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Explicitly correlated wave functions of the ground state and the lowest quintuplet state of the carbon atom

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Variational, nonrelativistic energies have been calculated for the ground state (^3P_g) and the lowest quintuplet state (^5S_u) of the carbon atom, with wave functions expressed in the basis of symmetry-projected, explicitly correlated Gaussian lobe functions. New exact limits of these energies have been estimated, amounting to $-37.844906(4)$ and $-37.691751(2)$ hartree. With finite nuclear masses and leading, scalar relativistic corrections included, respective experimental excitation energy of ^{12}C has been reproduced with accuracy of about 7 cm^{-1}.

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I. INTRODUCTION

Carbon has the richest chemistry among all elements. Literally thousands of scientific papers, reporting various calculations on carbon compounds, are written every year. On the other hand, determination of the carbon atom properties on the grounds of theory, with accuracy comparable to that offered by spectroscopic experiments, remains a challenge for computational chemistry. The present paper does not provide an ultimate solution of this problem. The aim is more modest—to demonstrate that an explicitly correlated wave function is able to yield about 10-μhartree energy accuracy for a six-electron atom and that an ansatz with inaccurate angular dependency of basis functions may prove to be more efficient than one that is seemingly better or at least more elegant.

For a long time, the best variational nonrelativistic energy of the carbon atom ground state was that obtained with the configuration interaction (CI) method in the year 1974 [1], using Slater orbitals corresponding to the angular momentum quantum number l up to 6, and up to quadruply excited configurations. That result still represents the most accurate published CI energy of this state. Recent CI calculation in which configurations were selected carefully, considering their energy contributions, but built from orbitals with l limited to 4, gave a little higher energy [2]. Comparison with the work devoted to the boron atom and anion (the latter being isoelectronic with the carbon atom's ground state) [3] makes it clear that orbitals with much higher l are needed for building a many-electron basis, capable of yielding the accuracy of about 1 mhartree. CI variational energies have been surpassed by those obtained in calculations with explicitly correlated Gaussian (ECG) functions [4,5], but the best result reported is still about 1.5 mhartree above the estimate of exact nonrelativistic energy [6]. This estimate is approached well by nonvariational (or at least not strictly variational) methods—coupled clusters with exponential correlation factor (CC-F12) [7], diffusion quantum Monte Carlo simulations [8,9], and the "free complement" method [10]. In the latter, regularized Krylov sequences of functions generated by the system's Hamiltonian are used as the basis. The results, reported in cited references, differ, however, even by a few millihartree, and those for which standard deviations are given [8–10] do not overlap (Table II below). Calculations on the ^5S_u state (the one spin quintuplet below the ionization limit of the carbon atom, known widely for the sp^3 orbital hybridization model) [1,8,10] yielded somewhat more consistent results, with the discrepancies reaching several hundred microhartree.

A comparison of theoretical results with spectroscopic data does not require absolute energies of states. Good agreement with experimental excitation energy of the carbon atom from the ground state to the ^5S_u state (and other states too, but they are not the subject of the present paper) has been achieved in multiconfiguration Hartree-Fock calculations [11], with omitted correlation of 1s core electrons. According to the same reference publication, the leading relativistic energy corrections contribute about 90 cm^{-1}. They are partially taken into consideration in the present paper.

For few-electron systems, for which high accuracy is desired, an explicitly correlated ansatz, used in the variational framework, is most effective. Unfortunately, the associated computational cost grows rapidly with the number of electrons. Despite technological progress, on both computer hardware and the software side, almost two decades passed between first publications of the ground-state energies, computed with nearly microhartree accuracy, for beryllium [12] and boron [13,14] atoms. Concerning the analytical forms of explicitly correlated basis functions, many of them are tractable for two- and three-electron systems, while only the Hylleraas-CI method and ECGs are competitive in practice for four-electron atoms and atomic ions. Both methods provided energies accurate to a few nanohartree [15–17]. The latter ansatz is at present the one applicable for systems containing five and more electrons, due to the relatively simple form of integrals appearing in Hamiltonian matrix elements. Other types of basis functions are used too, but occurrence of complicated many-electron integrals, without known analytical solutions, forces resorting to stochastic techniques [8–10] or using the resolution of identity [7] for reduction of their complexity.

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In the present calculation, the ansatz of explicitly correlated Gaussian lobe functions (called also "Gaussians with shifted centers," see Ref. [18] for an example) is employed. This ansatz was applied, with success, in studies of small molecules, molecular ions, and van der Waals complexes [19–23]. Free atoms have spherical symmetry, therefore their exact wave functions are eigenfunctions of not only the Hamiltonian but also the square of angular momentum ($\hat{L}^2$) and the z component of angular momentum ($\hat{L}_z$) operators. Basis functions χ for atomic states are constructed, as a rule, so that the relations $\hat{L}^2\chi = L(L+1)\chi$ and $\hat{L}_z\chi = M\chi$ are fulfilled *a priori* for particular values of L and M quantum numbers [4,13,14,24–27]. In contrast, a lobe function centered off the nucleus is not an eigenfunction of these operators. Convergence towards the desired state may, however, be enforced by variational optimization of a trial wave function, with proper symmetry constraint. This method, introduced in earlier papers devoted to high L states of the lithium atom [28] and various states of many-electron harmonium [29–33], will be briefly described in the next section. Atomic units are used unless stated otherwise.

II. METHODS

A. Nonrelativistic wave function

The stationary Schrödinger equation is solved with the nonrelativistic Hamiltonian of the n-electron atom:

$$\hat{H} = -\frac{\nabla^2_{\rm nuc}}{2m_{\rm nuc}} + \sum_{i=1}^{n}\left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i}\right) + \sum_{i>j=1}^{n}\frac{1}{r_{ij}}. \qquad (1)$$

The wave function, depending on spatial ($\mathbf{r}_i$) and spin (s_i) coordinates,

$$\Psi(\mathbf{r}_1, s_1, \dots, \mathbf{r}_n, s_n) = \sum_{I=1}^{K} C_I \hat{A}\Theta_I(s_1,\dots,s_n)\hat{P}\chi_I(\mathbf{r}_1,\dots,\mathbf{r}_n), \qquad (2)$$

with proper permutational symmetry ensured by $\hat{A}$ and primitives χ_I being explicitly correlated Gaussian lobe functions,

$$\chi_I(\mathbf{r}_1,\dots,\mathbf{r}_n) = \exp\left[-\sum_{i=1}^{n}\alpha_{I,i}(\mathbf{r}_i - \mathbf{R}_{I,i})^2 - \sum_{i>j=1}^{n}\beta_{I,ij}r_{ij}^2\right], \qquad (3)$$

is not an eigenfunction of $\hat{L}^2$ for nonzero $\mathbf{R}_{I,i}$ vectors. Deviation of $\langle L^2\rangle$ from the exact $L(L+1)$ eigenvalue is effectively diminished by the procedure of variational energy minimization, in which nonlinear parameters $\alpha_{I,i}$, $\beta_{I,ij}$ and $\mathbf{R}_{I,i}$ are optimized. Linear coefficients are determined by solution of the eigenvalue problem, for a given set of nonlinear parameters. The convergence towards the desired state is ensured by the spatial symmetry projector $\hat{P}$, proper for an irreducible representation of a selected finite point group. Action of $\hat{P}$ upon basis functions annihilates a finite subset of their unwanted components, the symmetry properties of which are specific to representations other than the desired one of the K_h infinite point group. Particularly, the A_2 representation of the C_{4v} point group was used for the symmetry projector of the ^3P_g state:

$$\hat{P}(^3P_g) = \hat{E} + \hat{C}_4^1 + \hat{C}_2 + \hat{C}_4^3 - \hat{\sigma}_{v1} - \hat{\sigma}_{v2} - \hat{\sigma}_{d1} - \hat{\sigma}_{d2}. \qquad (4)$$

Confinement of all $\mathbf{R}_{I,i}$ vectors to the xy plane ensures proper parity (even) of the wave function. Lifting this constraint while using the projector proper to the A_{2g} representation of the D_{4h} group offered only negligible energy lowering at substantial increase of computation time even for small basis sets, therefore this alternative path has been abandoned at an early stage of the work. The A_{1u} representation of the O_h point group was employed for the ^5S_u state. The symmetry projector is simply too long (48 operations) to be written here explicitly. Identity and all rotation operators, that form the O group, enter this projector with coefficients equal to 1, and remaining operators (products of the former with the inversion operator) enter with coefficients equal to -1.

Single spin functions,

$$\Theta(s_1,\dots,s_6) = [\alpha(1)\beta(2) - \beta(1)\alpha(2)][\alpha(3)\beta(4) - \beta(3)\alpha(4)]\alpha(5)\alpha(6) \qquad (5)$$

for the triplet, and

$$\Theta(s_1,\dots,s_6) = [\alpha(1)\beta(2) - \beta(1)\alpha(2)]\alpha(3)\alpha(4)\alpha(5)\alpha(6) \qquad (6)$$

for the quintuplet, are sufficient to ensure convergence to correct variational limits, as the spatial functions are nonorthogonal.

The optimizations of basis set parameters were carried out for infinite nuclear mass. The eigenvalue problem was then solved, in the same basis, for various isotopes of carbon. The center-of-mass (CM) motion was not separated explicitly from the Hamiltonian, as the wave function depends on relative coordinates only ($\mathbf{r}_i$ in all equations is the vector of coordinates of the ith electron relative to the nucleus). In such a case, the total kinetic-energy operator in the laboratory coordinate frame, acting upon the wave function (or a basis function), gives the same result as the action of the kinetic-energy operator of relative motion, because $\hat{T} = \hat{T}_{\rm CM} + \hat{T}_{\rm rel}$, and $\hat{T}_{\rm CM}\Psi_{\rm rel} = 0$ for any definition of internal coordinates [34].

B. Relativistic corrections

The relativistic corrections to the energy are obtained in the perturbative series in the fine-structure constant $\alpha = \frac{1}{4\pi\epsilon_0}\frac{e^2}{\hbar c}$. In atomic units, the value of α is equal to the reciprocal of the speed of light in vacuum, $c = 137.036$. With the rest mass energy omitted, successive terms in the expansion

$$E = E^{(0)} + E^{(2)} + E^{(3)} + \cdots \qquad (7)$$

are calculated as expectation values of respective operators, with known nonrelativistic wave function. $E^{(0)}$ is the nonrelativistic energy, $E^{(2)}$ contains the Breit-Pauli corrections, and higher-order terms are the QED (radiative) corrections. The Breit-Pauli Hamiltonian contains the $\hat{H}_{\rm RS}$ operator, which is responsible for the scalar relativistic correction, shifting the energies of whole terms, and the fine and hyperfine structure operators. Only the former is being considered in this paper.

TABLE I. Nonrelativistic energies, squares of angular momentum, and virial ratios for $^{\infty}$C. For extrapolated results, standard deviations of the least significant digit are given in parentheses in the bottom row of the table.

	^3P_g			^5S_u		
K	Energy	$\langle L^2 \rangle$	$-\frac{V}{T}$	Energy	$\langle L^2 \rangle$	$-\frac{V}{T}$
88	−37.833555219	2.00015841	2.000005668	−37.688655780	0.00018743	2.000004222
129	−37.838026763	2.00009725	1.999990991	−37.690127107	0.00008282	2.000009232
189	−37.840615636	2.00008198	2.000002689	−37.690927579	0.00006823	2.000001843
277	−37.842526491	2.00005762	1.999986861	−37.691351361	0.00004046	1.999999213
406	−37.843672608	2.00003558	1.999993489	−37.691561153	0.00002250	2.000000133
595	−37.844247698	2.00002376	1.999995273	−37.691666242	0.00000907	2.000000081
872	−37.844533602	2.00001554	1.999997023	−37.691707096	0.00000554	1.999999854
1278	−37.844711824	2.00000879	1.999999330	−37.691727292	0.00000336	1.999999806
1873	−37.844794050	2.00000523	1.999999866	−37.691739801	0.00000138	2.000000038
2745	−37.844851675	2.00000255	2.000000012	−37.691745022	0.00000069	1.999999997
4023	−37.844877180	2.00000125	2.000000010	−37.691747780	0.00000036	1.999999992
5896	−37.844889402	2.00000071	2.000000040			
E	−37.844906(4)	2		−37.691751(2)	0	

For fixed nucleus, the relativistic shift Hamiltonian

$$\hat{H}_{\mathrm{RS}} = \hat{H}_1 + \hat{H}_2 + \hat{H}_3 + \hat{H}_4 \tag{8}$$

consists of the following components:

$$\hat{H}_1 = -\frac{1}{8c^2} \sum_{i=1}^{n} \nabla_i^4 \tag{9}$$

is the mass-velocity correction,

$$\hat{H}_2 = \frac{Z\pi}{2c^2} \sum_{i=1}^{n} \delta(\mathbf{r}_i) \tag{10}$$

is the electron-nucleus Darwin term,

$$\hat{H}_3 = \frac{\pi}{c^2} \sum_{i>j=1}^{n} \delta(\mathbf{r}_{ij}) \tag{11}$$

represents the sum of the electron-electron Darwin term and spin-spin Fermi contact interaction (the latter after integration over spin variables [35]), and

$$\hat{H}_4 = \frac{1}{2c^2} \sum_{i>j=1}^{n} \left(\frac{\nabla_i \cdot \nabla_j}{r_{ij}} + \frac{\mathbf{r}_{ij} \cdot [(\mathbf{r}_{ij} \cdot \nabla_i)\nabla_j]}{r_{ij}^3} \right) \tag{12}$$

describes the interaction of magnetic dipoles arising from orbital motion of the electrons. Expectation values of $\hat{H}_1$, $\hat{H}_2$, and $\hat{H}_3$ are known to converge slowly, because these operators sample the wave function for short interparticle distances, where ECG functions have an incorrect analytical behavior (they do not describe the wave function's cusps). This deficiency may be overcome by regularization of the problem [36]; the respective technique is, however, not implemented yet in the author's program, so direct formulas were used in the calculations.

III. RESULTS AND DISCUSSION

The most time-consuming part of the calculations was the optimization of nonlinear parameters of basis functions. It was commenced with very small sets, with sizes of 1, 2, and 3 (stages 1, 2, and 3), respectively. Basis enlarging was performed, with reuse of previously optimized functions in mind. Therefore, functions from stage $k-2$ were appended to the set obtained at stage k. Consequently, the successive basis sizes formed Narayana's cows sequence [37]. Each new basis was optimized, function by function, in cycles. Then the expectation value of the $\hat{L}^2$ operator and the virial ratio of potential and kinetic energies $(-\frac{V}{T})$ were computed. The results are given in Table I, beginning with 88 ECGs. The convergence of the energy and $\langle L^2 \rangle$ was substantially better for the ^5S_u state, therefore the calculations for this state were finished with 4023 basis functions, while the basis of 5896 functions was additionally built for the ground state.

There is no regularity to be found among virial ratios. Their values, close to 2, indicate only that all parameters were optimized reasonably well. No parameter scaling based on virial ratios was attempted. On the other hand, the squares of angular momentum converge to known exact limits, making it possible to try to extrapolate the energies as functions of $x = \langle L^2 \rangle - L(L+1)$. There is no theoretical foundation for this extrapolation, other than an observation that the deviation of $\langle L^2 \rangle$ is linearly proportional to the rotation energy error, and the assumption that the latter is a slowly varying fraction of the total-energy error. Extrapolation to $x = 0$ with least-squares linear regression (Fig. 1), using five points for each state, yields estimates of exact nonrelativistic energies of the $^{\infty}$C atom. For the ground state, this estimate differs by about 0.1 mhartree from the previous one [6] and is certainly more precise.

The energy convergence with projected ECG lobe functions appears better than that with ECGs multiplied by a proper polynomial of electrons coordinates, which are eigenfunctions of $\hat{L}^2$ (Table II). The energies obtained in the present paper, for 189 and 406 functions, are lower than those published in Refs. [4,5], computed with 500 and 1000 basis functions, respectively. The best published result of diffusion quantum Monte Carlo simulation [9] is surpassed with 872 functions, while final variational energy is lower by about 400 μhartree. This difference exceeds by far the numerical uncertainty of that simulation. The present result is matched

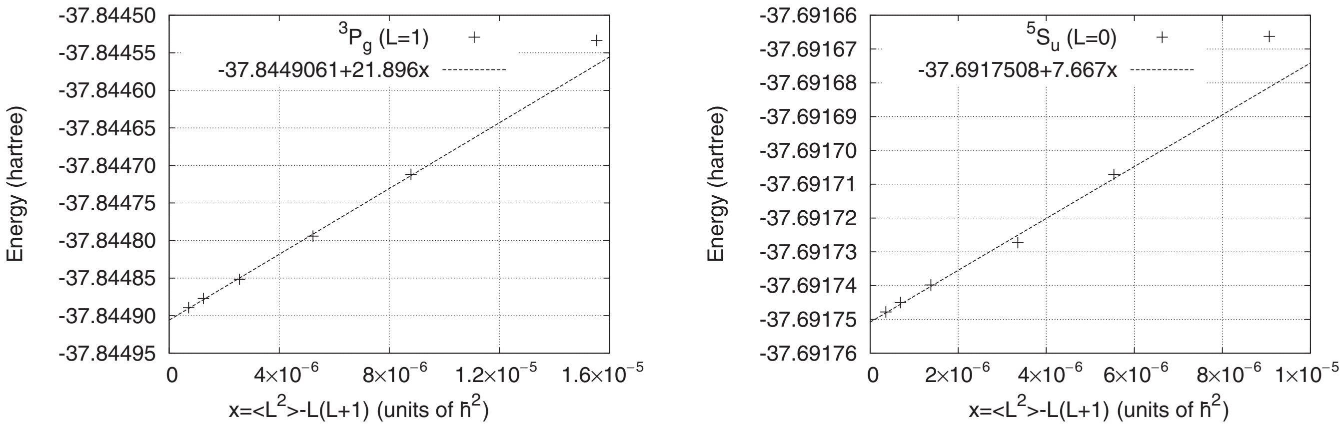

FIG. 1. Energy dependency on the deviation of $\langle L^2\rangle$ from exact value.

only by the FC-CFT method by Nakatsuji *et al.* [10], at least for the ground state, but with significantly wider error margins.

Nonadiabatic calculations were carried out with nuclear masses $m_{^{12}C} = 21\,868.6618$, $m_{^{13}C} = 23\,697.6661$, and $m_{^{14}C} = 25\,520.3468$, calculated from known molar masses of carbon isotopes ($12u$, $13.003355u$, and $14.003241u$, respectively)—dividing them by the Avogadro number and subtracting six electron masses. The same basis sets were used as for fixed nucleus, only the linear coefficients in the wave functions [Eq. (2)] were obtained independently for each isotope. Extrapolations were also based on an assumption that the gap from the best variational energy to the limit, and standard deviation of extrapolated energy, do not change with the nuclear mass. For a given state, the differences of nonrelativistic energies of isotopes converge very quickly and remain stable, therefore only the results obtained with the two largest basis sets are given in Table III. The effect of finite nuclear mass contributes -39.78 μhartree (or -8.731 cm^{-1}) to the energy of $^3P_g \rightarrow {}^5S_u$ excitation of ^{12}C. The isotopic shift between ^{13}C and ^{12}C is equal to 3.071 μhartree (0.674 cm^{-1}), and agrees perfectly with the experimental result, which amounts to 0.670(5) cm^{-1} [38]. Therefore a reliable prediction of the isotopic shift between ^{14}C and ^{12}C (5.692 μhartree or 1.249 cm^{-1}) is possible with nonrelativistic wave functions.

Even with finite nuclear mass taken into account, the nonrelativistic theory is not sufficient to calculate accurate energy differences between atomic states. The ground-state term has a fine structure. According to spectroscopic data [38], the terms of ^{12}C, with $J = 1$ and 2, appear, respectively, at 16.4167(13) and 43.4135(13) cm^{-1} above that with $J = 0$. The calculation of this split could not be completed in this paper, because of lacking implementation of expectation values of spin-orbit and spin-spin coupling operators. At this stage, it is only possible to refer theoretical results to weighted average energy of the ^3P_g term:

$$E_{\text{exp}}(^3P_g) = \tfrac{1}{9}[E(^3P_0) + 3E(^3P_1) + 5E(^3P_2)] \\ = 29.591\ \text{cm}^{-1}. \tag{13}$$

The ^5S_u term appears at 33 735.121(18) cm^{-1}, so the reference "excitation energy" amounts to 33 705.530 cm^{-1}. Subtraction of extrapolated, nonrelativistic energies (Table III) gives 33605(1) cm^{-1}, which misses the experimental result by about 100 cm^{-1}.

The convergence of relativistic shifts and their components, for fixed nucleus, is illustrated with the data presented in Table IV. As expected, the mass-velocity and electron-nucleus Darwin terms are dominant and their convergence with increasing number of basis functions is unsatisfactory.

TABLE II. Comparison of calculated, nonrelativistic energies of $^{\infty}$C.

Method	^3P_g	^5S_u
CI-SDTQ ($l_{\max} = 6$) [1]	-37.8393	-37.6893
CI (selected configurations, $l_{\max} = 4$) [2]	-37.8352652	
ECG, K=500 [4]	-37.84012879	
ECG, K=1000 [5]	-37.843333	
CCSD(T)-F12 [7]	-37.844334	
DMC [8]	$-37.84185(5)$	$-37.69026(3)$
DMC [9]	$-37.84446(6)$	
FC-CFT [10]	$-37.845004(282)$	$-37.690998(99)$
Estimated exact [6]	-37.8450	
Present paper (ECG lobes)		
Variational	-37.844889402	-37.691747780
Extrapolated	$-37.844906(4)$	$-37.691751(2)$

TABLE III. Nonrelativistic energies of carbon isotopes. Extrapolated results are given with the standard deviations of the least significant digit in parentheses.

K	$E(^{12}C)$	$E(^{13}C)$	$E(^{14}C)$	$E(^{13}C)-E(^{12}C)$	$E(^{14}C)-E(^{12}C)$
			^3P_g		
4023	−37.843165183	−37.843297308	−37.843410138	−0.132125	−0.244955
5896	−37.843177408	−37.843309534	−37.843422363	−0.132126	−0.244955
E	−37.843194(4)	−37.843326(4)	−37.843439(4)		
			^5S_u		
2745	−37.690072810	−37.690201865	−37.690312073	−0.129055	−0.239263
4023	−37.690075568	−37.690204623	−37.690314831	−0.129055	−0.239263
E	-37.690079(2)	-37.690208(2)	-37.690318(2)		

The differences between the results obtained in the two successive largest basis sets still exceed 10 μhartree, for both states. The expectation value of $\hat{H}_3$, which contains the two-electron Dirac delta operator, converges also slowly but the differences fall below 1 μhartree. The orbit-orbit interaction energies behave nonmonotonically, and appear to be converged within 0.1 μhartree. Fortunately, the errors of individual components cancel to some extent, owing to the optimization of nonlinear parameters of the wave function [39], so that five decimal digits of total relativistic scalar corrections for both states seem to be stable and converged even better than their nonrelativistic energies. There is, however, no perspective to extrapolate these corrections to the infinite basis set limit. The results agree fairly well with published relativistic corrections, obtained with less accurate wave functions [11,35] ($\langle\hat{H}_1\rangle$, $\langle\hat{H}_2\rangle$, and $\langle\hat{H}_3\rangle$). The orbit-orbit

TABLE IV. Convergence of the components of relativistic shift for $^{\infty}$C and comparison with literature data.

K	$\langle\hat{H}_1\rangle$	$\langle\hat{H}_2\rangle$	$\langle\hat{H}_3\rangle$	$\langle\hat{H}_4\rangle$	$\langle\hat{H}_{RS}\rangle$
			^3P_g		
88	−0.077592107	0.062485440	0.001154713	−0.000014929	−0.013966884
129	−0.077878128	0.062750198	0.001139876	−0.000013589	−0.014001643
189	−0.078232316	0.063087664	0.001130461	−0.000012954	−0.014027145
277	−0.078470993	0.063317266	0.001127264	−0.000012110	−0.014038574
406	−0.078622237	0.063461817	0.001121835	−0.000012169	−0.014050755
595	−0.078756303	0.063591427	0.001118551	−0.000012462	−0.014058786
872	−0.078842674	0.063674480	0.001115578	−0.000012629	−0.014065244
1278	−0.078927592	0.063758450	0.001114301	−0.000012773	−0.014067614
1873	−0.078982156	0.063811519	0.001113287	−0.000012783	−0.014070133
2745	−0.079013248	0.063842513	0.001112827	−0.000012847	−0.014070755
4023	−0.079034180	0.063862568	0.001112179	−0.000012871	−0.014072305
5896	−0.079045823	0.063874616	0.001111739	−0.000012842	−0.014072309
HF[a]	−0.07799	0.06300	0.00132		−0.01367
MCHF[b]	−0.078935	0.063934	0.001319		−0.013682
DMC[c]	−0.0790(2)	0.0639(2)	0.001115(8)	−0.000017(2)	−0.0140(3)
			^5S_u		
88	−0.075975991	0.061299742	0.001088726	0.000055146	−0.013532377
129	−0.076395863	0.061707535	0.001085135	0.000055467	−0.013547726
189	−0.076664784	0.061964780	0.001082663	0.000056176	−0.013561165
277	−0.076929320	0.062222229	0.001080459	0.000055542	−0.013571089
406	−0.077035132	0.062326668	0.001077918	0.000055280	−0.013575266
595	−0.077161830	0.062450289	0.001077187	0.000054941	−0.013579414
872	−0.077223369	0.062511108	0.001075924	0.000054808	−0.013581529
1278	−0.077236771	0.062524877	0.001075463	0.000054893	−0.013581537
1873	−0.077289679	0.062575932	0.001074897	0.000054992	−0.013583858
2745	−0.077300396	0.062587016	0.001074547	0.000054987	−0.013583846
4023	−0.077320425	0.062606802	0.001074403	0.000055056	−0.013584164
HF[a]	−0.07623	0.06171	0.00127		−0.01325
MCHF[b]	−0.077202	0.062654	0.001278		−0.013270

[a] Hartree-Fock [35].

[b] Multiconfiguration Hartree-Fock [11]

[c] Quantum Monte Carlo [9].

term has been calculated only for the ground state, in the quantum Monte Carlo simulation [9].

Assuming the same scalar relativistic corrections for the ^{12}C isotope as for $^{\infty}$C (which is expected to be correct within a fraction of μhartree for total correction [40]) and adding their values obtained in the largest basis sets to extrapolated nonrelativistic energies from Table III, corrected energies are obtained: $E(^3P_g) = -37.857266$ and $E(^5S_u) = -37.703663$. Their difference amounts to 0.153603 hartree, or 33712 cm^{-1}. It is not possible to calculate its standard deviation, because of lacking error estimation for relativistic corrections. Assuming arbitrarily that the error range is doubled, it would amount to 2 cm^{-1}. The missing contribution of at least 5 cm^{-1} to the excitation energy might stem from radiative corrections.

Notice should be taken that the present result is almost equal to that published in Ref. [11] (33 711 cm^{-1}), but the latter is accurate owing to a fortunate cancellation of errors. The finite nuclear mass effect (about -9 cm^{-1}) was not taken into account there. The orbit-orbit magnetic interaction energy was also omitted, resulting in underestimated relativistic correction to the excitation energy in older calculations [11,35]. This term has the smallest absolute value among all components of scalar Breit-Pauli corrections, but is the one with opposite signs for ^3P_g and ^5S_u states. It contributes nearly 15 cm^{-1} to the excitation energy—almost 14% of the total contribution of relativistic corrections, amounting to 107 cm^{-1}.

IV. CONCLUSIONS

The optimized ECG lobe functions, projected onto proper representations of finite point groups, appear to be a powerful tool for studying the properties of atomic states. Quite surprisingly, they form a more efficient basis, giving lower variational energies at noticeably shorter expansions than the ECGs with preexponential factors, which are eigenfunctions of $\hat{L}^2$. For the first time, the nonrelativistic energies of a six-electron atom were calculated with accuracy better than 20 μhartree. Apparent weakness, manifesting itself in $\langle L^2 \rangle$ deviating from the exact eigenvalue of this operator, may be utilized for energy extrapolation, leading to new estimations of nonrelativistic energies of the lowest triplet and quintuplet states of the carbon atom.

There are ^1D_g and ^1S_g states of the carbon atom, stemming from the same orbital electron configuration as the ground state ($1s^2 2s^2 2p^2$), and with energies lower than that of the ^5S_u term. They were not studied here, due to excessive computational cost of the optimization of thousands of nonlinear parameters of explicitly correlated basis functions, and they are postponed to a future work. Realization of the present project lasted for about two years and engaged a varying number of modern CPU cores, reaching several hundreds working in parallel on calculation of matrix elements.

Concerning the goal to achieve spectroscopic accuracy of quantum-chemical calculations for the carbon atom, there is still a long way to go. The experimental accuracy of the energy difference of the two states considered here, amounting to 0.018 cm^{-1}, i.e., 82 nanohartree, is by two orders of magnitude better than what the present calculations may offer. The fine structure as well as the contribution of radiative corrections have to be addressed by future work.

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