

Fine-structure splittings in low-lying triplet states of the carbon atom

Pavel Rzhevskii^{1,*}, Dmitry Tumakov^{2,1,†}, Toreniyaz Shomenov^{3,1,‡} and Sergiy Bubín^{1,§}

¹Department of Physics, *Nazarbayev University*, Astana 010000, Kazakhstan

²*Institute for Theoretical Physics, University of Hamburg*, Hamburg 22607, Germany

³National Laboratory Astana, *Nazarbayev University*, Astana 010000, Kazakhstan



(Received 29 October 2024; accepted 22 October 2025; published 4 February 2026)

We present benchmark theoretical values of the fine-structure splittings in the ground $^3P^e$ and low-lying excited $^3P^e$ and $^3D^e$ states of the ^{12}C , ^{13}C , and ^{14}C isotopes of the neutral carbon atom. We handle the correlations in the dynamics of all particles (six electrons and a nucleus) in all considered states in the practically exact manner by employing very large expansions of the wave functions in terms of all-particle explicitly correlated Gaussian basis sets, whose nonlinear parameters were extensively optimized. The resulting wave functions were used to compute the fine-structure splittings for the three isotopes by including the leading-order spin-orbit and electron spin-spin corrections ($\propto\alpha^2$), contribution from the electron anomalous magnetic moment ($\propto\alpha^3$), and by taking into account the most significant couplings between the targeted and neighboring electronic states ($\propto\alpha^4$). Our results show a notable improvement in accuracy compared to any previous theoretical calculations, are in good agreement with the best available experimental data, and demonstrate that the calculations of six-electron systems are now sufficiently advanced for precision measurement applications.

DOI: [10.1103/v4jk-j7c9](https://doi.org/10.1103/v4jk-j7c9)

I. INTRODUCTION

Investigations of the atomic fine structure are foundational to both theoretical and applied physics. They offer insights that are relevant to many disciplines ranging from astrophysics, precision measurements, and atomic clocks to nanotechnology and medical imaging. Accurate atomic structure calculations represent a tool to test quantum electrodynamics (QED) by comparing theoretical predictions with experimental measurements, determine fundamental constants and nuclear properties, and even search for new physics beyond the standard model [1–8]. A common way to perform such calculations for light atoms is to include relativistic and QED effects perturbatively as a series in terms of the fine-structure constant α [9]. With this approach, the fine-structure intervals for helium and lithium have been calculated up to the orders of α^5 and $\alpha^5 \ln \alpha$, respectively [10,11]. Obtaining the same order of accuracy for larger, four- and five-electron systems is a challenging task—e.g., fine-structure calculations for beryllium and boron are currently limited to the α^3 contributions, while the α^4 effects are either completely neglected or estimated crudely [12–15].

The study of carbon fine structure is particularly important due to its prevalence in various matter environments ranging from interstellar clouds to complex chemical compounds on Earth that include life itself. Carbon is the fourth most abundant element in the universe and plays a significant role in the evolution of the interstellar medium (ISM) [16]. Thanks to the low ionization energy of 11.26 eV [17,18], carbon is predominantly present in the ionized form (C II) in the ISM, while a significant share of neutral carbon (C I) can be found in the UV-shielded dense clouds. Via inelastic collisions with electrons, protons, hydrogen, and other particles, both C I and C II contribute to the ISM cooling at low temperatures [19].

Recently, precise fine-structure calculations for the eight lowest Rydberg $^2P^o$ states of C II were reported with the accuracy exceeding that of the experiment [20]. When it comes to neutral carbon, the values of its fine-structure splittings derived from experimental data and compiled by Haris and Kramida [17,18] are currently far more accurate than any theoretical predictions. Moreover, there exist only a few theoretical calculations, and most of them concern the ground state only. One of the earliest calculations of C I was done by Veseth [21] back in 1988 in the framework of many-body perturbation theory. Veseth accounted for the electron anomalous magnetic moment and, approximately, coupling between the ground 2^3P^e and isoconfigurational 2^1D^e and 2^1S^e states. However, the values of the off-diagonal spin-orbit matrix element were estimated from experiment [22]. These semiempirical fine-structure intervals agreed with experimental measurements to within $0.1\text{--}0.2\text{ cm}^{-1}$. Since 1988, a slight improvement in the fine-structure calculations of the ground state has been made, but to this day there are still no accurate theoretical data for the excited states. The most accurate calculation remains the paper by Carette and Godefroid [23] who

*Contact author: pavel.rzhevskii@nu.edu.kz

†Contact author: dm.tumakov@gmail.com

‡Contact author: toreniyaz.shomenov@nu.edu.kz

§Contact author: sergiy.bubin@nu.edu.kz

employed multiconfiguration Hartree-Fock (MCHF) variational method. Their results for the $J = 1 \rightarrow 0$ and $J = 2 \rightarrow 1$ transitions (here and below J denotes the total angular momentum quantum number) differ from the experimental measurements by 0.03 and 0.08 cm^{-1} , respectively, but no uncertainty estimates were reported.

The main difficulty in accurate atomic structure calculations originates from the inability of standard quantum-chemical approaches based on expansions in terms of Slater determinants of spin orbitals to provide sufficiently converged results with reliable uncertainty estimates that can match the uncertainties of highly accurate spectroscopic measurements. Representation of the wave functions in terms of explicitly correlated basis sets allows one to overcome this difficulty and improve the accuracy by orders of magnitude, but it comes at a high computational cost, which scales very rapidly with the system size. So far, no such calculations (with sufficiently converged results) have been reported for atomic systems with six or more electrons. Recently, we have implemented new computational algorithms for calculations of states with dominant configuration containing up to two particles in p states or a single particle in a d state [24], which opens up new avenues in precision studies of systems with six and more electrons. In this work, we present the first state-of-the-art application of this algorithm.

We investigate the carbon fine-structure splittings for the ground and first excited triplet P^e states, and lowest triplet D^e state, calculated with highly optimized explicitly correlated Gaussian (ECG) basis sets. We include the $\mathcal{O}(\alpha^3)$ contribution from the electron anomalous magnetic moment and account for the dominant part of the $\mathcal{O}(\alpha^4)$ second-order perturbation correction directly evaluating off-diagonal spin-orbit and spin-spin mixing terms. In our calculations, we do not assume the Born-Oppenheimer approximation i.e., the nucleus is treated on an equal footing with electrons, which allows us to automatically account for all relevant recoil effects and determine isotopic shifts for the three naturally occurring carbon isotopes. Our calculated fine-structure intervals are the most accurate theoretical values reported to date and agree with the experimental data within 0.0001–0.01 cm^{-1} .

II. METHOD

A. Nonrelativistic Hamiltonian

Due to the translational invariance of the nonrelativistic Hamiltonian $H_{\text{NR}}^{(0)}$, we can separate it into two terms describing the center-of-mass motion and internal dynamics, $H_{\text{NR}}^{(0)} = H_{\text{NR,CM}}^{(0)} + H_{\text{NR,INT}}^{(0)}$. Since we are interested only in internal motion, this procedure allows us to eliminate three degrees of freedom, reducing the original N -particle problem to the $n = (N - 1)$ -particle problem. For atomic and ionic systems, it is most convenient to choose the origin of the internal coordinate system at the position of the nucleus. In this coordinate frame, the particles are specified by their position vectors $\mathbf{r}_i$ relative to the nucleus, charges q_i , and masses m_i . Thus, after separating out the center-of-mass motion, the nonrelativistic Hamiltonian in internal coordinates takes the form (atomic units are assumed throughout unless stated otherwise; in the following, the subscript “INT” in the operators is

omitted) [24,25]

$$\mathcal{H}_{\text{NR}}^{(0)} = \frac{1}{2} \sum_{i=1}^n \frac{1}{\mu_i} \mathbf{p}_i^2 + \frac{1}{2m_0} \sum_{j \neq i}^n \mathbf{p}_i' \mathbf{p}_j + \sum_{i=1}^n \frac{q_0 q_i}{r_i} + \sum_{j>i}^n \frac{q_i q_j}{r_{ij}}, \quad (1)$$

where m_0 and q_0 are the mass and charge, respectively, of the reference particle, $\mu_i = m_0 m_i / (m_0 + m_i)$ is the reduced mass of the i th particle, $\mathbf{p}_i$ is the momentum operator of particle i , $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$ is the distance between particles i and j , and the prime symbol denotes vector transpose. For a carbon atom, consisting of six electrons and a nucleus, $n = 6$, $q_0 = 6$, and for the electrons $q_i = -1$ and $m_i = 1$ ($i = 1, \dots, n$). For the nuclear masses m_0 of the ^{12}C , ^{13}C , and ^{14}C isotopes, we adopted the values of 21 868.663 8505 m_e , 23 697.667 827 m_e , and 25 520.350 607 m_e , respectively, derived from the AME 2020 atomic mass values [26].

B. Basis functions

To solve the Schrödinger equation with the nonrelativistic Hamiltonian (1), we employ the Rayleigh-Ritz variational method. The spatial part of the wave function is expanded in a basis of all-electron explicitly correlated Gaussians [25,27–29]. Extensive optimization of Gaussian parameters, which is based on the analytic energy gradient, combined with the very large expansions of wave functions, allows us to obtain highly accurate nonrelativistic wave functions and energies.

In this work, we considered the lowest even-parity S , P , and D states of carbon with the electronic configuration containing two p -electrons, or a single d -electron. The basis functions for these states were chosen as follows:

$$\phi_k^{(S)}(\mathbf{r}) = \exp[-\mathbf{r}'(A_k \otimes \mathbf{I})\mathbf{r}], \quad (2)$$

$$\phi_k^{(P)}(\mathbf{r}) = (x_{i_k} y_{j_k} - y_{i_k} x_{j_k}) \exp[-\mathbf{r}'(A_k \otimes \mathbf{I})\mathbf{r}], \quad (3)$$

$$\begin{aligned} \phi_k^{(D)}(\mathbf{r}) &= (x_{i_k} x_{j_k} + y_{i_k} y_{j_k} - 2z_{i_k} z_{j_k}) \\ &\times \exp[-\mathbf{r}'(A_k \otimes \mathbf{I})\mathbf{r}], \end{aligned} \quad (4)$$

where $\mathbf{r}$ is a $3n$ -component column vector containing position vectors of all particles and A_k is an $n \times n$ positive definite matrix of nonlinear variational parameters that is unique for each basis function ϕ_k :

$$\mathbf{r} = \begin{pmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \vdots \\ \mathbf{r}_n \end{pmatrix}, \quad A_k = \begin{pmatrix} (A_k)_{11} & (A_k)_{12} & \cdots & (A_k)_{1n} \\ (A_k)_{21} & (A_k)_{22} & \cdots & (A_k)_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ (A_k)_{n1} & (A_k)_{n2} & \cdots & (A_k)_{nn} \end{pmatrix}. \quad (5)$$

Integer indices i_k and j_k refer to particles carrying orbital angular momentum $l = 1$. Matrix $\mathbf{I}$ is a 3×3 identity matrix and the symbol $\otimes$ denotes the Kronecker product. The positive definiteness of matrix A_k ensures the square integrability of the wave function.

Our choice of prefactors in basis functions (2)–(4) corresponds to the projection of the orbital angular momentum $M_L = 0$. For P and D states, the basis functions $\phi_k^{(P)}$ and $\phi_k^{(D)}$ represent either two electrons carrying angular momentum $l = 1$ or, in the case $i_k = j_k$, a single electron carrying angular momentum $l = 2$. At the same time, the basis functions $\phi_k^{(S)}$ for S states correspond to all electrons occupying s orbitals.

Although this choice is not natural for systems with two p electrons (each basis function individually does not possess the proper rotational symmetry), the variational procedure guarantees convergence of the trial wave function, which is a linear combination of basis functions, to the true wave function. The details of the calculations with the basis functions (2)–(4) are described in Refs. [24,30].

C. Leading-order fine-structure Hamiltonian

The inclusion of relativistic and QED corrections for light atoms can be carried out systematically in the framework of nonrelativistic quantum electrodynamics (NRQED) by expanding the energy in powers of α :

$$E = E_{\text{NR}}^{(0)} + E^{(2)} + E^{(3)} + E^{(4)} + \dots, \quad (6)$$

where $E_{\text{NR}}^{(0)}$ represents the energy corresponding to the Schrödinger Hamiltonian (1), $E^{(2)}$ is the expectation value of the effective Dirac-Breit Hamiltonian that describes the leading-order relativistic effects, etc. The superscripts (0), (2), (3), etc. represent the power of α in each expansion term (some terms may also contain $\ln \alpha$). In general, the relativistic and QED effects lead to shifting and splitting of the energy levels. At leading-order $\mathcal{O}(\alpha^2)$, we can separate the contributions that result in an overall shift from those that cause splitting by writing the Dirac-Breit Hamiltonian $\mathcal{H}_{\text{R}}^{(2)}$ as follows:

$$\mathcal{H}_{\text{R}}^{(2)} = \mathcal{H}_{\text{SR}}^{(2)} + \mathcal{H}_{\text{FS}}^{(2)}, \quad (7)$$

where $\mathcal{H}_{\text{SR}}^{(2)}$ represents all leading-order scalar relativistic effects and $\mathcal{H}_{\text{FS}}^{(2)}$ describes the leading-order fine-structure splittings. $\mathcal{H}_{\text{SR}}^{(2)}$ includes the mass-velocity, Darwin, orbit-orbit, and Fermi contact spin-spin terms. Their expressions in internal coordinates can be found in Ref. [25].

The leading-order fine-structure Hamiltonian consists of two terms:

$$\mathcal{H}_{\text{FS}}^{(2)} = \mathcal{H}_{\text{SO}}^{(2)} + \mathcal{H}_{\text{SSNC}}^{(2)}, \quad (8)$$

where $\mathcal{H}_{\text{SO}}^{(2)}$ and $\mathcal{H}_{\text{SSNC}}^{(2)}$ are the spin-orbit interaction and the electron part of the noncontact (dipolar) spin-spin interaction, respectively. In internal coordinates, they are expressed as follows [31]:

$$\mathcal{H}_{\text{SO}}^{(2)} = \mathcal{H}_{\text{SO1}}^{(2)} + \mathcal{H}_{\text{SO2}}^{(2)}, \quad (9)$$

$$\mathcal{H}_{\text{SO1}}^{(2)} = -\alpha^2 \sum_{i=1}^n \frac{q_0 q_i}{2m_i} \left(\frac{1+2a_e}{m_i} + \frac{2(1+a_e)}{m_0} \right) \frac{s'_i}{r_i^3} [\mathbf{r}_i \times \mathbf{p}_i], \quad (10)$$

$$\begin{aligned} \mathcal{H}_{\text{SO2}}^{(2)} = & -\alpha^2 \sum_{j \neq i}^n \left\{ (1+a_e) \frac{q_0 q_i}{m_0 m_i} \frac{s'_i}{r_i^3} [\mathbf{r}_i \times \mathbf{p}_j] + \frac{q_i q_j}{2m_i} \frac{s'_i}{r_{ij}^3} \right. \\ & \times \left[(\mathbf{r}_i - \mathbf{r}_j) \times \left(\frac{1+2a_e}{m_i} \mathbf{p}_i - \frac{2(1+a_e)}{m_j} \mathbf{p}_j \right) \right] \Big\}, \end{aligned} \quad (11)$$

$$\mathcal{H}_{\text{SSNC}}^{(2)} = \alpha^2 \sum_{j>i}^n (1+a_e)^2 \frac{q_i q_j}{m_i m_j} \left[\frac{(s'_i s'_j)}{r_{ij}^3} - 3 \frac{(s'_i \mathbf{r}_{ij})(s'_j \mathbf{r}_{ij})}{r_{ij}^5} \right], \quad (12)$$

where s_i is the spin of the i th electron, $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ is the interparticle separation vector, and $a_e \approx \alpha/2\pi + \dots$ is the electron anomalous magnetic moment. Operators $\mathcal{H}_{\text{SO1}}^{(2)}$ and $\mathcal{H}_{\text{SO2}}^{(2)}$ are commonly referred to as spin-same-orbit and spin-other-orbit interactions. Note that $\mathcal{H}_{\text{FS}}^{(2)}$ effectively contains terms $\propto \alpha^3$ and higher through the electron magnetic moment anomaly. For a_e in our calculations, we adopt the CODATA 2022 recommended value of $1.159\,652\,180\,46 \times 10^{-3}$ [32].

D. Second-order perturbation theory contribution

Up to the fourth power of α , the fine structure can be expressed as the sum of the first-order and second-order perturbation theory contributions. The corresponding expression for the total J -dependent part of the energy in state $|\psi\rangle \equiv |nJM_JLS\rangle$ is

$$\begin{aligned} E_{nJ} = & \langle \psi | \mathcal{H}_{\text{FS}}^{(2)} | \psi \rangle + \sum_{\phi \neq \psi} \frac{|\langle \phi | \mathcal{H}_{\text{FS}}^{(2)} | \psi \rangle|^2}{E_\psi - E_\phi} \\ & + 2 \sum_{\phi \neq \psi} \frac{\langle \psi | \mathcal{H}_{\text{SR}}^{(2)} | \phi \rangle \langle \phi | \mathcal{H}_{\text{FS}}^{(2)} | \psi \rangle}{E_\psi - E_\phi} + \langle \psi | \mathcal{H}_{\text{FS}}^{(4)} | \psi \rangle. \end{aligned} \quad (13)$$

The first term in Eq. (13) contains the leading-order contribution of order $\mathcal{O}(\alpha^2)$ and anomalous magnetic moment correction of order $\mathcal{O}(\alpha^3)$ and higher. The second and third terms come from the second-order perturbation theory. The summation involves all eigenstates $|\phi\rangle$ of the nonrelativistic Hamiltonian (1). The last term comes from the higher-order effective Hamiltonian obtained by the Foldy-Wouthuysen transformation of the Dirac equation. The explicit expression for $\mathcal{H}_{\text{FS}}^{(4)}$ can be found in Refs. [11,33].

Both the diagonal and off-diagonal matrix elements of $\mathcal{H}_{\text{FS}}^{(2)}$ in this work were computed using the nonrelativistic wave functions expanded in terms of suitable ECG basis sets [24,30]. A general formalism of spin-dependent calculations with the ECG basis is given in Refs. [14,34]. For all triplet states of the carbon atom considered in this work, the dominant contribution at the $\mathcal{O}(\alpha^4)$ level comes from the second term. In fact, as will be demonstrated below, the bulk of that contribution originates from the off-diagonal terms corresponding to the isoconfigurational states, while the perturbation theory summation in Eq. (13) can be truncated when a desired level of numerical convergence is achieved. Note that the third term in Eq. (13) contains the off-diagonal matrix elements with the scalar relativistic Hamiltonian $\mathcal{H}_{\text{SR}}^{(2)}$. Due to rotational invariance of $\mathcal{H}_{\text{SR}}^{(2)}$, only the states with the same orbital angular momentum and spin as the targeted one do not vanish. In evaluating the matrix elements of $\mathcal{H}_{\text{SR}}^{(2)}$, we neglected the orbit-orbit interaction, since its contribution is expected to be about two orders of magnitude smaller than the largest corrections—the mass-velocity and Darwin [35–37]. In this work, we evaluated all off-diagonal matrix elements of $\mathcal{H}_{\text{SR}}^{(2)}$ directly, i.e., without resorting to any regularization techniques to improve numerical convergence. The direct approach sufficed for our purposes because the overall contribution of these second-order perturbation terms to the fine-structure splitting is small (on the order of 10^{-4} cm^{-1}).

TABLE I. Nonrelativistic energies of even-parity states of most common carbon isotopes. $\mathcal{K}$ denotes the ECG basis size used in the calculations. Entries marked with ∞ correspond to the extrapolated energies when $\mathcal{K} \rightarrow \infty$. The first column is the electronic configuration of the outer shells $2np$. Figures in parentheses represent the numerical uncertainty of the extrapolation.

Conf.	State	$\mathcal{K}$	Energy			
			^{12}C	^{13}C	^{14}C	$^{\infty}\text{C}$
$2p^2$	2^3P^e	9000	−37.843 182	−37.843 314	−37.843 427	−37.844 894
		∞	−37.843 189(7)	−37.843 321(7)	−37.843 434(7)	−37.844 901(7)
	2^1D^e	6000	−37.796 832	−37.796 964	−37.797 077	−37.798 543
		∞	−37.796 850(19)	−37.796 983(19)	−37.797 095(19)	−37.798 562(19)
	2^1S^e	6000	−37.744 670	−37.744 802	−37.744 915	−37.746 380
		∞	−37.744 684(14)	−37.744 816(14)	−37.744 929(14)	−37.746 394(14)
$2p3p$	3^1P^e	6000	−37.529 425	−37.529 558	−37.529 670	−37.531 139
		∞	−37.529 437(11)	−37.529 569(11)	−37.529 682(11)	−37.531 150(11)
	3^3D^e	9000	−37.525 489	−37.525 621	−37.525 734	−37.527 203
		∞	−37.525 497(8)	−37.525 629(8)	−37.525 742(8)	−37.527 211(8)
	3^3S^e	6000	−37.520 789	−37.520 921	−37.521 034	−37.522 502
		∞	−37.520 820(32)	−37.520 952(32)	−37.521 065(32)	−37.522 534(32)
	3^3P^e	9000	−37.517 959	−37.518 091	−37.518 204	−37.519 673
		∞	−37.517 970(12)	−37.518 103(12)	−37.518 216(12)	−37.519 684(12)
	3^1D^e	6000	−37.512 299	−37.512 431	−37.512 544	−37.514 013
		∞	−37.512 327(28)	−37.512 459(28)	−37.512 572(28)	−37.514 041(28)
	3^1S^e	6000	−37.506 044	−37.506 176	−37.506 289	−37.507 758
		∞	−37.506 091(47)	−37.506 223(47)	−37.506 336(47)	−37.507 805(47)
$2p4p$	4^1P^e	6000	−37.476 057	−37.476 189	−37.476 302	−37.476 189
		∞	−37.476 079(22)	−37.476 211(22)	−37.476 324(22)	−37.476 211(22)
	4^3D^e	6000	−37.474 919	−37.475 051	−37.475 164	−37.476 631
		∞	−37.474 945(26)	−37.475 077(26)	−37.475 190(26)	−37.476 658(26)
	4^3S^e	6000	−37.473 505	−37.473 637	−37.473 750	−37.475 218
		∞	−37.473 574(69)	−37.473 706(69)	−37.473 819(69)	−37.475 286(69)
	4^3P^e	6000	−37.472 535	−37.472 667	−37.472 780	−37.474 247
		∞	−37.472 567(32)	−37.472 699(32)	−37.472 812(32)	−37.474 280(32)
	4^1D^e	6000	−37.470 546	−37.470 679	−37.470 791	−37.472 259
		∞	−37.470 583(36)	−37.470 715(36)	−37.470 828(36)	−37.472 295(36)
	4^1S^e	6000	−37.468 255	−37.468 387	−37.468 387	−37.469 967
		∞	−37.468 376(122)	−37.468 509(122)	−37.468 512(122)	−37.470 089(122)

The evaluation of the fourth term with $\mathcal{H}_{\text{FS}}^{(4)}$ in Eq. (13) represents a more challenging computational task and we did not include it in the present calculations as its contribution is much less significant. However, we do provide rough estimates of the numerical uncertainty that results from neglecting this contribution.

Note that a series in α , similar to Eq. (13), can be written for the matrix element of any operator if the wave functions of the initial and final states are expanded in a perturbation series using the relativistic Hamiltonian of the desired order. The convergence of the truncated perturbation sums, however, must be examined individually in each case.

III. RESULTS AND DISCUSSION

A. Nonrelativistic energies

We consider the fine structure of the carbon atom in its ground 2^3P^e and the two lowest excited triplet states of even parity – 3^3D^e and 3^3P^e . In the perturbation theory summation in Eq. (13), we included off-diagonal matrix elements with other even-parity states (the elements containing states of

mixed parity vanish due to the inversion symmetry) corresponding to electronic configurations $1s^22s^22p^2$, $1s^22s^22p3p$, and $1s^22s^22p4p$. All these states are listed in Table I. To demonstrate the level of convergence at the nonrelativistic level of theory, for each state we show its energy for the largest basis size and the result of extrapolation to the infinite basis size. In fact, all values shown in Table I represent the most accurate nonrelativistic energies of carbon to date. For the targeted states (2^3P^e , 3^3P^e , and 3^3D^e), we used 9000 ECGs, while for all other states, we restricted ourselves to smaller expansions of just 6000 ECGs since they contribute to fine-structure splittings only in the second order of the perturbation theory. Despite adopting highly efficient optimization algorithms that involve analytic energy gradient of the energy with respect to the Gaussian nonlinear parameters [24,30], these calculations represent a major computational effort that required many months of continuous computing on a parallel system using well over a thousand CPU cores.

In our calculations, we do not account for the finite nuclear size effects. Using the leading-order finite nuclear size Hamiltonian from Ref. [38], we found its contribution to the nonrelativistic energies to be only several microhartrees,

TABLE II. The values of the spin-orbit matrix elements, $\langle \cdot | \mathcal{H}_{SO}/\alpha^2 | \cdot \rangle$, for the three targeted triplet states in the case of ^{12}C isotope. The presented matrix elements correspond to the largest possible value of the total angular momentum J . Note that certain matrix elements vanish due to the rotational symmetry. The numbers in parentheses represent the extrapolation uncertainty. All values are in a.u.

$\langle \cdot \cdot \rangle$	2^3P^e	3^3D^e	3^3P^e
2^3P^e	1.196 676(5)	0.60781(4)	-0.142 59(4)
2^1D^e	1.981 759(3)	-0.9280(2)	-0.2332(2)
2^1S^e	-3.832 767(4)	0	0.2977(2)
3^1P^e	0.525 18(2)	1.725 78(2)	1.153 95(4)
3^3D^e	0.607 81(4)	1.880 577(6)	1.437 137(6)
3^3S^e	0.7682(1)	0	1.949 57(1)
3^3P^e	-0.142 59(4)	1.437 137(6)	0.923 47(1)
3^1D^e	-0.294 80(4)	-1.987 95(6)	1.327 97(1)
3^1S^e	0.5665(1)	0	-2.5863(1)
4^1P^e	-0.278 45(3)	0.0120(4)	0.2312(2)
4^3D^e	0.330 96(3)	0.0434(6)	-0.2191(4)
4^3S^e	0.4326(2)	0	-0.1901(9)
4^3P^e	0.089 24(2)	-0.0730(6)	-0.0133(3)
4^1D^e	0.178 08(2)	0.2225(9)	-0.1199(5)
4^1S^e	0.3379(3)	0	-0.4061(9)

which is about four orders of magnitude lower than the leading-order $\mathcal{O}(\alpha^2)$ relativistic corrections. The correction for the fine-structure intervals due to finite nuclear size is on the order of 10^{-6} cm^{-1} , which is also much smaller than the achieved accuracy of 10^{-2} cm^{-1} .

Our ground-state energy of the ^{12}C isotope, $-37.843\,182\,304$ hartree, computed with 9000 ECGs, is about 5 $\mu\text{hartree}$ lower and, thus, more accurate than the value of $-37.843\,177\,408$ obtained by Strasburger [39] with 5896 ECG lobe functions. A similar level of accuracy is maintained in our calculations for the excited states. However, a fair comparison with other high-precision calculations for carbon is difficult because of the lack of sufficiently accurate reference data. For the 2^1D^e state of ^{12}C , Carette and Godefroid [23] reported the value of $-37.798\,111$ hartree obtained using MCHF method, which compares reasonably well with our result of $-37.798\,543$ with 6000 ECGs and extrapolated to $-37.798\,562(19)$ hartree.

B. Fine-structure splittings

The values of the spin-orbit and spin-spin matrix elements for the targeted states are presented in Tables II and III. One may notice that the matrix elements between the states corresponding to the same electronic configurations are noticeably larger than those between the states with different configurations. The contribution from the states with a distinct configuration to the fine-structure splitting of the given term is further reduced by their larger energy separation. Another point to note is that the spin-spin matrix elements are two to four orders of magnitude smaller than the corresponding spin-orbit values. Yet the inclusion of the electron spin-spin noncontact interaction is important for achieving the desired accuracy of our results.

TABLE III. The values of the electron spin-spin matrix elements, $\langle \cdot | \mathcal{H}_{SSNC}/\alpha^2 | \cdot \rangle \times 10^3 \text{ a.u.}$, for the the three targeted triplet states of ^{12}C . We show the matrix elements that correspond to the largest possible value of the total angular momentum J .

$\langle \cdot \cdot \rangle$	2^3P^e	3^3D^e	3^3P^e
2^3P^e	-13.3515(2)	-4.7792(5)	3.8632(3)
3^3D^e	-4.7792(5)	0.5624(2)	-0.4069(3)
3^3S^e	0	2.1812(4)	0
3^3P^e	3.8632(3)	-0.4069(3)	-1.419 21(1)
4^3D^e	-2.946(3)	0.2418(4)	0.042(2)
4^3S^e	0	0.9589(7)	0
4^3P^e	-2.2978(2)	0.1193(4)	0.8248(2)

The main results of this work—the calculated values of the fine-structure splittings for ^{12}C —are presented in Table IV. In order to help understand the relative importance of each contribution, in this table we provide the splittings computed at different levels of theory (α^2 , α^3 , and α^4). It can be clearly seen that the inclusion of the second-order corrections has a crucial role in bringing the calculated values close to the experimental ones, with an accuracy of about 0.01 cm^{-1} . This becomes particularly important for the 3^3P^e and 3^3D^e states that have the $2p3p$ configuration and for which neighboring states with the same configuration sit close to each other on the energy scale.

The data in Table IV are visualized in Fig. 1 (in all diagrams, v_{ab} denotes the energy difference between the levels with $J = a$ and $J = b$). Interestingly, for five out of six fine-structure splittings studied in this work, the second-order α^4 correction turns out to be notably larger than the α^3 correction due to the electron magnetic moment anomaly. What should also be emphasized is that at the α^4 level of theory, by far the largest contribution comes from the couplings with isoconfigurational states. For each considered fine-structure splitting, we also provide the results of the best previous theoretical calculations. The most accurate values for the ground state were reported by Carette and Godefroid [23], and Froese Fischer and Tachiev [40]. Both of these works involved MCHF calculations within the Breit-Pauli approximation. For the excited triplet states, the only available result is by Stancalie [43], obtained with the general-purpose relativistic atomic structure package GRASP [44] that accounts for the Breit interaction and QED effects. Overall, our calculations provide significantly more accurate fine-structure intervals with the improvement of nearly three orders of magnitude, in particular for the excited states.

For our final results, we provide three uncertainties that contribute to the overall uncertainty of fine-structure splittings. These are the uncertainty of the ECG basis truncation, the uncertainty that comes from the truncation of the second-order perturbation theory summation, and, finally, the estimated uncertainty due to omission of $\langle \mathcal{H}_{FS}^{(4)} \rangle$ and higher-order terms in Eq. (13). To determine the basis truncation uncertainty, we analyze the convergence of the numerical results with the increase of the basis size. The uncertainty due to the truncation of the second-order perturbation series

TABLE IV. Fine-structure splittings (in cm^{-1}) for the ground and lowest excited triplet states of ^{12}C . δ_{AMM} stands for the α^3 contribution due to the electron anomalous magnetic moment. δ_{offdiag} are the α^4 second-order perturbation theory corrections: $\delta_{\text{offdiag}}^{\text{isoconf}}$ denotes the contribution of the isoconfigurational states only, while $\delta_{\text{offdiag}}^{\text{full}}$ stands for the contribution of all states. The final theoretical values are shown with three separate numerical uncertainties: the first represents the ECG basis truncation uncertainty, second is the uncertainty due to the finite number of states used in the second-order perturbation theory, and the last one is an uncertainty due to the omitted $\langle \mathcal{H}_{\text{FS}}^{(4)} \rangle$ term in (13).

Transition	Contribution	^{12}C
$2^3P_1^e \rightarrow 2^3P_0^e$	α^2	16.2830(2)
	$\alpha^2 + \delta_{\text{AMM}}$	16.3268(2)
	$\alpha^2 + \delta_{\text{AMM}} + \delta_{\text{offdiag}}^{\text{isoconf}}$	16.4191(2)
	$\alpha^2 + \delta_{\text{AMM}} + \delta_{\text{offdiag}}^{\text{full}}$	16.4168(2)(9)(300)
		16.39
MCHF [23]		16.33
Experiment [41]		16.416 7122(18)
NIST ASD		16.416 7122(6)
$2^3P_2^e \rightarrow 2^3P_1^e$	α^2	26.9610(2)
	$\alpha^2 + \delta_{\text{AMM}}$	27.0355(2)
	$\alpha^2 + \delta_{\text{AMM}} + \delta_{\text{offdiag}}^{\text{isoconf}}$	26.9831(2)
	$\alpha^2 + \delta_{\text{AMM}} + \delta_{\text{offdiag}}^{\text{full}}$	26.9836(2)(9)(300)
		26.92
MCHF [23]		26.70
Experiment [42]		26.996 7422(17)
NIST ASD		26.996 7422(10)
$3^3D_2^e \rightarrow 3^3D_1^e$	α^2	21.8764(1)
	$\alpha^2 + \delta_{\text{AMM}}$	21.9329(1)
	$\alpha^2 + \delta_{\text{AMM}} + \delta_{\text{offdiag}}^{\text{isoconf}}$	21.2041(7)
	$\alpha^2 + \delta_{\text{AMM}} + \delta_{\text{offdiag}}^{\text{full}}$	21.2060(7)(8)(300)
		18.9
MCHF [43]		21.193 35(28)
NIST ASD		
$3^3D_3^e \rightarrow 3^3D_2^e$	α^2	32.9129(1)
	$\alpha^2 + \delta_{\text{AMM}}$	32.9979(1)
	$\alpha^2 + \delta_{\text{AMM}} + \delta_{\text{offdiag}}^{\text{isoconf}}$	33.3534(3)
	$\alpha^2 + \delta_{\text{AMM}} + \delta_{\text{offdiag}}^{\text{full}}$	33.3516(3)(9)(300)
		29.1
MCHF [43]		33.364 85(23)
NIST ASD		
$3^3P_1^e \rightarrow 3^3P_0^e$	α^2	11.0130(1)
	$\alpha^2 + \delta_{\text{AMM}}$	11.0417(1)
	$\alpha^2 + \delta_{\text{AMM}} + \delta_{\text{offdiag}}^{\text{isoconf}}$	12.3827(55)
	$\alpha^2 + \delta_{\text{AMM}} + \delta_{\text{offdiag}}^{\text{full}}$	12.3832(55)(38)(300)
		9.0
MCHF [43]		12.392 52(31)
NIST ASD		
$3^3P_2^e \rightarrow 3^3P_1^e$	α^2	21.4304(3)
	$\alpha^2 + \delta_{\text{AMM}}$	21.4863(3)
	$\alpha^2 + \delta_{\text{AMM}} + \delta_{\text{offdiag}}^{\text{isoconf}}$	20.4701(55)
	$\alpha^2 + \delta_{\text{AMM}} + \delta_{\text{offdiag}}^{\text{full}}$	20.4717(55)(18)(300)
		16.3
MCHF [43]		20.473 96(19)
NIST ASD		

is conservatively estimated as the sum of absolute contributions coming from the states with the electronic configuration $1s^2 2s^2 2p 4p$. To verify the numerical convergence of the sums

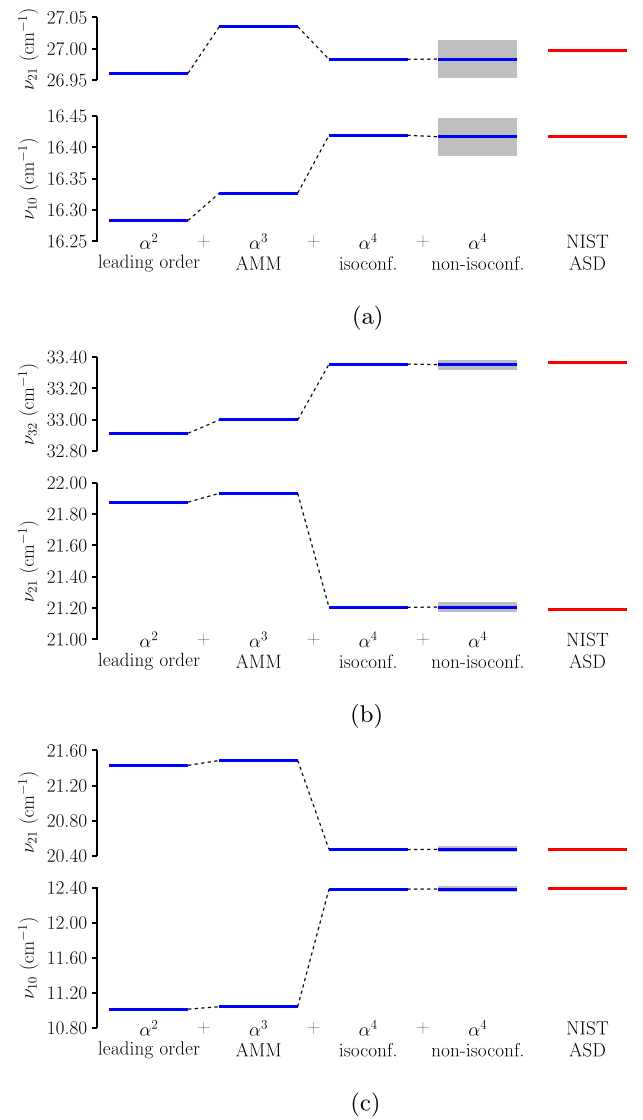


FIG. 1. Fine-structure transition energies in carbon ^{12}C : (a) $J = 2 \rightarrow 1$ and $J = 1 \rightarrow 0$ fine-structure splittings for the ground 2^3P^e state, (b) $J = 3 \rightarrow 2$ and $J = 2 \rightarrow 1$ fine-structure splittings for the 3^3D^e state, and (c) $J = 2 \rightarrow 1$ and $J = 1 \rightarrow 0$ fine-structure splittings for the 3^3P^e state. The gray shade indicates the estimated uncertainty of theoretical calculations.

in Eq. (13), we also experimented with the inclusion of two extra excited states with $1s^2 2s^2 2p 5p$ configurations and found their contributions to be negligibly small for the level of accuracy aimed in our calculations. A rough estimate of the uncertainty due to the omitted term $\langle \mathcal{H}_{\text{FS}}^{(4)} \rangle$ was done as follows. For a hydrogenlike atom, α^4 QED contribution to the fine-structure splitting depends on the nuclear charge as Z^6 . Owing to this strong dependence, we may assume that the largest contribution to the carbon fine-structure splittings comes from the electron-nucleus interaction. The effective charge felt by p electrons in carbon ground configuration can be estimated using the Slater's rules [45], which gives $Z_{\text{eff}}^C = 3.25$. Taking the value of α^4 QED contribution to the fine-structure splitting in hydrogen ($\approx 2.55 \times 10^{-5} \text{ cm}^{-1}$)

[46], and multiplying it by $(Z_{\text{eff}}^{\text{C}})^6$, we obtain the value of about 0.03 cm^{-1} . If we use the values of the fine-structure QED contributions for lithium [11] or helium [47,48], find their effective charges, and apply the same argument about nuclear charge dependence, then for carbon we obtain the values around $0.03\text{--}0.05 \text{ cm}^{-1}$, which ensures the consistency of our simple estimate. In Table IV, the uncertainty due to the missing $\langle \mathcal{H}_{\text{FS}}^{(4)} \rangle$ and higher-order terms was set to 0.03 cm^{-1} for all transitions, assuming an order-of-magnitude estimate.

It is interesting to compare our fine-structure splittings for neutral carbon with recent ECG calculations of the five-electron carbon cation by Stanke *et al.* [20]. The 2^2P^o ground state splitting of 63.37 cm^{-1} in C^+ is notably larger in magnitude. This can be attributed to a larger effective nuclear charge felt by the p electron, and the fact that the leading-order contribution to the fine-structure splitting from the one-electron part of the spin-orbit interaction scales as Z_{eff}^4 . Another noteworthy feature is the sharp reduction of the fine-structure splitting in C^+ , from 63.37 cm^{-1} in the ground 2^2P^o state to only 11.15 cm^{-1} in the first excited 3^2P^o state. This behavior can be explained by the fact that the carbon cation has only one valence electron, so the splitting originates from its interaction with the nucleus and the electron core. When this electron is excited to a higher orbital, the interaction strength decreases rapidly. In contrast, neutral carbon has two valence electrons, and in the 3^3P^e state only one of them is excited to a higher orbital. The other valence electron remains in a lower-energy orbital, where its interaction with the nucleus and the rest of the electrons is only weakly affected. Moreover, this remaining electron feels a slightly larger effective nuclear charge due to the reduced screening from the excited valence electron. Consequently, the fine-structure intervals in neutral carbon are reduced only moderately as one moves from the ground to excited states.

Fine-structure calculations for the odd-parity carbon states were not included in this work. Nevertheless, our method allows the construction of accurate nonrelativistic wave functions for odd-parity states with dominant $2pns$ configurations as well as for some states with dominant $2pnd$ and $2p^3$ configurations. These calculations are currently under way and will be reported in a separate study. We expect to resolve the fine-structure intervals with accuracy comparable to that achieved in the present work. However, reaching the same level of accuracy for the excited S^o and D^o states is not currently possible, as we do not yet have a well-developed and highly efficient algorithm for generating ECG basis sets corresponding to such states.

It is worth noting that while the existing experimental data for carbon are more accurate than our state-of-the-art calculations, for other six-electron systems (namely, the boron anion or nitrogen cation), comparably accurate experimental measurements are not yet available. When applied to these systems, our method may provide precise values of the fine-structure intervals and guide future experimental studies.

C. Fine-structure isotopic shifts

As our calculations do not assume the Born-Oppenheimer approximation and both the wave function and all effective operators have nuclear mass dependence, we can extract the isotopic shifts in the fine-structure splittings, $\Delta\nu$, relative to

TABLE V. Isotopic shifts of fine-structure intervals relative to ^{12}C . Numbers in parentheses represent numerical uncertainties.

Transition	$\Delta\nu \times 10^5 (\text{cm}^{-1})$		
	^{13}C	^{14}C	^{15}C
$2^3P_1^e \rightarrow 2^3P_0^e$ Veseth [50] Kozlov <i>et al.</i> [49] NIST ASD	7.91(4) 10.3 9.27 7.47(8)	14.70(8)	102.5(5)
$2^3P_2^e \rightarrow 2^3P_1^e$ Veseth [50] Kozlov <i>et al.</i> [49] Carette and Godefroid [23] NIST ASD	14.81(8) 15.0 20.1 14 13.78(16)	27.46(14)	191.9(1.0)
$3^3D_2^e \rightarrow 3^3D_1^e$	9.53(4)	17.68(7)	123.5(5)
$3^3D_3^e \rightarrow 3^3D_2^e$	16.08(6)	29.82(10)	208.4(7)
$3^3P_1^e \rightarrow 3^3P_0^e$	7.17(2)	13.30(3)	93.0(2)
$3^3P_2^e \rightarrow 3^3P_1^e$	9.12(3)	16.91(6)	118.2(4)

^{12}C . They are given in Table V. The reported isotopic shifts include the leading-order contribution ($\alpha\alpha^2$), AMM correction ($\alpha\alpha^3$), and the contribution from the second-order perturbation theory summation ($\alpha\alpha^4$), where only isoconfigurational states were considered. We provide only the numerical uncertainty, as the uncertainty associated with truncating the perturbation series and omitting higher-order QED terms is estimated to be much smaller.

For the isotopic shift in the ground state of ^{13}C , we also list the most accurate literature values, as well as the data from NIST Atomic Spectra Database [17,18]. Unlike ^{12}C and ^{14}C isotopes, ^{13}C has nonzero nuclear spin ($I = 1/2$) and therefore possesses hyperfine structure. Haris and Kramida [17] obtained fine-structure splittings of ^{13}C by taking the center of gravity of the experimental measurements of the hyperfine structure (HFS) transitions. As one can see it in Table V, our values of the isotopic shifts are notably larger than the NIST values [17] and are off by 4.9σ and 5.8σ for $J = 1 \rightarrow 0$ and $J = 2 \rightarrow 1$ transitions, respectively (here σ denotes the combined uncertainty obtained as the square root of the sum of the theoretical and experimental uncertainties). Interestingly, the other theoretical calculations also yielded larger values. Kozlov *et al.* [49] used an all-electron configuration interaction method with Dirac-Breit Hamiltonian and obtained the values of $\Delta\nu_{01} = 9.27 \times 10^{-5} \text{ cm}^{-1}$ and $\Delta\nu_{12} = 20.1 \times 10^{-5} \text{ cm}^{-1}$ for $J = 1 \rightarrow 0$ and $J = 2 \rightarrow 1$ transitions, respectively. The many-body perturbation theory calculations carried out by Veseth [50] gave the values of $\Delta\nu_{01} = 10.3 \times 10^{-5} \text{ cm}^{-1}$ and $\Delta\nu_{12} = 15.0 \times 10^{-5} \text{ cm}^{-1}$. The MCHF calculations done by Carette and Godefroid [23], combined with the relativistic corrections of Veseth [50], give the value of $\Delta\nu_{12} = 14 \times 10^{-5} \text{ cm}^{-1}$, which lies closer to the NIST value of $13.78 \times 10^{-5} \text{ cm}^{-1}$. However, the actual numerical uncertainty of all results in Refs. [23,49,50] cannot be assessed easily and is probably quite large, on the order of 30%–50% of the reported absolute values.

To better understand the origin of the discrepancy between our theoretical isotopic shifts and the NIST ASD values, we

performed a more detailed analysis. The fine-structure levels of ^{13}C reported in NIST ASD were obtained by Haris and Kramida as weighted averages of experimental hyperfine transition frequencies, with the weights equal to the relative theoretical intensities (which corresponds to weighting the hyperfine energy levels by their statistical weights). From a theoretical standpoint, the values obtained this way include hyperfine structure contributions of order $\mathcal{O}(\alpha^4)$, while the contributions of orders $\mathcal{O}(\alpha^3)$ and $\mathcal{O}(\alpha^2)$ are canceled exactly. Therefore, to enable a consistent comparison with the NIST ASD data, we incorporated in our calculations the hyperfine interaction of ^{13}C using the Hamiltonian from Ref. [13]. Then, we calculated the fine-structure levels by weighting the HFS components with the inclusion of the dominant second-order perturbative contribution of order $\mathcal{O}(\alpha^4)$, namely, the coupling between states with different J but the same total angular momentum $F = I + J$, where I is the nuclear spin. We do not provide the details of the hyperfine structure calculations since they are not the primary focus of the current work; however, it is worth mentioning that our values of the second-order shift are in good agreement with the calculations of Jönsson and Froese Fischer [51]. Using their hyperfine coupling constants, one obtains second-order corrections of 1.2×10^{-6} and $2.7 \times 10^{-7} \text{ cm}^{-1}$ for the $F = 1/2$ and $F = 3/2$ levels, respectively, which compare well with our results of 1.2×10^{-6} and $2.5 \times 10^{-7} \text{ cm}^{-1}$.

After weighting the HFS components, we obtained the fine-structure isotopic shifts of $(\Delta\nu)_{10}^{\text{weighted}} = 7.86(4) \times 10^{-5} \text{ cm}^{-1}$ and $(\Delta\nu)_{21}^{\text{weighted}} = 14.93(8) \times 10^{-5} \text{ cm}^{-1}$ for $J = 1 \rightarrow 0$ and $J = 2 \rightarrow 1$ transitions, respectively. With these corrections, the discrepancy with the NIST ASD values decreases to 4.4σ for the $J = 1 \rightarrow 0$ transition but increases to 6.4σ for the $J = 2 \rightarrow 1$ transition.

The remaining disagreement may originate from fine-hyperfine mixing or an inaccurate estimate of the QED contribution. Resolving this issue will require further in-depth

study and could be the subject of future work. Nevertheless, the isotopic shifts in the fine-structure splittings reported here represent a significant improvement in theoretical accuracy compared to previous works.

IV. CONCLUSIONS

In this work, we report accurate, state-of-the-art calculations of carbon fine structure performed in the framework of the variational ECG approach. We studied the three lowest triplet states: 2^3P^e , 3^3D^e , and 3^3P^e . Our fine-structure splitting values agree with the experimental data at a level of 0.01 cm^{-1} or better. The largest source of uncertainty for most transitions comes from the neglected $\mathcal{O}(\alpha^4)$ QED effects. By employing a non-Born-Oppenheimer approach, we determined the isotopic shifts for all carbon isotopes. For the ground state of ^{13}C , however, the results differ from the experimental values by 4–6 estimated uncertainties, which requires further investigations. Along with the fine-structure splittings, we report the most accurate nonrelativistic energies for the 15 lowest even-parity states of carbon. This work demonstrates the capability of the ECG approach for six-electron systems, pushing the limits of precision physics applications to larger systems.

ACKNOWLEDGMENTS

This work was supported by Nazarbayev University FD-CRGP Grant No. 040225FD4706. We acknowledge the use of Shabyt high-performance computer cluster at Nazarbayev University, where most of the numerical calculations were carried out.

DATA AVAILABILITY

The data that support the findings of this article are available from the authors upon reasonable request.

-
- [1] S. G. Karshenboim, Precision physics of simple atoms: QED tests, nuclear structure and fundamental constants, *Phys. Rep.* **422**, 1 (2005).
 - [2] R. Sánchez, W. Nörtershäuser, G. Ewald, D. Albers, J. Behr, P. Bricault, B. A. Bushaw, A. Dax, J. Dilling, M. Domschy, *et al.*, Nuclear charge radii of $^9,^{11}\text{Li}$: The influence of halo neutrons, *Phys. Rev. Lett.* **96**, 033002 (2006).
 - [3] P. Mueller, I. A. Sulai, A. C. C. Villari, J. A. Alcántara-Núñez, R. Alves-Condé, K. Bailey, G. W. F. Drake, M. Dubois, C. Eléon, G. Gaubert *et al.*, Nuclear charge radius of ^8He , *Phys. Rev. Lett.* **99**, 252501 (2007).
 - [4] R. Pohl, A. Antognini, F. Nez, F. D. Amaro, F. Biraben, J. M. R. Cardoso, D. S. Covita, A. Dax, S. Dhawan, L. M. P. Fernandes, *et al.*, The size of the proton, *Nature (London)* **466**, 213 (2010).
 - [5] X. Zheng, Y. R. Sun, J.-J. Chen, W. Jiang, K. Pachucki, and S.-M. Hu, Laser spectroscopy of the fine-structure splitting in the 2^3P_J levels of ^4He , *Phys. Rev. Lett.* **118**, 063001 (2017).
 - [6] M. S. Safronova, D. Budker, D. DeMille, D. F. J. Kimball, A. Derevianko, and C. W. Clark, Search for new physics with atoms and molecules, *Rev. Mod. Phys.* **90**, 025008 (2018).
 - [7] B. Maaß, T. Hüther, K. König, J. Krämer, J. Krause, A. Lovato, P. Müller, K. Pachucki, M. Puchalski, R. Roth *et al.*, Nuclear charge radii of $^{10,11}\text{B}$, *Phys. Rev. Lett.* **122**, 182501 (2019).
 - [8] M. Puchalski, J. Komasa, and K. Pachucki, Hyperfine structure of the 2^3P state in ^9Be and the nuclear quadrupole moment, *Phys. Rev. Res.* **3**, 013293 (2021).
 - [9] W. E. Caswell and G. P. Lepage, Effective Lagrangians for bound state problems in QED, QCD, and other field theories, *Phys. Lett. B* **167**, 437 (1986).
 - [10] K. Pachucki and V. A. Yerokhin, Fine structure of heliumlike ions and determination of the fine structure constant, *Phys. Rev. Lett.* **104**, 070403 (2010).
 - [11] M. Puchalski and K. Pachucki, Quantum electrodynamics corrections to the $2P$ fine splitting in Li, *Phys. Rev. Lett.* **113**, 073004 (2014).
 - [12] C. Chen, Energies, expectation values, fine structures and hyperfine structures of the ground state and excited states for boron, *Eur. Phys. J. D* **69**, 128 (2015).
 - [13] M. Puchalski, J. Komasa, and K. Pachucki, Fine and hyperfine splitting of the low-lying states of ^9Be , *Phys. Rev. A* **104**, 022824 (2021).

- [14] M. Stanke, A. Kędziorowski, and L. Adamowicz, Fine structure of the beryllium ^3P states calculated with all-electron explicitly correlated Gaussian functions, *Phys. Rev. A* **105**, 012813 (2022).
- [15] S. Nasiri, D. Tumakov, M. Stanke, A. Kędziorowski, L. Adamowicz, and S. Bubin, Fine structure of the doublet P levels of boron, *Phys. Rev. Res.* **6**, 043225 (2024).
- [16] T. Henning and F. Salama, Carbon in the universe, *Science* **282**, 2204 (1998).
- [17] K. Haris and A. Kramida, Critically evaluated spectral data for neutral carbon (C I), *Astrophys. J. Suppl. Ser.* **233**, 16 (2017).
- [18] A. E. Kramida, Y. Ralchenko, J. Reader, and NIST ASD Team, NIST Atomic spectra database (ver. 5.11), 2023, <http://physics.nist.gov/asd>.
- [19] A. Dalgarno and R. A. McCray, Heating and ionization of HI regions, *Annu. Rev. Astron. Astrophys.* **10**, 375 (1972).
- [20] M. Stanke, A. Kędziorowski, S. Nasiri, L. Adamowicz, and S. Bubin, Fine structure of the ^2P energy levels of singly ionized carbon (C II), *Phys. Rev. A* **108**, 012812 (2023).
- [21] L. Veseth, Refined many-body calculations of atomic fine structure, *J. Phys. B* **21**, 1719 (1988).
- [22] L. Veseth, Spin-extended Hartree-Fock calculation of atomic fine structure, *J. Phys. B* **14**, 795 (1981).
- [23] T. Carette and M. R. Godefroid, Theoretical study of the $C^{-4}S_{3/2}^o$ and $^2D_{3/2,5/2}^o$ bound states and C ground configuration: Fine and hyperfine structures, isotope shifts, and transition probabilities, *Phys. Rev. A* **83**, 062505 (2011).
- [24] T. Shomenov and S. Bubin, Explicitly correlated Gaussians for high-precision variational calculations of S^e , P^e , and D^e states of quantum systems: An efficient algorithm, *Phys. Rev. E* **108**, 065308 (2023).
- [25] S. Bubin, M. Pavanello, W.-C. Tung, K. L. Sharkey, and L. Adamowicz, Born–Oppenheimer and non-Born–Oppenheimer, atomic and molecular calculations with explicitly correlated Gaussians, *Chem. Rev.* **113**, 36 (2013).
- [26] M. Wang, W. Huang, F. Kondev, G. Audi, and S. Naimi, The AME 2020 atomic mass evaluation (II). Tables, graphs and references, *Chin. Phys. C* **45**, 030003 (2021).
- [27] S. F. Boys, The integral formulae for the variational solution of the molecular many-electron wave equations in terms of Gaussian functions with direct electronic correlation, *Proc. R. Soc. London Ser. A* **258**, 402 (1960).
- [28] K. Singer, The use of Gaussian (exponential quadratic) wave functions in molecular problems. I. General formulae for the evaluation of integrals, *Proc. R. Soc. London A* **258**, 412 (1960).
- [29] J. Mitroy, S. Bubin, W. Horiuchi, Y. Suzuki, L. Adamowicz, W. Cencek, K. Szalewicz, J. Komasa, D. Blume, and K. Varga, Theory and application of explicitly correlated Gaussians, *Rev. Mod. Phys.* **85**, 693 (2013).
- [30] S. Bubin and L. Adamowicz, Matrix elements of N -particle explicitly correlated Gaussian basis functions with complex exponential parameters, *J. Chem. Phys.* **124**, 224317 (2006).
- [31] A. Kędziorowski, M. Stanke, and L. Adamowicz, Atomic fine-structure calculations performed with a finite-nuclear-mass approach and with all-electron explicitly correlated Gaussian functions, *Chem. Phys. Lett.* **751**, 137476 (2020).
- [32] P. J. Mohr, D. B. Newell, B. N. Taylor, and E. Tiesinga, CODATA recommended values of the fundamental physical constants: 2022, *Rev. Mod. Phys.* **97**, 025002 (2025).
- [33] M. Puchalski and K. Pachucki, Quantum electrodynamics $m\alpha^6$ and $m\alpha^6 \ln \alpha$ corrections to the fine splitting in Li and Be^+ , *Phys. Rev. A* **92**, 012513 (2015).
- [34] D. Tumakov, P. Rzhetskii, T. Shomenov, and S. Bubin, Relativistic corrections in the ground and excited states of positronic beryllium, *Phys. Rev. A* **109**, 042826 (2024).
- [35] I. Hornyák, S. Nasiri, S. Bubin, and L. Adamowicz, ^2S Rydberg spectrum of the boron atom, *Phys. Rev. A* **104**, 032809 (2021).
- [36] M. Stanke, E. Palikot, K. L. Sharkey, and L. Adamowicz, Benchmark calculations of the ^2D Rydberg spectrum of lithium, *Mol. Phys.* **119**, e1925765 (2021).
- [37] S. Nasiri, L. Adamowicz, and S. Bubin, Benchmark calculations of the energy spectra and oscillator strengths of the beryllium atom, *J. Phys. Chem. Ref. Data* **50**, 043107 (2021).
- [38] K. Pachucki and V. A. Yerokhin, QED theory of the nuclear recoil with finite size, *Phys. Rev. Lett.* **130**, 053002 (2023).
- [39] K. Strasburger, Explicitly correlated wave functions of the ground state and the lowest quintuplet state of the carbon atom, *Phys. Rev. A* **99**, 052512 (2019).
- [40] C. F. Fischer and G. Tachiev, Breit–Pauli energy levels, lifetimes, and transition probabilities for the beryllium-like to neon-like sequences, *At. Data Nucl. Data Tables* **87**, 1 (2004).
- [41] S. Yamamoto and S. Saito, Laboratory observation of the $^3P_1 - ^3P_0$ transition of the neutral carbon atom by submillimeter-wave absorption spectroscopy, *Astrophys. J.* **370**, L103 (1991).
- [42] H. Klein, F. Lewen, R. Schieder, J. Stutzki, and G. Winnewisser, Precise laboratory observation of the $^3P_2 \leftarrow ^3P_1$ fine-structure transitions of ^{12}C and ^{13}C , *Astrophys. J.* **494**, L125 (1998).
- [43] V. Stancalie, Contribution to the theoretical investigation of electron and photon interaction with carbon atom and its ions, *J. Phys.: Conf. Ser.* **576**, 012010 (2015).
- [44] P. Jönsson, G. Gaigalas, J. Bieroń, C. Froese Fischer, and I. Grant, New version: Grasp2K relativistic atomic structure package, *Comput. Phys. Commun.* **184**, 2197 (2013).
- [45] J. C. Slater, Atomic shielding constants, *Phys. Rev.* **36**, 57 (1930).
- [46] M. Haidar, Z.-X. Zhong, V. I. Korobov, and J.-P. Karr, Non-relativistic QED approach to the fine- and hyperfine-structure corrections of order $m\alpha^6$ and $m\alpha^6(m/M)$: Application to the hydrogen atom, *Phys. Rev. A* **101**, 022501 (2020).
- [47] K. Pachucki and V. A. Yerokhin, Reexamination of the helium fine structure, *Phys. Rev. A* **79**, 062516 (2009).
- [48] K. Pachucki and V. A. Yerokhin, Publisher’s note: Reexamination of the helium fine structure [Phys. Rev. A 79, 062516 (2009)], *Phys. Rev. A* **80**, 019902 (2009).
- [49] M. G. Kozlov, I. I. Tupitsyn, and D. Reimers, Coefficients for sensitivity of fine-structure transitions in carbonlike ions to α variation, *Phys. Rev. A* **79**, 022117 (2009).
- [50] L. Veseth, Isotopic shift in atomic fine structure, *Phys. Rev. A* **32**, 1328 (1985).
- [51] P. Jönsson and C. F. Fischer, Large-scale multiconfiguration Hartree-Fock calculations of hyperfine-interaction constants for low-lying states in beryllium, boron, and carbon, *Phys. Rev. A* **48**, 4113 (1993).