Large-scale nonrelativistic multireference configuration interaction calculation of the ground state ^3P of the carbon atom

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Abstract

The ground state ^3P energy of the carbon atom which is given from large-scale nonrelativistic multireference configuration interaction (MRCI) calculations is presented. The maximum angular momentum of orbitals used is 9 (i.e., m-symmetry). The orbitals used are the Hartree-Fock orbitals for occupied orbitals and natural orbitals for the correlating orbitals. The number of expansion terms in the largest MRCI wave function is 6,235,756. The MRCI energy obtained is –37.844698 hartree. The full configuration interaction (FCI) energy limit is estimated: the estimated energy is –37.84475 hartree. Moreover, the energy contribution from the orbitals having higher angular momentum is estimated. The final estimated energy is –37.84487 hartree.

1. INTRODUCTION

The electronic structure of atoms is described by the wave function Ψ, which is given from the Schrödinger equation:

$$H\Psi = E\Psi . \tag{1}$$

Here, H is the nonrelativistic Hamiltonian:

$$H = \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_i - r_i^{-1} \right) + \sum_{i<j}^{N} r_{ij}^{-1}, \tag{2}$$

where r_i is the distance between the i-th electron and the nuclei, and r_{ij} is the distance between the i-th electron and the j-th electron. Eq.(1) is solved by various methods, e.g., configuration interaction (CI), coupled cluster (CC), many-body perturbation theory (MBPT), or explicitly

correlated function (ECF) methods. In particular, the ECF method is powerful and gives highly accurate results. Unfortunately, it is very difficult to apply the ECF method to many-electronic systems because of appearance of complicated Hamiltonian matrix elements. Even the calculation for the carbon atom with 6 electrons is difficult.

The CI method can be applied to many-electronic atoms and is extensively used because the CI wave function is simple form. The CI wave function is expressed by a linear combination of excited configuration state functions (CSFs) from a reference configuration Φ:

$$\Psi = \Phi + \sum_i C_i^{\mathrm{S}} \Phi_i^{\mathrm{S}} + \sum_i C_i^{\mathrm{D}} \Phi_i^{\mathrm{D}} + \sum_i C_i^{\mathrm{T}} \Phi_i^{\mathrm{T}} + \sum_i C_i^{\mathrm{Q}} \Phi_i^{\mathrm{Q}} + \cdots, \tag{3}$$

where Φ_i^{S}, Φ_i^{D}, Φ_i^{T}, and Φ_i^{D} are singly, doubly, triply, and quadruply excited CSFs from Φ, respectively. Actual calculations use truncated CI wave functions because the full CI (FCI) wave function is very large. The simplest truncated CI wave function is a linear combination of singly and doubly excited configurations from a single reference configuration: this CI wave function is called a 'single reference singly and doubly excited CI' (SRSDCI) one. The SRSDCI wave function only considers two-body effects. It is important to further incorporate many-body effects into the CI wave function. Most important many-body effect is described by quadruply excited configurations. To effectively consider the many-body effects, multiple reference configurations are employed. Such the CI wave function is called a 'multireference singly and doubly excited CI' (MRSDCI) one. Since the MRSDCI wave function can incorporate the many-body effects beyond the two-body effect, the MRSDCI energy converges rapidly to the FCI one. Therefore, the MRSDCI method is superior about consideration of the many-body effects.

A defect of the CI wave function is to restrict incorporation of the higher partial wave component of the electron pair. Correct wave function must include inter-electronic distances. The inter-electronic distance between the electron 1 and 2, r_{12}, is expanded as

$$r_{12} = \sum_{l=0}^{\infty} \frac{4\pi}{(2l+1)} \left(-\frac{1}{2l-1} \frac{r_<^l}{r_>^{l-1}} + \frac{1}{2l-3} \frac{r_<^{l+2}}{r_>^{l+1}} \right) \sum_{m=-l}^{l} Y_l^{-m} (\theta_1 \varphi_1) \, Y_l^m (\theta_2 \varphi_2), \tag{4}$$

where $r_>$ is the greater of r_1 and r_2, $r_<$ is the lesser, and Y_l^m is the spherical harmonics. As seen from Eq.(4), the CI wave function must be used orbitals having infinite angular momentum. In actual CI calculations, however, only the orbitals with finite angular momentum can be used. The maximum angular momentum used is less than 10 usually because the CI wave function becomes large size.

Our aim is to obtain the ground state energy of the carbon atom from large-scale nonrelativistic

MRSDCI calculations. Furthermore, the FCI energy limit and the higher λ effect were estimated by extrapolation techniques. To this end, the Hartree-Fock (HF) calculation for the ground state ^3P of the carbon atom was first performed. Subsequently, SRSDCI and MRSDCI calculations were carried out. The present CI calculations employed the HF orbitals for occupied ones and the natural orbitals (NOs) for the correlating ones.

The orbital is usually expanded by Slater-type functions (STFs) and Gauss-type functions (GTFs). This work adopted a set of B-splines[1,2]. The B-splines of order K $\{B_{i,K}(r)\}$ are piecewise polynomials of degree $K-1$ on a knot sequence in a cavity of radius R. The knot sequence $\{t_i\}$ is a set of points defined on an interval $[0, R]$. $B_{i,K}(r)$ is nonzero in the interval $[t_i, t_{i+K})$. The advantage of B-splines is that they are very flexible and are relatively free from computational linear dependence. Thus, it is possible to apply a single B-spline set to the expansion of orbitals, irrespective of orbital symmetry, without loss of accuracy. Atomic calculations with the B-spline set will give highly accurate results. The atomic HF calculations with the B-spline set gives highly accurate energies.[3,4]

The next section explains basis functions used, NO construction procedures, and extrapolation procedures. The third section summarizes the ground state energy of the carbon atom and discusses comparison with the other CI energies and the estimated exact value.

2. COMPUTATIONAL ASPECT

The B-spline set used for the present calculations were constructed on the exponential knot sequence[5], with endpoints of K-fold multiplicity. The knot sequence $\{t_i\}_{i=1, 2, \ldots, N+K+2}$ can be written as

$$\{t_i\}_{i=1, \ldots, K} = 0, \tag{5}$$

$$\{t_i\}_{i=K+1, \ldots, N+2} = R_1 \left(\frac{R}{R_1}\right)^{\frac{i-K-1}{N-K+2}}, \tag{6}$$

$$\{t_i\}_{i=N+3, \ldots, N+K+2} = R, \tag{7}$$

where R_1 is the initial interval. Since the first and last terms of the B-splines with K-fold multiplicity are nonzero at $r = 0$ and at $r = R$, respectively, the N-term B-spline set was constructed omitting them, in order to satisfy the boundary conditions. This work employed the parameters, $N = 100$, $R = 60$ (bohr), $K = 9$, and $R_1 = 10^{-4}$ (bohr).

Our CI calculations used the HF orbitals for occupied orbitals and the NOs for the correlating orbitals. The NOs were generated by a series of SRSDCI calculations with the reference space consisting of the HF configurations.

Let us now explain the generating procedure for NOs. First, the SRSDCI calculation was carried out with the HF orbitals in the sp-space, to obtain sp-NOs. Subsequently, d-NOs were generated

by the SRSDCI calculation with the sp-NOs. The NOs with higher angular momentum than d-NOs were generated in the same way, step by step. The $spdf$-NOs were truncated until 30-terms for each symmetry. NOs with higher symmetry greater than f were truncated so that the energy loss was less than -10^{-6} hartree at each step. Finally, we obtained an orbital set ($30s30p30d30f30g28h27i25k25l24m$). SRSDCI and MRSDCI calculations were carried out using this orbital set.

To estimate the FCI limit for the energy, a further series of MRSDCI calculations was carried out using the orbital set, increasing the reference configurations which were selected for the largest weight in the previous MRSDCI wave function. The FCI limits of the MRSDCI energies (E_{CI}) were estimated by extrapolating E_{CI} to $w_{ref}=1$, where w_{ref} is the weight of reference space. The convergence pattern of E_{CI}, E_{CI+Q}, and E_{AV} were analyzed with respect to w_{ref}. E_{CI+Q} is E_{CI} plus the quadruple correction[6]. E_{AV} is the average of E_{CI} and E_{CI+Q}. Although E_{AV} has no physical meaning, E_{AV} is very useful for estimating the FCI limit.

The higher λ effect for the MRSDCI energies was also estimated by extrapolating the energy contributions due to the respective λ-NOs to $\lambda \to \infty$. To treat the systems on equal footing, we extrapolated the CI energies to $\lambda \to \infty$ using E_{CI} with $w_{ref} \approx 0.998$. The energy contribution ΔE_λ is plotted on a log-log scale, and it was fitted by a linear relation. The energy contribution from the NOs having angular momentum greater than 9 ($E_{\lambda>9}$) was estimated as

$$E_{\lambda>9} = \sum_{\lambda=10}^{\infty} \Delta E_\lambda. \tag{8}$$

The FCI energy limit including the higher λ effect was finally obtained.

The HF calculations with the B-spline set were carried out using our atomic self-consistent field program code based on the algorithm of Roothaan and Bagus[7]. All CI calculations were performed by the program ATOMCI[8,9].

3. RESULTS AND DISCUSSION

Table 1 summarizes the CI energies and the quadruple corrected energies of SRSDCI and MRSDCI calculations, together with other CI works. Each CI calculation is denoted as SRSDCI(λ) and MRSDCI(λ), where λ is the maximum angular momentum of the orbital set used. The MRSDCI(m) energy is -37.844698 hartree. The difference between this energy and the SRSDCI(m) energy -37.837750 hartree is large. This shows that the many-body effects are large. The quadruple corrected SRSDCI(m) energy is -37.844757 hartree. This energy is very near to the MRSDCI(m)

energy. Table 2 lists the weights of principal reference configurations of the MRSDCI(m) wave function. Although the main configuration of the MRSDCI(m) function is the HF configuration, the weights of doubly excited configurations from the HF configuration are also large. These doubly excited configurations induce quadruply excited configurations from the HF configuration. This shows that quadruply excited configurations are important.

Table 1. CI energies (E_{CI}) and quadruple corrected energies (E_{CI+Q}) of SRSDCI, MRSDCI, and other CI works (in hartree). N_{CI} is the number of expansion terms in CI wave function.

Method	Orbital set	N_{CI}	E_{CI}	E_{CI+Q}
This work				
SRSDCI(p)	($30s30p$)	7,483	–37.777320	–37.780176
SRSDCI(d)	($30s30p30d$)	13,438	–37.828576	–37.835389
SRSDCI(f)	($30s30p30d30f$)	19,333	–37.834933	–37.841916
SRSDCI(g)	($30s30p30d30f30g$)	25,228	–37.836558	–37.843559
SRSDCI(h)	($30s30p30d30f30g28h$)	30,590	–37.837172	–37.844178
SRSDCI(i)	($30s30p30d30f30g28h27i$)	35,477	–37.837457	–37.844464
SRSDCI(k)	($30s30p30d30f30g28h27i25k$)	39,777	–37.837608	–37.844616
SRSDCI(l)	($30s30p30d30f30g28h27i25k25l$)	43,877	–37.837696	–37.844703
SRSDCI(m)	($30s30p30d30f30g28h27i25k25l24m$)	47,753	–37.837750	–37.844757
MRSDCI(p)	($30s30p$)	150,780	–37.779846	–37.779965
MRSDCI(d)	($30s30p30d$)	961,515	–37.834542	–37.834671
MRSDCI(f)	($30s30p30d30f$)	2,262,542	–37.841772	–37.841873
MRSDCI(g)	($30s30p30d30f30g$)	3,519,573	–37.843481	–37.843586
MRSDCI(h)	($30s30p30d30f30g28h$)	3,889,442	–37.844110	–37.844218
MRSDCI(i)	($30s30p30d30f30g28h27i$)	4,559,555	–37.844401	–37.844509
MRSDCI(k)	($30s30p30d30f30g28h27i25k$)	5,796,821	–37.844555	–37.844664
MRSDCI(l)	($30s30p30d30f30g28h27i25k25l$)	5,710,780	–37.844643	–37.844751
MRSDCI(m)	($30s30p30d30f30g28h27i25k25l24m$)	6,235,756	–37.844698	–37.844806
Other works				
DCI [a]	($4s3p2d2f$)	40	–37.77888	
SDCI [b]	($6s6p6d4f$)	181	–37.7507	
FCI [c]	($7s6p5d3f$)	234	–37.83378	
SDTQCI [d]	($10s9p8d8f6g4h2i$)	993	–37.8393	
selected CI [f]	($7s6p5d4f3g$)	1,080	–37.835365	

[a] A.W. Weiss (Ref.10).

[b] H.F. Schaefer et al. (Ref.11).

[c] A. Bunge et al. (Refs.12 and 13).

[d] F. Sasaki and M. Yoshimine (Ref.14).

[f] M.B. Ruiz and R. Tröger (Ref.15).

Table 2.   Weight of principle reference configurations

w_{Ref}	Configuration
0.970720	$1s^2\, 2s^2\, 2p^2$
0.141121	$1s^2\, 2s^1\, 2p^2\, 3d^1$
0.132360	$1s^2\, 2p^4$
0.071498	$1s^2\, 2s^1\, 2p^1\, 3s^1\, 3p^1$

Let us compare with other CI works: the doubly excited CI (DCI) energy of Weiss[10], the singly and doubly excited CI (SDCI) energy of Schaefer et al.[11], the FCI energy of Bunge et al.[12,13], the singly, doubly, triply, and quadruly excited CI (SDTQCI) of Sasaki and Yoshimine[14], and the selected CI energy of Ruiz and R. Tröger[15]. All other CI works listed in Table 1 used STFs. The FCI energy –37.83378 hartree is smaller than MRSDCI(f) energy –37.841772 hartree. The SDTQCI energy is also smaller than the MRSDCI(i) energy. This reason is that the FCI and the SDTQCI calculations used small orbital set.

The CI energy –37.844698 hartree was obtained from the largest MRSDCI(m) calculation. The FCI limit energy was estimated by extrapolation E_{CI} to $w_{\text{ref}} = 1$. Fig. 1 shows the convergence pattern of E_{CI}, $E_{\text{CI+Q}}$, and E_{AV} against the weight of reference space. This extrapolations estimated FCI energy limit –37.84475 hartree. The rest many-body effect ($\sim$ –0.00005 hartree) is very small because the weight of reference space of the MRSDCI wave function is very near to 1: $w_{\text{ref}} \approx 0.998$.
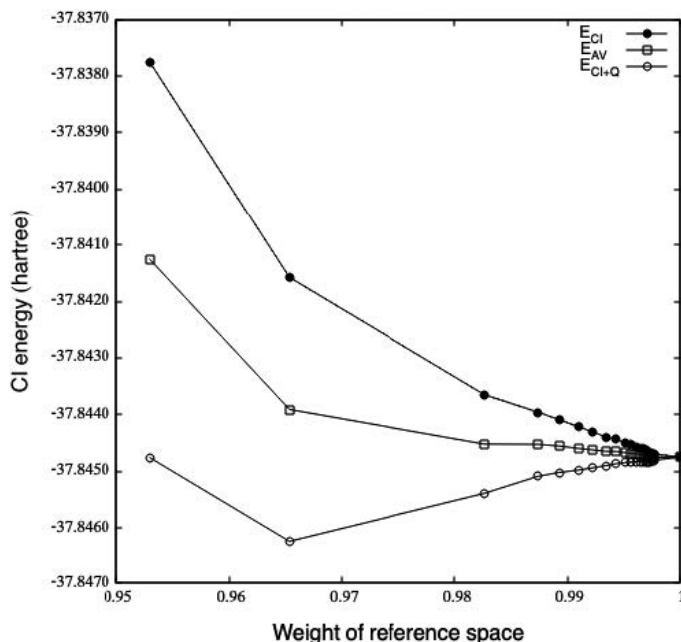

Fig. 1.   Convergence of CI energy with respect to the weight of the reference space.

The higher λ effect for the CI energies was also estimated by extrapolating the energy contributions due to the respective λ-NOs to $\lambda \rightarrow \infty$. Fig.2 shows the energy contribution to the CI energy from the respective λ-NOs, on a log-log scale. It reveals that the energy contribution by adding λ-NOs ($-\Delta E_\lambda$) converges linearly at $\lambda \geq 4$. This correlation can be expressed as

$$-\Delta E_\lambda = a\lambda^{-b}, \tag{9}$$

where a and b are fitting parameters. The energy contribution from the NOs having angular momentum greater than 9 are estimated as Eq.(8). The energy contribution –0.00012 hartree was obtained. Thus, the energy –37.84487 hartree was obtained. Table 3 lists the energies of this work and the estimated exact value. The two extrapolations estimated the energy lowering ~ 0.00017 hartree. The total energy of FCI limit + higher λ is quite near to the estimated exact value: the difference is ~ –0.0001 hartree.
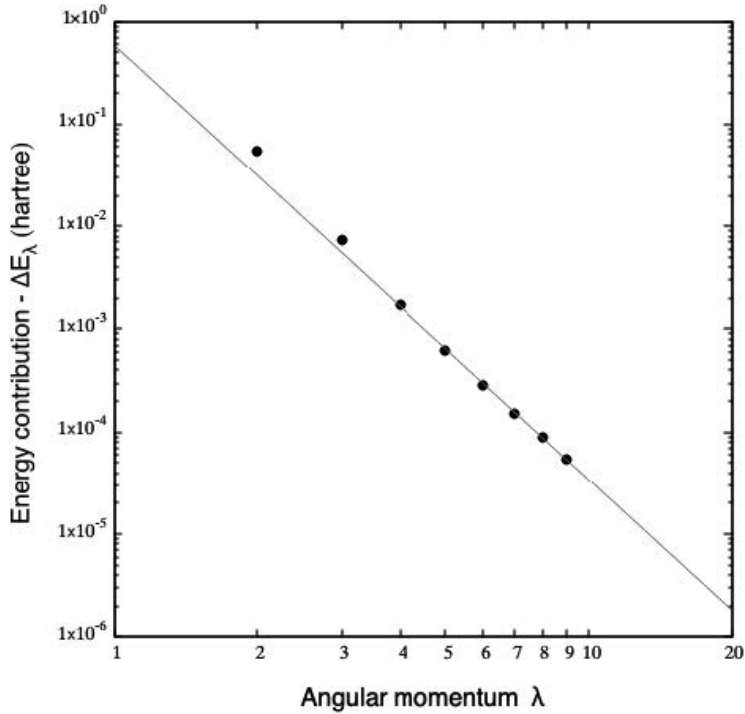

Fig. 2   Contributions to CI energy from the respective λ orbitals.

Table 3.   Extrapolated energies and estimated exact value (in hartree).

Method	Reference	Energy
MRSDCI(m)	This work	–37.844698
FCI limit	This work	–37.84475
FCI limit + higher λ	This work	–37.84487
Estimated exact value	Ref.16	–37.8450

In summary, the ground state energy of the carbon atom –37.844698 hartree was given from the MRSDCI(m) wave function expanded with 6,235,756 CSFs. Furthermore, the FCI limit energy –37.84475 hartree and the FCI limit + higher λ energy –37.84487 hartree were estimated by the extrapolation techniques. Although the MRSDCI(m) energy is very near to the estimated exact value, the remaining many-body and higher λ effects are still large. The present calculation is probably the limit of the CI calculation for the carbon atom.

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