
$^{12}C^{2+}$	$2\,^1S_0$	2000	−36.533 148 788	−1509.7554	1199.1146	42.4169	−2.3963	−36.547 559 684
		4000	−36.533 149 029	−1509.7926	1199.1534	42.4155	−2.3963	−36.547 559 914
		6000	−36.533 149 098	−1509.8448	1199.2045	42.4092	−2.3963	−36.547 560 377
		8000	−36.533 149 131	−1509.8420	1199.2076	42.4081	−2.3963	−36.547 560 149
		10 000	−36.533 149 149	−1509.8919	1199.2478	42.4077	−2.3963	−36.547 560 710
		10 000[a]	−36.533 149 159(35)	−1509.9152	1199.2626	42.4076	−2.3963	−36.547 561 174(500)
	$3\,^1S_0$	2000	−35.702 788 412	−1417.4557	1132.2895	39.3873	0.6127	−35.715 843 846
		4000	−35.702 791 828	−1417.7682	1132.6512	39.3539	0.6127	−35.715 846 418
		6000	−35.702 792 293	−1417.8611	1132.7478	39.3523	0.6127	−35.715 846 767
		8000	−35.702 792 471	−1417.8923	1132.7824	39.3522	0.6127	−35.715 846 774
		10 000	−35.702 792 551	−1417.9022	1132.7983	39.3512	0.6127	−35.715 846 589
		10 000[a]	−35.702 792 578(110)	−1417.9024	1132.7984	39.3512	0.6127	−35.715 846 619(200)
$^{13}C^{2+}$	$2\,^1S_0$	2000	−36.533 280 234	−1509.7771	1199.1275	42.4173	−2.3876	−36.547 691 114
		4000	−36.533 280 475	−1509.8143	1199.1663	42.4158	−2.3876	−36.547 691 344
		6000	−36.533 280 544	−1509.8665	1199.2174	42.4096	−2.3876	−36.547 691 807
		8000	−36.533 280 577	−1509.8636	1199.2205	42.4085	−2.3876	−36.547 691 579
		10 000	−36.533 280 594	−1509.9136	1199.2607	42.4081	−2.3876	−36.547 692 141
		10 000[a]	−36.533 280 604(35)	−1509.9368	1199.2755	42.4080	−2.3876	−36.547 692 604(500)
	$3\,^1S_0$	2000	−35.702 911 862	−1417.4760	1132.3017	39.3877	0.6207	−35.715 967 282
		4000	−35.702 915 279	−1417.7885	1132.6635	39.3543	0.6207	−35.715 969 854
		6000	−35.702 915 744	−1417.8814	1132.7601	39.3527	0.6207	−35.715 970 203
		8000	−35.702 915 921	−1417.9126	1132.7947	39.3525	0.6207	−35.715 970 211
		10 000	−35.702 916 001	−1417.9226	1132.8105	39.3516	0.6207	−35.715 970 025
		10 000[a]	−35.702 916 028(110)	−1417.9227	1132.8107	39.3515	0.6207	−35.715 970 055(200)
$^{14}C^{2+}$	$2\,^1S_0$	2000	−36.533 392 482	−1509.7956	1199.1385	42.4176	−2.3803	−36.547 803 349
		4000	−36.533 392 723	−1509.8328	1199.1773	42.4162	−2.3803	−36.547 803 579
		6000	−36.533 392 792	−1509.8850	1199.2284	42.4099	−2.3803	−36.547 804 042
		8000	−36.533 392 825	−1509.8821	1199.2315	42.4088	−2.3803	−36.547 803 815
		10 000	−36.533 392 843	−1509.9321	1199.2717	42.4084	−2.3803	−36.547 804 376
		10 000[a]	−36.533 392 853(35)	−1509.9553	1199.2865	42.4083	−2.3803	−36.547 804 840(500)
	$3\,^1S_0$	2000	−35.703 017 284	−1417.4934	1132.3122	39.3880	0.6275	−35.716 072 691
		4000	−35.703 020 700	−1417.8059	1132.6740	39.3546	0.6275	−35.716 075 263
		6000	−35.703 021 165	−1417.8988	1132.7706	39.3530	0.6275	−35.716 075 612
		8000	−35.703 021 343	−1417.9300	1132.8051	39.3528	0.6275	−35.716 075 620
		10 000	−35.703 021 423	−1417.9399	1132.8210	39.3519	0.6275	−35.716 075 434
		10 000[a]	−35.703 021 450(110)	−1417.9401	1132.8212	39.3519	0.6275	−35.716 075 464(200)
$^{\infty}C^{2+}$	$2\,^1S_0$	2000	−36.534 851 968	−1510.0359	1199.2817	42.4220	−2.2843	−36.549 262 665
		4000	−36.534 852 209	−1510.0731	1199.3205	42.4206	−2.2843	−36.549 262 895
		6000	−36.534 852 278	−1510.1253	1199.3716	42.4143	−2.2843	−36.549 263 358
		8000	−36.534 852 311	−1510.1225	1199.3747	42.4132	−2.2843	−36.549 263 130
		10 000	−36.534 852 328	−1510.1724	1199.4149	42.4128	−2.2843	−36.549 263 692
		10 000[a]	−36.534 852 338(35)	−1510.1957	1199.4297	42.4127	−2.2843	−36.549 264 156(500)
	$3\,^1S_0$	2000	−35.704 388 000	−1417.7190	1132.4484	39.3920	0.7159	−35.717 443 246
		4000	−35.704 391 417	−1418.0316	1132.8102	39.3586	0.7159	−35.717 445 820
		6000	−35.704 391 883	−1418.1245	1132.9068	39.3570	0.7159	−35.717 446 170
		8000	−35.704 392 060	−1418.1557	1132.9414	39.3569	0.7159	−35.717 446 178
		10 000	−35.704 392 140	−1418.1656	1132.9573	39.3559	0.7159	−35.717 445 993
		10 000[a]	−35.704 392 167(110)	−1418.1658	1132.9574	39.3559	0.7159	−35.717 446 023(200)

[a] Several additional optimization cycles were performed.

$\alpha^4 E_{\mathrm{HQED}}$) correction is calculated. E_{QED} for singlet states of a four-electron atom has the form [31,32]

$$E_{\mathrm{QED}} = \sum_{i=1,j<i}^{4} \langle\Psi| \left[\frac{164}{15} + \frac{14}{3}\ln\alpha\right]\delta^3(\mathbf{r}_{ij}) - \frac{7}{6\pi}P\left(1/r_{ij}^3\right)|\Psi\rangle + \sum_{i=1}^{4}\left[\frac{19}{30} + \ln(\alpha^{-2}) - \ln k_0\right]\frac{4q_0}{3}\langle\Psi|\delta^3(\mathbf{r}_i)|\Psi\rangle, \tag{9}$$

which includes the Araki-Sucher term, $\langle\Psi|P(1/r_{ij}^3)|\Psi\rangle/(4\pi)$, defined as

$$\langle\Psi|P\left(1/r_{ij}^3\right)|\Psi\rangle(4\pi) = \frac{4}{\pi}\lim_{a\to 0}\int \delta^3(\mathbf{r})\Psi^*(\mathbf{r})\Psi(\mathbf{r}) \times \left[\frac{1}{r^3}\Theta(r-a) + 4\pi\delta^3(\mathbf{r})(\gamma + \ln a)\right], \tag{10}$$

and the Bethe logarithm, $\ln k_0$, defined as

$$\ln k_0 = \frac{\langle\Psi|\sum_{i=1}^4 \mathbf{p}_i\left(\hat{H}_{\mathrm{int}}^{\mathrm{BO}} - E_{\mathrm{int}}^{\mathrm{BO}}\right)\ln\left[2\frac{\left(\hat{H}_{\mathrm{int}}^{\mathrm{BO}} - E_{\mathrm{int}}^{\mathrm{BO}}\right)}{\alpha^2}\right]\sum_{j=1}^4 \mathbf{p}_j|\Psi\rangle}{2\pi q_0\sum_{i=1}^4\langle\Psi|\delta^3(\mathbf{r}_i)|\Psi\rangle}, \tag{11}$$

where Θ is the step function, γ is the Euler constant, $\hat{H}_{\mathrm{int}}^{\mathrm{BO}}$ is the internal Hamiltonian in the Born-Oppenheiner approximation, and $E_{\mathrm{int}}^{\mathrm{BO}}$ is its eigenvalue.

While E_{QED} contribution is relatively simple to evaluate, the calculation of the complete α^4 correction is a formidable task. So far, such a complete calculation was only performed for one- and two-electron atoms [33–35], including the calculations of some lowest ^{1}S states of the helium atom [36–38]. In general, the algorithm for the α^4 correction involves some first- and second-order quantities, which, when computed individually, are divergent. The complexity of this algorithm can be assessed, for example, by the inspection of Eq. (3.58) in Ref. [38]. This complexity prevented us from calculating the full α^4 correction in the present work. However, it is known that the α^4 correction is dominated by the so-called one-loop term (see Eq. (2.56) in Ref. [38]) that can be determined using the following formula:

$$E_{\mathrm{HQED}} \simeq 4\pi q_0^2\left(\frac{139}{128} + \frac{5}{192} - \frac{\ln 2}{2}\right)\langle\Psi|\sum_{i=1}^{4}\delta^3(\mathbf{r}_i)|\Psi\rangle. \tag{12}$$

This formula has been employed here to approximately determine the contribution from the α^4 QED effects.

The numerical values of the fine structure constant and the Hartree-wave-number conversion factor used in this work were taken from [39]. They are: $\alpha = 7.297\,352\,537\,6 \times 10^{-3}$, 1 hartree = $2.194\,746\,313\,705 \times 10^5$ cm^{-1}.

III. RESULTS

The calculations performed in this work involved the following three steps. In the first step we performed

TABLE II. Convergence of the nonrelativistic and relativistic transition $2\,^1S_0 \to 3\,^1S_0$ energy values (in cm^{-1}) for different isotopes of C^{2+} with the number of basis functions. Again, the values in parentheses are estimates of the remaining theoretical uncertainty.

Basis size	^{12}C^{2+}, nonrel.	^{12}C^{2+}, rel.	^{13}C^{2+}, nonrel.	^{13}C^{2+}, rel.	^{14}C^{2+}, nonrel.	^{14}C^{2+}, rel.	$^{\infty}$C^{2+}, nonrel.	$^{\infty}$C^{2+}, rel.
2000	182 243.038	182 540.527	182 244.792	182 542.281	182 246.291	182 543.780	182 265.773	182 563.260
4000	182 242.341	182 540.013	182 244.095	182 541.767	182 245.594	182 543.266	182 265.076	182 562.746
6000	182 242.254	182 540.038	182 244.008	182 541.792	182 245.507	182 543.291	182 264.989	182 562.771
8000	182 242.222	182 539.986	182 243.977	182 541.741	182 245.475	182 543.239	182 264.957	182 562.719
10 000	182 242.208	182 540.150	182 243.963	182 541.905	182 245.461	182 543.403	182 264.944	182 562.883
10 000[a]	182 242.205(20)	182 540.245(170)	182 243.959(20)	182 542.000(170)	182 245.458(20)	182 543.498(170)	182 264.940(20)	1825 62.978(170)
Experiment [14]		182 519.88						

[a] Several additional optimization cycles were performed.

nonrelativistic variational calculations where the ECGF basis set for each state was grown to the size of 10 000 functions by incrementally enlarging the basis by 20 functions, optimizing them one by one with the gradient-based method, and, after this optimization was completed, cycling over all functions in the basis set and reoptimizing each of them once. After the 10 000-function basis was generated, several additional cyclic optimizations were performed to get the final basis set for each of the two states. The optimization of the exponential parameters of the basis functions have been performed only for the $^{12}C^{2+}$ isotope. In the calculations of other isotopes, as well as in the calculations with the infinite nuclear mass $^{\infty}C^{2+}$, only the linear expansion coefficients were varied. Our experience with atoms and atomlike systems have shown that adjusting only linear coefficients is sufficient to accurately reproduce the small change of the wave function caused by the difference in the nuclear mass.

In Table I we show how the total nonrelativistic energy and the relativistic corrections for each isotope and for each of the two states converge with the number of basis functions. As the results indicate, nine to ten leading figures in the nonrelativistic energy value are essentially converged. The results also show that the relativistic corrections are not as tightly converged as is the nonrelativistic energy. This is clearly caused by a singular character of the operators representing those corrections. Also, while the value of the total nonrelativistic energy in the variational calculations always decreases when more functions are added to the basis set, the values of the relativistic corrections usually show some small fluctuations.

We should mention that generating the ECGF basis sets has been the most time consuming step of the calculations. Even though our computer code was very effectively parallelized and run on a cluster using up to 24 computer cores, which made it possible to significantly reduce the computational time, it still took several months to complete the calculations.

As the internal nonrelativistic Hamiltonian depends on the reduced masses of the electrons, the nonrelativistic energy varies with the nuclear mass. Thus, the nonrelativistic wave functions are slightly different for different isotopes and this, along with the fact that some of the relativistic operators depend explicitly on the nuclear mass, results in the total relativistic correction being mass dependent. This dependency, as well as the mass dependency of the total nonrelativistic energy, cause a small change of the transition energy depending on the mass of the nucleus. This change is shown in Table II as the function of the number of ECGFs in the basis set. As one can see, the transition energy obtained with 10 000 ECGFs increases by 1.755 cm^{-1} in going from $^{12}C^{2+}$ to $^{13}C^{2+}$ and increases again by 1.498 cm^{-1} between $^{13}C^{2+}$ and $^{14}C^{2+}$. Virtually all the shift values result from the mass dependency of the nonrelativistic energy. In Table II we also show the uncertainty of each contribution to the transition energy estimated based on the convergence pattern. These values indicate that the nonrelativistic contribution to the transition energy is converged very well (the uncertainty is about 0.020 cm^{-1}), while the contribution from the relativistic correction is converged somewhat worse, to about 0.170 cm^{-1}. We should note that the theoretical uncertainties shown in Tables I and II (which arise due to finiteness of the basis set) should be considered to be very rough estimates only. As experience shows, these estimates can easily be off by a factor of two or three, in particular in the case of relativistic energies and transitions, whose convergence often shows nonmonotonic behavior. This is probably one of the reasons why the estimated uncertainty of the total relativistic energy of the excited state in Table I happened to be smaller than the one of the ground state, while normally one should expect the opposite.

In the next step of the calculations we evaluated the leading QED corrections of the order of α^3 and α^4. As said, the calculations of these corrections in the present work were only performed for the case of an infinite carbon nuclear mass. As such, while they contribute to the transition energy value, they do not affect its isotope shifts. In the perturbation approach used to calculate the QED corrections we used the nonrelativistic zero-order $^{\infty}C^{2+}$ wave function expanded in terms of 10 000 Gaussians. In Table III we show the results of the calculations that include, besides the values of the corrections, also the values of the $\langle P(1/r_{ij}^3)\rangle/(4\pi)$ and $\ln k_0$ terms, which are the key components of the corrections. The reason for small uncertainties due to $\alpha^3 E_{\rm QED}$ correction in Table III is the finite size of the basis used in the calculations. In the case of $\alpha^4 E_{\rm HQED}$ correction, the uncertainties are much larger. These are the result of the approximate treatment of this correction in which only the dominant part is included.

The final set of results is presented in Table IV. It concerns the $2\,^1S_0 \rightarrow 3\,^1S_0$ transition energies determined for the $^{12}C^{2+}$, $^{13}C^{2+}$, and $^{14}C^{2+}$ isotopes by adding consecutive corrections to the value obtained at the nonrelativistic level with the infinite nuclear mass of the carbon nucleus. Our final value of the transition energy for $^{12}C^{2+}$ of 182 519.031(1000) cm^{-1} can be compared with the value of the transition energy of 182 519.88 cm^{-1} obtained experimentally [14]. The results presented in Table IV indicate that to achieve such an excellent sub-wave-number agreement between the calculations and the experiment, all corrections calculated in this work are needed. More careful analysis of the $E_{\rm HQED}$ correction shows that its contribution to the transition energy equal to 1.552 cm^{-1} is perhaps too large, as only 0.703 cm^{-1} separates the calculated value from the experimental result when this correction is not

TABLE III. The leading QED corrections for the $2\,^1S_0$ and $3\,^1S_0$ states of the C^{2+} ion. The Araki-Sucher term and the Bethe logarithm, as well as the total α^3 and α^4 QED corrections ($\alpha^3 E_{\rm QED}$ and $\alpha^4 E_{\rm HQED}$), obtained in the infinite-mass calculations with 10 000-term wave functions are shown. All values are in a.u.

State	$\langle P(1/r_{ij}^3)\rangle/(4\pi)$	$\ln k_0$	$\alpha^3 E_{\rm QED}$	$\alpha^4 E_{\rm HQED}$
$2\,^1S_0$	$-5.954\,323(3)$	6.5574(4)	$1.556\,166\,8(1) \times 10^{-3}$	$1.27(42) \times 10^{-4}$
$3\,^1S_0$	$-5.089\,253(5)$	6.5642(8)	$1.466\,578\,7(4) \times 10^{-3}$	$1.20(40) \times 10^{-4}$

TABLE IV. Convergence of the $2\,^1S_0 \rightarrow 3\,^1S_0$ transition energies for $^{12}\mathrm{C}^{2+}$, $^{13}\mathrm{C}^{2+}$, and $^{14}\mathrm{C}^{2+}$ including increasingly higher level corrections (finite-mass, relativistic, and QED) to the energies of the two states. All values are in cm^{-1}.

Contribution included	ΔE ($^{12}\mathrm{C}^{2+}$)	ΔE ($^{13}\mathrm{C}^{2+}$)	ΔE ($^{14}\mathrm{C}^{2+}$)
E_{nonrel} (inf. nucl. mass)	182 264.940(20)	182 264.940(20)	182 264.940(20)
E_{nonrel} (fin. nucl. mass)	182 242.205(20)	182 243.959(20)	182 245.458(20)
$\alpha^2 E_{\mathrm{rel}}$	182 540.245(170)	182 542.000(170)	182 543.498(170)
$\alpha^3 E_{\mathrm{QED}}$	182 520.583(170)	182 522.338(170)	182 523.836(170)
$\alpha^4 E_{\mathrm{HQED}}$	182 519.031(1000)	182 520.785(1000)	182 522.283(1000)
Experiment [14]	182 519.88		

included. Thus, the inclusion of the neglected part of the E_{HQED} correction seems indispensable in the calculations of heavier atoms. This point will be investigated in our future work.

The agreement obtained for $^{12}\mathrm{C}^{2+}$ also indicates that the $2\,^1S_0 \rightarrow 3\,^1S_0$ transition energies calculated for the $^{13}\mathrm{C}^{2+}$ and $^{14}\mathrm{C}^{2+}$ isotopes and shown in Table IV are also likely to be very precise. As they differ from the transition energy obtained for $^{12}\mathrm{C}^{2+}$ by almost two wave numbers, they can be experimentally determined and used to estimate the isotope ratio for the C^{2+} ions both in laboratory samples and in interstellar space.

IV. SUMMARY

There have been two goals in this work. The first concerned very accurate determination of the $2\,^1S_0 \rightarrow 3\,^1S_0$ transition energy for $^{12}\mathrm{C}^{2+}$ using the variational approach and explicitly correlated Gaussian basis functions at the nonrelativistic level and the perturbation-theory approach to calculate relativistic and QED energy corrections. This part of the work resulted in the transition energy value that differs from the experimental result by less than a wave number. Such an excellent agreement for a system where the relativistic corrections are significantly larger than for lighter four-electron atoms (e.g., Be or Li^-), indicates the NRQED approach works very well. A possible improvement of the approach that may further reduce the difference between the calculated and experimental transition energy values is to include the neglected component of the E_{HQED} correction. This will be considered in our future work.

The second goal concerned determination of the mass shifts (yet unmeasured) of the transition energy that occurs for the $^{13}\mathrm{C}^{2+}$ and $^{12}\mathrm{C}^{2+}$ isotopes. As those shifts are sufficiently high to be detected experimentally, their measurement would provide an excellent test of the theoretical model used in the calculations performed in this work.

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