

Accurate variational calculations of the ground $^2P^o(1s^22s^22p)$ and excited $^2S(1s^22s2p^2)$ and $^2P^o(1s^22s^23p)$ states of singly ionized carbon atom

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(Received 5 September 2011; accepted 9 November 2011; published online 5 December 2011)

In this article we report accurate nonrelativistic variational calculations of the ground and two excited states of C^+ ion. We employ extended and well optimized basis sets of all-electron explicitly correlated Gaussians to represent the wave functions of the states. The optimization of the basis functions is performed with a procedure employing the analytic gradient of the energy with respect to the nonlinear parameters of the Gaussians. The calculations explicitly include the effects due to the finite nuclear mass. The calculated transition energies between the three states are compared to the experimentally derived values. Finally, we present expectation values of some small positive and negative powers of the interparticle distances and contact densities. © 2011 American Institute of Physics. [doi:10.1063/1.3664900]

I. INTRODUCTION

Very accurate *ab initio* calculations of ground and excited states of small atoms serve an important purpose because they allow for direct and meaningful comparison between high-accuracy theoretical results and high-resolution experimental data. Through such comparison the theoretical models and techniques used in the calculations can be tested. Also, in some cases such calculations, particularly those performed on small atomic systems, can yield results that are more accurate than the available experimental data and thus can guide future remeasurement of these quantities. For example, we have recently investigated the Rydberg series of 2D states of the lithium atom in very accurate calculations carried out with explicitly correlated Gaussian functions.^{1,2} A total of nine states were computed. For the upper states the results obtained in the calculations enabled some refinement of the experimentally determined energies of those states.

The variational approach employing the explicitly correlated Gaussians for describing ground and excited states of small atoms is currently the only method that has been shown to be capable of delivering energies of these types of states with absolute accuracy of 10^{-7} – 10^{-8} hartree for systems with more than three electrons. An important feature of the method that enables achieving the high accuracy is the use of the analytic gradient of the energy in the variational optimizations of the exponential parameters of the Gaussians. In this work we assess what level of the energy convergence can be achieved with the method in calculations of ground and some lowest excited states of a five-electron system – the singly ionized carbon atom. Our effort is aimed to extend the very accurate atomic calculations beyond four-electron systems and to show that even larger systems can be tackled with similar accuracy as what is now possible for small atoms (i.e., sub

0.01 cm^{-1} accuracy) provided sufficient computer power becomes available.

The present calculations concern the ground $1s^22s^22p$ state of C^+ , as well as its $1s^22s^23p$ and $1s^22s^23s$ excited states. This is the first time these states are calculated with high accuracy.

The details of the algorithms for gradient-aided optimization were described in our previous works.^{3,4} All calculations have been made using a non-relativistic Hamiltonian corresponding to the internal motion, \hat{H}_{int} , that explicitly depends on the mass of the nucleus. This Hamiltonian is obtained by rigorously separating the kinetic energy of the center-of-mass motion from the laboratory frame Hamiltonian. It has the following form in atomic units:

$$\hat{H}_{\text{int}} = -\frac{1}{2} \left(\sum_{i=1}^n \frac{1}{\mu_i} \nabla_{\mathbf{r}_i}^2 + \sum_{\substack{i,j=1 \\ i \neq j}}^n \frac{1}{m_0} \nabla_{\mathbf{r}_i} \nabla_{\mathbf{r}_j} \right) + \sum_{i=1}^n \frac{q_0 q_i}{r_i} + \sum_{i>j=1}^n \frac{q_i q_j}{r_{ij}}, \quad (1)$$

where n is the number of electrons, \mathbf{r}_i is the distance between the i th electron and the nucleus, m_0 is the nucleus mass (21 868.66382 m_e , 23 697.66779 m_e , and 25 520.35057 m_e for the $^{12}\text{C}^+$, $^{13}\text{C}^+$, and $^{14}\text{C}^+$ isotopes, respectively, where $m_e = 1$ is the electron mass), q_0 is its charge, q_i are electron charges, and $\mu_i = m_0 m_i / (m_0 + m_i)$ are electron reduced masses ($m_i = m_e$, $i = 1, \dots, n$). Prime indicates the matrix/vector transpose.

As \hat{H}_{int} is explicitly dependent on the mass of the nucleus, it allows for direct calculation of energy levels of a particular isotope. It also allows infinite-nuclear-mass (INM) calculations by setting the mass of the nucleus in Eq. (1) to infinity. The purpose of performing INM calculations is to

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generate results which can be directly compared with literature data, which is usually obtained for an infinite nuclear mass.

II. METHOD

In this work we consider two types of states, the 2S and 2P states. Appropriate explicitly correlated Gaussian basis sets for calculations of such states are as follows:^{3,4}

$$\phi_k = \exp[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}], \quad (2)$$

$$\phi_k = z_{i_k} \exp[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}], \quad (3)$$

for the S and P states, respectively. In (3) the electron index, i_k , can range from 1 to n , A_k is an $n \times n$ symmetric matrix, \otimes is the Kronecker product, I_3 is a 3×3 identity matrix, and \mathbf{r} is a $3n$ -component vector of the electron coordinates.

Gaussians (2) and (3) have to be square integrable. This happens when the matrix A_k is positive definite. To assure that we use the following Cholesky factored form of A_k : $A_k = L_k L_k'$, where L_k is a lower triangular matrix with matrix elements ranging from ∞ to $-\infty$. A_k in such a form is automatically positive definite. The advantage of using L_k and not A_k as the matrix of the variational parameters is that the minimization can then be carried out without any constraints regarding their values. If the A_k elements were used as the variational parameters, constraints would have to be imposed to keep A_k positive definite. This would considerably hampered the efficiency of the energy minimization.

To implement the correct permutational symmetry of the wave function in the present calculations we used the spin-free formalism. In this formalism, an appropriate symmetry projector (the Young operator, which is a mixture of antisymmetrizers and symmetrizers) is applied to the spatial part of the wave function to impose certain symmetry properties. The spin component of the wave function is not used explicitly. The procedures for building such symmetry projectors are well known and can be found in Ref. 5. For our case of a system with five identical particles in a doublet state the Young operator can be chosen as $\hat{Y} = (1 - \hat{P}_{13})(1 - \hat{P}_{15} - \hat{P}_{35})(1 - \hat{P}_{24})(1 + \hat{P}_{12})(1 + \hat{P}_{34})$, where \hat{P}_{ij} denotes the permutation of the spatial coordinates of the i th and j th electrons. As the internal Hamiltonian (1) commutes with all electron permutations, in the calculation of the overlap and Hamiltonian matrix elements it is convenient to apply \hat{Y} to the *ket* basis functions only (as $\hat{Y}^\dagger \hat{Y}$, where \hat{Y}^\dagger is the adjoint of \hat{Y}).

For the 2P states, where basis functions (3) are used, in addition to the L_k parameters the optimization involves choosing index i_k (which can be considered as an integer variational parameter) for each function. This is only done when the function is first added to the basis set.

The generation of the basis set for each state has been performed separately and only for the ^{12}C isotope. For other isotopes, as well as for ^{13}C it is sufficient to adjust only the linear coefficients of the basis functions to obtain an equally accurate wave function (this is because the change of the wave function is quite small when the mass of the nucleus is changed). The generation of the basis is the most time con-

suming part of the calculations. The basis set for each state has been grown from a small number of randomly chosen basis functions to the size of 5100 functions. This process involved adding subsets of 10 functions one by one and minimizing the total energy with respect to the parameters of the basis functions using the analytic gradient. At this stage, the i_k indices of the Gaussians used for the 2P states were also optimized. After the addition of each subset was completed, the whole basis set was reoptimized by cycling over all functions one by one and optimizing their parameters. After the basis set size reached 5000, the number of optimization cycles performed after each addition of 10 new basis functions was increased from one to three.

Extensive optimization of the basis set may yield near linearly dependent basis functions. Most commonly these linear dependencies occur between two basis functions. Linear dependencies are undesirable because they may cause numerical instabilities and lead to inaccuracies (or even to a complete failure of the optimization procedure). The linear dependencies in our calculations are automatically detected and eliminated as necessary. This is done by checking the overlap of the basis function, whose nonlinear variational parameters were just optimized, with all other basis functions. If the overlap exceeds a certain threshold (close to unity if the basis functions are normalized) the parameters of the basis function are reset to their original values.

III. RESULTS AND DISCUSSION

The calculations described in this work have involved over one year of continuous computing on a multiprocessor system employing 16 to 24 cores. By far the most time-consuming step has been the generation and variational optimization of the basis sets. The energies of the three considered states obtained in the calculations are presented in Table I. We show how they converge with the number of basis functions. The estimated accuracies of our final energy values determined using 5100 basis functions are shown in parentheses. These accuracy estimates are based on extrapolating to the limit of an infinite basis size. It is interesting to note that the estimated accuracy for the excited 2S state is roughly twice lower than that for the ground 2P state, while in our previous calculations on B atom we found that the energy of the first excited 2S -state was approximately five times better converged than the energy of the ground state. This order of magnitude difference in the accuracy of the first excited 2S states of C^+ and B is not due to a lower quality of the C^+ calculations. In fact, the basis set generation and optimization for C^+ and B were performed in an essentially identical manner and required approximately the same amount of computer time. The reason for a less tightly converged energy in the case of C^+ is the fact that the wave function of the lowest excited 2S state of this system is dominated by the $(1s^2 2s 2p^2)$ configuration. This is different from the dominant configuration of the lowest 2S state of B, which is $(1s^2 2s^2 3s)$. Such a configuration is easier to describe with the basis functions (2) than the $(1s^2 2s 2p^2)$ configuration that results from a coupling of two p -electrons to an S state. This explains the somewhat slower convergence of the calculations of the $(1s^2 2s 2p^2)$

TABLE I. Total nonrelativistic energies of the three states of singly ionized carbon atom considered in this work. Values in parentheses in this and other tables show the estimated remaining difference between our most accurate results and the exact nonrelativistic limits.

State	Isotope	Basis size	Energy (a.u.)
${}^2P^o(1s^22s^22p)$	${}^{12}\text{C}$	1000	-37.42904399
		2000	-37.42914664
		3000	-37.42916243
		4000	-37.42916720
		4500	-37.42916835
	5100	-37.42916955(250)	
	${}^{13}\text{C}$	5100	-37.42930159
	${}^{14}\text{C}$	5100	-37.42941435
	${}^{\infty}\text{C}$	5100	-37.43088049
	${}^2S(1s^22s2p^2)$	${}^{12}\text{C}$	1000
2000			-36.99014116
3000			-36.99017648
4000			-36.99018714
4500			-36.99018985
5100		-36.99019298(500)	
${}^{13}\text{C}$		5100	-36.99032209
${}^{14}\text{C}$		5100	-36.99043234
${}^{\infty}\text{C}$		5100	-36.99186591
${}^2P^o(1s^22s^23p)$		${}^{12}\text{C}$	1000
	2000		-36.82898235
	3000		-36.82900448
	4000		-36.82901134
	4500		-36.82901305
	5100	-36.82901478(350)	
	${}^{13}\text{C}$	5100	-36.82914677
	${}^{14}\text{C}$	5100	-36.82925949
	${}^{\infty}\text{C}$	5100	-36.83072508

state of ${}^{12}\text{C}^+$ in terms of the number of basis functions. The convergence could probably be improved if prefactors in the form of dot-products $\mathbf{r}_i^t \mathbf{r}_j$ are included in some basis functions.

The energies shown in Table I also include results for the ${}^{13}\text{C}^+$ and ${}^{14}\text{C}^+$ isotopes, as well as the ${}^{\infty}\text{C}^+$ results, obtained with 5100 basis functions. Our variational upper bound for the ground state energy of ${}^{\infty}\text{C}^+$, -37.43088049 hartree, can be compared with the best literature value of -37.43073(4) hartree obtained using the diffusion Monte Carlo method.⁶ The present work clearly achieves much higher accuracy.

The energy values taken from Table I have been used to calculate the transition energies shown in Table II.

These energies are compared with the values derived from the experimental data for ${}^{12}\text{C}^+$.⁷ Let us first examine the lowest ${}^2P^o(1s^22s^22p) \leftarrow {}^2S(1s^22s2p^2)$ transition. Our best estimate for this transition is 96 344.64(50) cm^{-1} . From the experiment one obtains two values, 96 430.32 and 96 493.74 cm^{-1} , which correspond to the ${}^2P_{3/2}^o(1s^22s^22p) \leftarrow {}^2S_{1/2}(1s^22s2p^2)$ and ${}^2P_{1/2}^o(1s^22s^22p) \leftarrow {}^2S_{1/2}(1s^22s2p^2)$ transitions, respectively. As our calculations do not include relativistic effects and, in particular, the spin-orbit interaction, we do not distinguish between the two transitions. The difference between our nonrelativistic transition energy, which, as can be seen, is a rather well converged

TABLE II. Nonrelativistic transition energies for C⁺ ion compared with the corresponding experimental values.⁷ The experimental data is for the ${}^{12}\text{C}$ isotope. Due to substantial fine-structure splitting the transition energies derived from experiment vary depending on the total angular momentum number J . In this table we give the smallest and the largest possible transition energy.

Transition	Isotope	Basis	ΔE (cm^{-1})
${}^2P^o(1s^22s^22p) \leftarrow {}^2S(1s^22s2p^2)$	${}^{12}\text{C}$	1000	96 375.75
		2000	96 350.56
		3000	96 346.28
		4000	96 344.99
		4500	96 344.64
	5100	96 344.22(50)	
	${}^{13}\text{C}$	5100	96 344.87(50)
	${}^{14}\text{C}$	5100	96 345.41(50)
	${}^{\infty}\text{C}$	5100	96 352.56(50)
	${}^2P_{3/2}^o(1s^22s^22p) \leftarrow {}^2S_{1/2}(1s^22s2p^2)$	expt.	
${}^2P_{1/2}^o(1s^22s^22p) \leftarrow {}^2S_{1/2}(1s^22s2p^2)$	expt.		96 493.74
${}^2P^o(1s^22s^22p) \leftarrow {}^2P^o(1s^22s^23p)$	${}^{12}\text{C}$	1000	13 1728.98
		2000	13 1720.83
		3000	13 1719.45
		4000	13 1718.99
		4500	13 1718.86
	5100	13 1718.75(20)	
	${}^{13}\text{C}$	5100	13 1718.76(20)
	${}^{14}\text{C}$	5100	13 1718.77(20)
	${}^{\infty}\text{C}$	5100	13 1718.89(20)
	${}^2P_{3/2}^o(1s^22s^22p) \leftarrow {}^2P_{1/2}^o(1s^22s^23p)$	expt.	
${}^2P_{1/2}^o(1s^22s^22p) \leftarrow {}^2P_{3/2}^o(1s^22s^23p)$	expt.		13 1735.52
${}^2S(1s^22s2p^2) \leftarrow {}^2P^o(1s^22s^23p)$	${}^{12}\text{C}$	1000	35 353.22
		2000	35 370.27
		3000	35 373.17
		4000	35 374.00
		4500	35 374.22
	5100	35 374.53(50)	
	${}^{13}\text{C}$	5100	35 373.89(50)
	${}^{14}\text{C}$	5100	35 373.35(50)
	${}^{\infty}\text{C}$	5100	35 366.33(50)
	${}^2S_{1/2}(1s^22s2p^2) \leftarrow {}^2P_{1/2}^o(1s^22s^23p)$	expt.	
${}^2S_{1/2}(1s^22s2p^2) \leftarrow {}^2P_{3/2}^o(1s^22s^23p)$	expt.		35 241.78

quantity, and the experimental energies clearly shows the importance of the relativistic effects whose magnitude exceeds 100 cm^{-1} . For the other two transitions shown in Table II the importance of the relativistic effects is similar.

Finally, in Table III we show expectation values of some low positive and negative powers of the nucleus–electron and electron–electron distances, as well as nucleus–electron and electron–electron contact densities. As one can see, with the increasing level of the electron excitation the average nucleus–electron and electron–electron distances become larger. Also, as expected, upon increasing the number of p electrons in the dominant configuration in the wave function, the $\langle \delta(\mathbf{r}_{ne}) \rangle$ average value decreases, as those electrons have nodes at the nucleus. The higher value of $\langle \delta(\mathbf{r}_{ne}) \rangle$ for the excited ${}^2P^o(1s^22s^23p)$ state than for the ground ${}^2P^o(1s^22s^22p)$ state likely results from a contraction of the core electrons ($1s^22s^2$) as the valence p electron becomes more excited and diffuse.

TABLE III. Expectation values of various powers of interparticle distances and Dirac δ -functions. All values are in a.u.

State	Isotope	Basis	$\langle 1/r_{ne}^2 \rangle$	$\langle 1/r_{ee}^2 \rangle$	$\langle 1/r_{ne} \rangle$	$\langle 1/r_{ee} \rangle$	$\langle r_{ne} \rangle$	$\langle r_{ee} \rangle$	$\langle r_{ne}^2 \rangle$	$\langle r_{ee}^2 \rangle$	$\langle \delta(\mathbf{r}_{ne}) \rangle$	$\langle \delta(\mathbf{r}_{ee}) \rangle$	
$^2P^o(1s^22s^22p)$	^{12}C	1000	27.803431	2.7590853	2.83130611	1.00811079	0.98450347	1.62068501	1.5854653	3.4244656	25.5973	0.67165	
		2000	27.803730	2.7589262	2.83130741	1.00809257	0.98453538	1.62076834	1.5856989	3.4249711	25.6317	0.67032	
		3000	27.803781	2.7588990	2.83130727	1.00808915	0.98454123	1.62078324	1.5857398	3.4250598	25.6471	0.67010	
		4000	27.803794	2.7588883	2.83130716	1.00808807	0.98454306	1.62078799	1.5857531	3.4250887	25.6485	0.66982	
		4500	27.803798	2.7588855	2.83130714	1.00808778	0.98454354	1.62078921	1.5857565	3.4250961	25.6487	0.66978	
		5100	27.803801	2.7588833	2.83130715	1.00808756	0.98454381	1.62079004	1.5857586	3.4251006	25.6490	0.66972	
	^{13}C	5100	27.804000	2.7588994	2.83131689	1.00809035	0.98454096	1.62078568	1.5857495	3.4250824	25.6492	0.66973	
		^{14}C	5100	27.804170	2.7589132	2.83132520	1.00809274	0.98453852	1.62078196	1.5857418	3.4250669	25.6495	0.66973
	$^{\infty}\text{C}$	5100	27.806383	2.7590919	2.83143328	1.00812376	0.98450683	1.62073352	1.5856406	3.4248652	25.6526	0.66980	
	$^2S(1s^22s2p^2)$	^{12}C	1000	27.318659	2.7285426	2.79772109	0.99518010	1.05450457	1.72402476	1.9657591	4.0722536	25.0209	0.65318
			2000	27.319470	2.7282534	2.79772232	0.99514206	1.05465158	1.72432533	1.9670784	4.0749356	25.0736	0.65160
3000			27.319606	2.7282110	2.79772477	0.99513968	1.05466302	1.72435102	1.9672076	4.0751972	25.0877	0.65112	
4000			27.319650	2.7281938	2.79772483	0.99513784	1.05466964	1.72436497	1.9672730	4.0753305	25.0988	0.65093	
4500			27.319661	2.7281894	2.79772492	0.99513743	1.05467136	1.72436866	1.9672897	4.0753650	25.0999	0.65089	
5100			27.319671	2.7281856	2.79772525	0.99513751	1.05467127	1.72436891	1.9672933	4.0753729	25.1004	0.65081	
^{13}C		5100	27.319873	2.7281993	2.79773429	0.99513881	1.05467171	1.72437067	1.9673027	4.0753908	25.1007	0.65082	
		^{14}C	5100	27.320044	2.7282111	2.79774200	0.99513992	1.05467209	1.72437218	1.9673107	4.0754062	25.1010	0.65082
$^{\infty}\text{C}$		5100	27.322277	2.7283639	2.79784232	0.99515434	1.05467700	1.72439178	1.9674148	4.0756059	25.1040	0.65089	
$^2P^o(1s^22s^23p)$		^{12}C	1000	27.839634	2.5849030	2.74157451	0.85896296	1.58534303	2.74236759	5.9141472	12.0760081	25.7814	0.67597
			2000	27.839972	2.5847379	2.74158646	0.85896422	1.58523384	2.74223459	5.9140310	12.0760896	25.8236	0.67493
	3000		27.840034	2.5846965	2.74158795	0.85896352	1.58521739	2.74221611	5.9140278	12.0761316	25.8310	0.67418	
	4000		27.840058	2.5846854	2.74158831	0.85896312	1.58521434	2.74221465	5.9140578	12.0762076	25.8438	0.67410	
	4500		27.840062	2.5846831	2.74158850	0.85896318	1.58521216	2.74221152	5.9140462	12.0761875	25.8443	0.67409	
	5100		27.840066	2.5846805	2.74158869	0.85896323	1.58520963	2.74220782	5.9140298	12.0761596	25.8448	0.67404	
	^{13}C	5100	27.840266	2.5846962	2.74159834	0.85896578	1.58520596	2.74220193	5.9140073	12.0761142	25.8451	0.67405	
		^{14}C	5100	27.840437	2.5847096	2.74160658	0.85896796	1.58520281	2.74219690	5.9139881	12.0760755	25.8453	0.67406
	$^{\infty}\text{C}$	5100	27.842659	2.5848836	2.74171372	0.85899628	1.58516196	2.74213148	5.9137386	12.0755720	25.8484	0.67413	

IV. SUMMARY

Very accurate nonrelativistic variational calculations using a finite-nuclear-mass Hamiltonian have been performed for the ground and two excited states of the singly ionized carbon atom using all-electron explicitly correlated Gaussian functions. The total and transition energies have been determined; the latter ones with the absolute precision of $0.2\text{--}0.5\text{ cm}^{-1}$. These are by far the most accurate calculations of this system and thus the present results are of benchmark quality. The comparison with the experiment shows that it is indispensable to account for the relativistic effects including the spin-orbit interaction to obtain quantitative agreement of the calculated transition energies with the results of high-resolution spectroscopic measurements. The development of capabilities to calculate the relativistic corrections with all-electron Gaussians used in the present calculations will be pursued in the future.

ACKNOWLEDGMENTS

The authors thank University of Arizona Research Computing Services for using resources on SGI Altix ICE 8200 computer cluster, where all calculations reported in this article were performed.

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