

Correlation Energy of the Ground State of C^+

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The energy results of an accurate configuration-interaction calculation of the ground state of C are reported. Special emphasis is placed on the quantitative assessment of all sources of truncation errors. In this way, the nonrelativistic energy is estimated to be -37.8436 ± 0.0015 a.u. (C), in agreement with previous estimates obtained by different methods. Nesbet's calculation is interpreted in the light of the present results.

I. INTRODUCTION

In accurate electronic-structure calculations, it is very common practice to talk of the energy results in terms of the percentage of correlation energy (CE) obtained.¹ However, since the definition of the CE involves the total nonrelativistic energy, which is not well known, its use as a yardstick with which to measure the accuracy of computed energies has to be made with some reservations.

Veillard and Clementi have recently estimated the CE of the ground state of C to be -0.1551 a.u.² on the basis of previous relativistic calculations³ and of a recent updating of the experimental data⁴; but their value includes the Lamb shift, which they estimate to be 0.0014 a.u., i.e., a more reasonable value for the CE would be -0.1565 a.u., in excellent agreement with a previous semiempirical estimate of -0.1564 a.u.⁵ The CE shall be estimated here on the basis of a recent configuration-interaction (CI) calculation^{6,7} and a study of the errors involved in the various truncations: truncations of the *spdf* Slater-type orbital (STO) basis (Sec. II), of the full CI expansion (Sec. III), and of orbitals with higher angular momentum (Sec. IV). In Sec. V, the CE's of C , C^{2+} , and C^{4+} are compared. Finally, in Sec. VI, Nesbet's calculation⁸ is interpreted in the light of our results.

II. STO BASIS

If an optimized STO and orbital basis is constructed in a systematic manner, it is possible to find patterns of convergence for expectation values, in particular for the energy, permitting the estimation of the "saturation remainders." (Within each shell and l symmetry type, "saturation" with STO's is achieved when no new STO's can be found which give any substantial improvement in the

energy.)

The STO's from a *nominal* Hartree-Fock (HF) function⁹ are used as a starting point. Next, several STO's are optimized in the L shell relative to a doubly excited L -shell CI expansion. The STO basis obtained at this stage already accounts for two thirds of the K -shell CE. This is partly due to the fact that K -shell correlating functions penetrate considerably into the L shell. The reverse is not true; this is why it is more economical, in terms of the number of STO's, to start by doing an L -shell optimization. The K -shell optimization which follows is quite simple, the energetically important STO's being very much localized.

The STO parameters used in this work are given elsewhere.¹⁰ For the L shell, the saturation remainders are about 0.00010 a.u. for s -type STO's, 0.00010 , 0.00017 , and 0.00010 a.u. for p -, d -, and f -type STO's, respectively. The overall saturation remainders for the intershell are probably smaller than 0.00020 a.u. For the K shell, they can be estimated very accurately, from the C^{4+} *spdf* energy limit,¹¹ and the computation of the exclusion effects (see Sec. V).

The STO basis employed is $7s6p4d3f$.

III. APPROXIMATION OF THE FULL CI

The terms of the CI expansion are selected according to a combined partial energy and eigenvector component criterion. For a function Φ_i , the partial energy is defined as $E_i = \langle \Phi_i | H | \Phi_i \rangle \cdot c_i / c_0$, where Φ_0 is an appropriate reference function (HF or a short CI) and the c_i 's are eigenvector components. It is possible to find a value of the modulus of the eigenvector component (EIG) below which the terms crowd together, most of them contributing very little to the energy; a few of these, however, do have sizable partial energies

and one can set a tolerance (TOL) such that the terms for which the absolute value of the partial energy exceeds TOL are separated from the rest.

The three large divisions of the CI expansion: *K* shell, *L* shell, and intershell excitations, are quite independent of each other, inasmuch as the partial energies and eigenvector components of one of them are not appreciably affected by the presence of the other two. The *K*-shell, *L*-shell, and intershell CI expansions are hence investigated first independently; the best energies obtained for each of them are indicated in Table I together with the energies of their most relevant truncations. Estimates for the various *spdf* energy limits are given in the last column of Table I; the entries of column 3 are estimates obtained from the configuration search by adding all partial energies of the terms which were discarded (this estimate is usually good to within 10%).¹² The CI truncation error of the final wave function (-0.00284 a.u.) is calculated by adding the following partial energies: *K*- and *L*-shell truncations equals -0.00138 a.u.; intershell truncations equals -0.000645 a.u.; triple and quadruple *KL* truncations equals -0.000315 a.u., and triple and quadruple *KL* truncations from subclasses not considered equals -0.00050 a.u.

IV. HIGHER HARMONICS

The energy effect of *g*, *h*, and higher harmonics in the *L* shell is estimated for each electron pair according to an empirical procedure which gives very accurate predictions for the He isoelectronic series.¹¹ It is illustrated in Table II for the $(s_2)^2$ excitations. It is based on the existence of a general pattern for the contributions $e(i, l)$ of the different orbitals (*i, l*) to the energy, when these are written in the manner shown in Table II. The

TABLE II. Diagram for estimation of $e(i, l)$ values for $(s_2)^2$ excitations.

$d_1 = 4100^a$							
$d_2 = 580$	$f_1 = 1000$						
$d_3 = 20^b$	$f_2 = 150$	$g_1 = 370$					
$d_4 = 1$	$f_3 = 10^b$	$g_2 = 60$	$h_1 = 180$				
.	$f_4 = 0$	$g_3 = 5$	$h_2 = 35$	$i_1 = 110$			
.	.	$g_4 = 0$	$h_3 = 2$	$i_2 = 22$.	.	.
.

^aIn units of 10^{-6} a.u.

^bComputed with CI wave functions.

energy $e(i, l)$ is obtained by adding the partial energies of the excitations in which (*i, l*) occurs; only those excitations of (*i, l*) are considered in which (*i, l*) occurs paired with itself or with another orbital (*i', l'*) for which $|e(i', l')| > |e(i, l)|$. One finds (a) $|e(i, l)| > |e(i, l+1)| > |e(i+1, l)|$, (b) the vertical ratios $e(i, l)/e(i+1, l)$ usually decrease smoothly for a given *i* value for increasing *l*.

Once a few of the $e(i, l)$'s have been obtained, the remaining ones are predicted according to the rules indicated above: In this way, we have estimated the effect of the *g, h*, and higher orbitals on the expansion of $(s_2)^2$, to be of the order of 0.0010 a.u. Analogously, we find 0.00045 and 0.0030 a.u. for the pairs $(p_1)^2$ and s_2p_1 , respectively. For the intershell, similar arguments lead to an estimate of the error in the CE of 0.00020 a.u. Similar considerations can be applied to the *K* shell, but a more accurate procedure is employed in this case, as described in Sec. V.

V. CORRELATION ENERGY

A. Saturation Remainders and Higher Harmonic

In *K* Shell

The difference between the CE of the *K* shell of

TABLE I. Steps in the configuration search.

Wave function	Number of terms	Energy	CI error ^a (<i>7s6p4d3f</i>)	Saturation remainders	<i>spdf</i> -energy ^b limit
<i>L</i> shell: HF interacting terms	83	-37.78222			
<i>L</i> shell: EIG=0.01, TOL=0.000065	51	-37.78360			
<i>L</i> shell: EIG=0.01, TOL=0.000150	39	-37.78231			
<i>L</i> shell: best expansion	179	-37.78560	-0.000400	-0.000470	-37.78647
<i>K</i> shell: best expansion	49	-37.72985	-0.000035	-0.000960 ^c	-37.73085
Intershell: best expansion	110	-37.69957	-0.000450	-0.0002	-37.70022
<i>K</i> shell+intershell: best expansion	159	-37.74080	-0.000485	-0.00116	-37.74245
<i>K</i> shell+ <i>L</i> shell: best expansion	215	-37.82437	-0.000435	-0.00143	-37.82624
Final wave function (full CI)	234	-37.83378	-0.00284 ^d	-0.00163	-37.83835

^aThis is the energy error due to the CI truncation for our *7s6p4d3f* basis.

^bThe error in this column is about 10% of the sum of columns 3 and 4.

^cSee Sec. V.

^dThis value differs from the one given in Ref. 6, in which the preliminary truncation error of the (*K+L*) shell function was mistakenly omitted.

C and that of C^{4+} is due mainly to the following effects: (a) the exclusion of the s_2 orbital from the K -shell expansion of C, which amounts to 0.002 57 a. u.; (b) the partial exclusion of the p_1 orbital from the K -shell expansion of C due to the presence of the $(p_1)^2$ pair in the L shell (about 0.000 58 a. u.); (c) an effective exclusion of all ${}^1S(s_1s_x)$ ${}^1S(s_2)^2{}^3P(p_1)^2$ configurations from the K -shell expansion of C due to the fact that s_1 is an HF orbital of C but not of C^{4+} (about 0.000 47 a. u.); and (d) the absence from the C^{4+} function of configurations (s_xd_y) , (p_xf_y) , ${}^3S(s_xs_y)$, etc., which do not form a 1S state. The latter effect (about 0.000 45 a. u.) opposes the other three; these can be estimated *a priori* from C^{4+} functions expressed in a basis which includes the HF orbitals of C (see Table III). Of special significance is the estimate of the partial exclusion effect of orbital p_1 . We consider the following model for the K -shell wave function of C:

$$\Psi(K \text{ shell } C) = \alpha[\Psi(K \text{ shell } C^{4+}) \times (s_2)^2 \times {}^3P(p_1)^2] \quad (1)$$

Then:

$$\begin{aligned} c_k(C^{4+}) \alpha \{ (s_2)^2 \times 1/\sqrt{3} [(p_1^0 | p_1^0) - (p_1^1 | p_1^1) - (p_1^{\bar{1}} | p_1^{\bar{1}})] \\ \times (p_1^0 p_1^1 |) \} = 1/\sqrt{3} \cdot c_k(C^{4+}) \cdot (s_2 p_1^{\bar{1}} p_1^0 p_1^1 | s_2 p_1^1) \\ = c_k(C) \cdot (s_2 p_1^{\bar{1}} p_1^0 p_1^1 | s_2 p_1^1) \end{aligned} \quad (2)$$

where the spin orbitals to the left of the bar have α spin, those to the right, β spin. It is seen that the expansion coefficient of $(p_1)^2(s_2)^2(p_1)^2$ is reduced by a factor of $\sqrt{3}$ with respect to the one of $(p_1)^2$ in C^{4+} ; it can be easily verified that the corresponding partial energy must be reduced accordingly by a factor of 3. Analogously, for con-

TABLE III. Comparison of K -shell correlation energies of C and C^{4+} .

	C	C^{4+}
E_0^a	-37.688 55	-32.360 19
K Shell CI ^b	-37.729 89	-32.404 61
$\Delta E = E - E_0$	-0.041 34	-0.044 42
$\Delta E - \sum (s_x d_y) - \sum {}^3S(s_1 s_2)$	-0.040 89 ^c	
Exclusion of s_2		0.002 57 ^d
Partial exclusion of p_1		0.000 58 ^e
$-\sum (s_1 s_x) = s_x \neq s_2$		0.000 47 ^f
$\Delta E + \text{Exc}$		-0.040 80
Total exclusion effects = Exc		0.003 62

^a E_0 = energy of ground configuration.

^bObtained with our $7s6p4d3f$ basis.

^cComputed by subtracting the corresponding partial energies relative to HF.

^dComputed as the energy difference between two full CI's for C^{4+} , with and without orbital s_2 .

^eSee text.

^fSum of partial energies relative to HF.

TABLE IV. Angular energy limits for C^{4+} .

	($7s6p4d3f$)	Ref. 11	"Exact"
s		-32.376 286	-32.376 289 ^a
sp	-32.400 89	-32.401 336	-32.401 344 ^a
spd		-32.404 655	-32.404 679 ^a
$spdf$	-32.404 61		-32.405 57 ^a
$spdfg$			-32.405 88 ^a
$E(\text{total})$			-32.406 25 ^b

^aReference 11, upper bounds estimated from rates of convergence of NSO expansions.

^bC. L. Pekeris, Phys. Rev. 112, 1649 (1958).

figurations of the type ${}^1S(p_1 p_x) {}^1S(s_2)^2 {}^3P(p_1)^2$, the expansion coefficients and partial energies are reduced by factors of $(\frac{2}{3})^{1/2}$ and $\frac{2}{3}$, respectively. In C^{4+} the partial energy of $(p_1)^2$ is -0.000 060 a. u.; hence we must expect -0.000 020 a. u. in C, i. e., an exclusion effect of 0.000 040 a. u. The sum of the partial energies for $(p_1 p_x)$ is -0.001 63 a. u.; the corresponding exclusion effect is of 0.000 54 a. u. Thus, the predicted over-all exclusion effect of p_1 to the K -shell correlation energy is 0.000 58 a. u., as reported in Table III. From Table XIV of Ref. 6, one may compute *a posteriori* a combined partial energy of -0.001 08 a. u. for p_1 in the K shell, which gives an over-all exclusion effect of 0.000 61 a. u.

Assuming then that all the differences between the CE's of the K shells of C and C^{4+} can be accounted for, their errors should be the same. The total error in C^{4+} may be obtained on the basis of angular energy limits (Table IV).

B. Estimate of the Nonrelativistic Energy

All energy errors discussed previously are combined as described in Table V, to give CE = -0.1550 \pm 0.0015 a. u. In Table VI we give the partition of the calculated CE in terms of the ϵ parameters of HF orbitals and of pairs of HF orbitals: These are defined as the sum of the partial energies of the corresponding excitations.

C. Comparison of C and C^{2+} Ground States

A qualitatively correct description of the CE relationships between neutral first-row atoms and their respective ions has been given by McKoy and Sinanoğlu.¹³ Two specific questions require detailed answers: (i) What are the relationships between the wave functions of C and C^{2+} ?, and (ii) Of what help can be, say, a C^{2+} wave function in the determination of a wave function for C?

We let Φ_k be a normalized term of the (normalized) C^{2+} wave function, with a CI coefficient $c_k(C^{2+})$, and set $\alpha \{ \Phi_k(p_1^0 p_1^1 |) \}$ to be the corresponding term of the (normalized) C wave function,

TABLE V. Estimate of the total nonrelativistic energy.

Energies in a.u. (C)	
<i>spdf</i> energy limit	-37.838 35 ± 0.0005 ^a
Contributions of <i>g</i> , <i>h</i> , and higher orbit- als to <i>K</i> shell	-0.000 68 ^b
Same, to (<i>s</i> ₂) ² excitations	-0.0010
Same, to (<i>p</i> ₁) ² excitations	-0.000 45
Same, to <i>s</i> ₂ <i>p</i> ₁ excitations	-0.0030
Same, to intershell	-0.0002
Total <i>g</i> , <i>h</i> , and higher	-0.0053 ± 0.0010
Total nonrela- tivistic energy	-37.8436 ± 0.0015
HF energy	-37.6886 ^c
Correlation ener- gy (estimate)	-0.1550 ± 0.0015

^aSee Table I.^bSee Table IV.^cReference 9.

with a CI coefficient $c'_k(C)$. We shall consider the following model for the C wave function:

$$c'_k(C) = c_k(C^{2+}), \quad (3)$$

such that $\alpha\{\Phi_k(p_1^0 p_1^1)\}$ is normalized if and only if the antisymmetrizer does not annihilate any term of $\{\Phi_k(p_1^0 p_1^1)\}$. The normalized coefficient $c_k(C)$ can be readily obtained from $c'_k(C)$ in a way similar to the one shown in Eq. (2). In general, the partial energies $E_k(C)$ are not related to the $E_k(C^{2+})$'s in a simple way, except for the cases already considered in Sec. VA; fortunately, however, these are the only relevant nontrivial cases.

A C^{2+} wave function with $E = 36.5300$ a.u. (C) was obtained with our $7s6p4d3f$ basis.¹⁴ The comparative results can be summarized as follows: (a) For the *K* shell, an analysis similar to the one given in Sec. VA is valid. (b) For the (*s*₂)² excitations, the model of Eq. (3) is approximately valid for (*s*₁)²(*p*₁)⁴, but fails otherwise by about 100% with no fixed pattern in the signs of the deviations. An analysis similar to (a) gives a fair agreement between the (*s*₂)² CE's, but this should be interpreted rather as a numerical coincidence. (c) The *s*₁*s*₂ excitations satisfy the model extremely well. The search of *s*₁*s*₂ excitations for C^{2+} constitutes a foolproof method to find those of C. (d) The quadruple-excited configurations of C^{2+} behave likewise. This is of utmost practical importance for estimating truncation errors in the expansion of the (*s*₁)²(*s*₂)² excitations of C. (e) There are many single

and triple excitations in C^{2+} which do not appear in C. These arise because *s*₁ and *s*₂ are HF orbitals of C but not of C^{2+} , and they can be readily identified.

VI. COMPARISON WITH PREVIOUS WORK

Previous work has been reviewed recently by Nesbet,⁸ except for Weiss's pioneer calculations.¹⁵ Weiss's emphasis is related to the computation of transition probabilities rather than to the determination of wave functions; however, his *spdf* *L*-shell energy error [half of which seems to come from an incomplete description of the (*s*₁)²(*s*₂)²(*p*₁)² degenerate space] is only -0.0077 a.u.; i. e., it is the best variational *L*-shell calculation of C previous to this work.

Nesbet's method is well known⁸; the following analysis of his work is based on our results: (a) Nesbet does not include *g*, *h*, and higher harmonics. We have estimated their energy contributions as -0.0053 ± 0.0010 a.u. (see Table V), i. e., about 3% of the correlation energy. Hence, Nesbet's results are to be compared with any of our *spdf* energy values; estimated exact values for CI and Nesbet methods are given for completeness (see Table VII). (b) Nesbet's result for $e(1s, 1s)$ gives a relative idea about the quality of his *spdf* functions: he gets $e(1s, 1s) = -0.040867$ a.u., while we get (*K*-shell CI - *S*₁ excitations) a similar value: -0.04085 a.u. (c) The sum $e(1s\alpha, 2s\alpha) + e(1s\alpha, 2s\beta) + e(1s\beta, 2s\alpha) + e(1s\beta, 2s\beta)$ is lower than the CE of the corresponding intershell CI by about 8%, a behavior already observed for Be.¹⁶ For *s*₁*p*₁ excitations this behavior is reversed,¹⁷ and hence the estimate for Nesbet's "exact" intershell CE is only 3% lower than the CI estimate. (d) Our results show that for C ground state, the sum of the exact one- and two-particle Bethe-Goldstone increments¹⁸ corresponding to the *L* shell is lower than the exact CI value by about 3%. (e) A further error is introduced in Nesbet's method when the *K*-shell, intershell, and *L*-shell

TABLE VI. Partition of the calculated correlation energy.

	Energy
E_{HF} (Ref. 9)	-37.688 547
$\epsilon(s_2, s_2)$	-0.028 626
$\epsilon(s_2, p_1)$	-0.021 625
$\epsilon(p_1, p_1)$	-0.008 433
$\epsilon(s_2)$	-0.035 456
$\epsilon(s_1, s_1)$	-0.040 575
$\epsilon(s_1)$	-0.000 447
$\epsilon(s_1, s_2)$	-0.005 446
$\epsilon(s_1, p_1)$	-0.004 623
$E(\text{total})$	-37.833 778

TABLE VII. Interpretation of Nesbet's results.

	Nesbet ^a	Nesbet ^b (exact)	CI (calc)	CI (extrap)	CI (<i>spdf</i> limit)	CI (exact)
(<i>s</i> ₁) ² excitations	-0.040 867	-0.042 53 ^c	-0.040 85	-0.040 89	-0.041 85	-0.042 53 ^c
<i>s</i> ₁ <i>s</i> ₂ + <i>s</i> ₁ <i>p</i> ₁	-0.012 185	-0.0126	-0.011 47 ^d	-0.011 92 ^d	-0.012 12 ^d	-0.012 32 ^d
<i>s</i> ₂ + <i>p</i> ₁ + (<i>s</i> ₂) ² + <i>s</i> ₂ <i>p</i> ₁ + (<i>p</i> ₁) ²	-0.100 110	-0.1051	-0.097 05	-0.097 45	-0.097 92	-0.1024

^aReference 8.

^bEstimated by adding to Nesbet's result the difference between columns 6 and 4.

^cIn this case CI and Nesbet's methods coincide.

^dIntershell + *s*₁ excitations which are linear combinations of *s*₁*s*₂- and *s*₁*p*₁-excited determinants.

expansions are lumped together: there is a lack of additivity of 0.0039 a. u., which is only partially compensated by triple- and quadruple-excited *KL*-shell excitations (-0.0018 a. u.).

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