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Configuration-interaction study of atoms. I. Correlation energies of B, C, N, O, F, and Ne

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The configuration-interaction method has been used to calculate the wave functions and energies for the ground state and some selected excited states of the atoms B to Ne. A systematic way of selecting atomic orbital basis and configurations has been developed and is reported in some detail. The calculated total correlation energies range from 95 to 97% of the empirical correlation energy. Calculated term energies of the carbon atom are within 2% of the spectroscopic values. The correlation energies were analyzed in terms of contributions from various classes of configurations, and these contributions were compared with results of previous work. The energy contributions from the class of configurations of triple and higher electron excitations are estimated to be of the order of (3–4)% of the total correlation energy, which is larger than previous estimates of (1–3)% for these atoms.

I. INTRODUCTION

The configuration-interaction (CI) method has been successfully applied to accurate quantitative studies of the correlation effects in small atoms containing as many as four electrons.[1] However, because the computational difficulty of an atomic CI calculation increases rapidly with the number of electrons involved, only few CI calculations of high quality have been reported for atoms beyond Be.[2-5] Instead, various pair-correlation approximations,[6] which assume essentially that the total energy can be given by the Hartree-Fock (HF) value plus a sum of independently calculated pair-correlation energies, have been applied to a large number of atoms and ions with considerable success[7] (~90% of the correlation energy or better). Recent calculations[4, 8-11] have shown, however, that pair-correlation approximations usually overestimate the correlation energy by 3–15% depending on the definition of the pair. The main reason for this is the neglect of the pair-pair interaction. A CI calculation will of course include the pair-pair interaction automatically. Thus, it is worthwhile to investigate more thoroughly the possibility of performing, with a reasonable amount of computational effort, large scale CI calculations that would yield accurate results for atoms beyond Be.

The main computational hurdle one must overcome in order to carry out large CI calculations for atoms lies perhaps in the evaluation of the Hamiltonian matrix elements between various configurations. This is especially true if one uses a symmetry adapted CI expansion; i.e., the configurations are eigenfunctions of L^2 and S^2. The complexity of atomic configurations constructed from orbitals of higher angular momenta is such that elementary methods for evaluating Hamiltonian matrix elements between these configurations become hopelessly slow and impracticable for large CI calculations. In order to overcome this hurdle, one of us (F.S.) developed a powerful method[12] by which any Hamiltonian matrix element can be found, in terms of sums of integrals over radial functions, with relative ease. With this hurdle out of the way, we are able to concentrate our effort on removing as much as possible the incompleteness of the orbital basis, which is the main source of uncertainty in the results of most correlation energy calculations, by inclusion of not only a sufficient number of orbitals of lower angular momenta but also orbitals of higher angular momenta. In addition, we may be able to estimate, with reasonable assurance, the energy contributions from the configurations of triple and higher excitations, which are formed by exciting three or more electrons from the HF configuration, by explicitly including a large number of these configurations in our CI wave function.

A remaining difficulty is the large number of configurations which arise for even relatively small systems, especially when triple and quadruple excitations are included; our largest calculation included 2650 configurations. Techniques, implemented in our computer programs, for the handling of large arrays of data and for the calculation of approximate natural orbitals have allowed us to surmount these difficulties as well.

This paper reports the results of large CI calculations carried out for the first row atoms, B–Ne. Our study of these atoms is aimed at three objectives. The first is to obtain CI wave functions for not only one atom but rather a series of atoms as accurately as possible with minimal computational effort. Second, the quality of interest usually involves an energy difference between some states of an atom or atoms. Therefore, a systematic method of selecting an orbital basis set and a set of configurations was developed to assure as much as possible the same degree of accuracy for different states. Details of this method will be given in Sec. II. Finally, the contributions of triple and higher electron excitations to the correlation energies for atoms beyond Be are still uncertain; they are usually assumed to be negligibly small. We investigated this effect by direct calculations in which a large number of configurations of higher excitations were included in the CI expansions. We also performed an analysis of the computed correlation energy in terms of the contribution of individual orbitals and classes of configurations. This analysis gives information concerning the importance of higher excitations. The result of these analyses are presented in Sec. III.

II. CALCULATIONS

A total wave function Ψ is expanded as

$$\Psi = C_{\mathrm{HF}}\Phi_{\mathrm{HF}} + \sum_{I} C_I \Phi_I , \qquad (1)$$

where C_{HF} and C_I are variationally determined coefficients, Φ_{HF} is the Hartree-Fock state function, and Φ_I are configuration state functions (CSF). The CSF are linear combinations of Slater determinants which are eigenfunctions of L^2 and S^2.

Classes of CSF

We used the HF state function as a reference CSF in all calculations. The other CSF will be divided into two major classes essentially according to their electron excitation with respect to the HF state, namely single-double (SD) excitations and triple-quadruple (TQ) excitations (in the present calculations excitations higher than quadruple are not considered). Because CSF used are symmetry adapted, the above definitions are not exact although descriptive. In the present work the SD class includes those CSF that interact with the HF state function, that is, those which have formally a nonvanishing Hamiltonian matrix element with the HF state function. Double orbital excitations that have formally a zero matrix elements with the HF state function are included in the class of TQ excitations.

These two classes are further subdivided according to the HF orbitals out of which electrons are excited. Thus, for the atomic systems considered here we have a total of six elementary classes of CSF, HF, SD_K, SD_{KL}, SD_L, TQ_{KL}, and TQ_L, and these classes are mutually disjoint by construction, which means that CSF of single excitation are in either SD_K or SD_L and none in SD_{KL}. We shall use these terms or any combinations of them in describing CI wave functions and adopt a convention that a term without a subscript means a major class and a union of elementary classes in different major classes will be denoted by four letters, for example, $\mathrm{SD} = \mathrm{SD}_K + \mathrm{SD}_{KL} + \mathrm{SD}_L$ and $\mathrm{SDTQ}_L = \mathrm{SD}_L + \mathrm{TQ}_L$.

Atomic Orbitals

The same number of atomic orbitals, 35 orbitals in total, is used for all atoms studied in this work. These orbitals are in turn expanded in 47 Slater-type functions (STF). Table I gives the compositions of the STF basis and atomic orbital set. The size and composition of these basis sets are arrived at as a compromise between accuracy and practicability. They are determined from the results of preliminary calculations on the carbon atom. These calculations indicated that a basis set of this size should be large enough to give 95% or more of the correlation energy and yet not yield an excessively large number of configurations.

As shown in Table I, our STF basis can be thought of as a union of three distinct sets. The first is the Hartree-Fock set $\{\chi_i\}_{\mathrm{HF}}$, for which we used the accurate set of Bagus *et al.*[13] for all systems except for the ^5S state of C, where calculations were performed to obtain the HF set. The Hartree-Fock orbitals ($1s$, $2s$, $2p$) constructed from the $\{\chi_i\}_{\mathrm{HF}}$ are used in all calculations.

The second is the K-shell set $\{\chi_i\}_K$ consisting of 20 STF of l values ranging from 0 to 6 (or s to i) namely $2s$, $3s$, $4s$, $3p$, $4p$, $5p$, four $3d$, four $4f$, three $5g$, two $6h$ and one $7i$-type STF. To facilitate optimization of the orbital exponents and also to avoid excessive linear dependence among basis functions a common exponent is selected for s-

TABLE I. Composition of STF basis and atomic orbital set.

Symmetry	*s*	*p*	*d*	*f*	*g*	*h*	*i*	Total
STF basis								
HF	5	4	0	0	0	0	0	9
K shell	3	3	4	4	3	2	1	20
L shell	2	2	4	4	3	2	1	18
Total	10	9	8	8	6	4	2	47
Atomic orbitals								
HF	2	1	0	0	0	0	0	3
K shell	3	3	3	2	2	1	1	15
L shell	3	3	3	3	2	2	1	17
Total	8	7	6	5	4	3	2	35

type and also for the p-type STF; for other orbital symmetry types exponents are selected to form a so-called "even tempered" set. This means that within each symmetry the exponents ζ_j are given by

$$\zeta_j = \zeta_0 R^{j-1}, \quad j = 1, 2, \ldots, n \tag{2}$$

where ζ_0 and R are constants to be determined, and n is the number of STF of the same symmetry. We did not vary R and used a fixed value of $R = \sqrt{2}$. (With this value of R we believe that an adequate range of exponents could be spanned yet excessive linear dependence among STF could be avoided.) The value of ζ_0 was determined by optimization for each symmetry. Optimization of $\{\chi_i\}_K$ was carried out in K-shell CI calculations, which include all CSF of the SD_K class that could be generated from the atomic orbital set constructed from the $\{\chi_i\}_K$ together with the $\{\chi_i\}_{\mathrm{HF}}$, by orthonormalizing individual χ_i to the Hartree-Fock orbitals. With the optimized $\{\chi_i\}_K$ the approximate natural orbitals (ANO) for the K shell, $(\overline{1s}, \overline{2s}, s_1, s_2, \ldots, \overline{2p}, p_1, p_2, \ldots, d_1, d_2, \ldots)$ were generated.

The third is the L shell set $\{\chi_i\}_L$ consisting of 18 STF. The types of STF employed are the same as those for the $\{\chi_i\}_K$, except $3s$, $4s$, and two $4p$ types are used. With a parallel procedure to that used for the K shell, optimization of the L-shell exponents was carried out and approximate natural orbitals $(\overline{1s}', \overline{2s}', s_1', s_2', \ldots, \overline{2p}', p_1', p_2', \ldots, d_1', d_2', \ldots)$ were obtained.

The atomic orbital set used in a full CI calculation was then constructed by orthonormalizing the subsets of the K- and L-shell ANO sets to the HF orbitals in a special order. From both sets ANO are selected according to their occupation numbers; the number of selected ANO for each symmetry are given in Table I. Because of the way we selected triple and quadruple excitations, which will be described below, it is important that at least the leading ANO selected in each symmetry of both sets remain essentially unchanged by orthonormalization to the Hartree-Fock orbitals and themselves. Therefore, the ANO were orthonormalized in the following order. For each symmetry the leading ANO in the L-shell set was first orthonormalized to the Hartree-Fock orbitals if they exist. (For our purposes we disregard the first two s and one p ANO which are nearly the same as the occupied Hartree-Fock orbitals.) Next, the leading ANO in the K shell was orthonormalized to the HF orbitals and leading L-shell ANO. This was followed by orthonormalization of the remainder of the L-shell set and lastly the remainder of the K-shell set. For example, the order for the p orbitals would be $2p, p_1', p_1, p_2', p_3', p_2, p_3$.

Notice that we have retained the HF orbitals as the leading members of the orbital set used in the full CI (including both K and L shell correlation) calculations. This was done to *minimize* the contribution to the correlation energy from higher than double excitations, following our observation that the electronic energy in comparable calculations which include single and double excitations nearly always increases if HF orbitals are replaced by their NO counterparts.

Configurations

All possible CSF of the class of single-double excitations that could be generated with the atomic orbital set described above were included in the full CI calculations. The numbers of these CSF

TABLE II. Numbers and classes of configuration state functions used in the CI calculations.

Class		B(^2P)	C(^3P)	C(^1D)	C(^1S)	C(^5S)	N(^4S)	O(^3P)	F(^2P)	Ne(^1S)
Hartree-Fock	(HF)	1	1	1	1	1	1	1	1	1
Single and double										
K shell	(SD_K)	122	122	116	110	116	109	109	109	103
KL intershell	(SD_{KL})	315	332	295	273	284	284	602	591	255
L shell	(SD_L)	235	281	329	261	120	256	782	871	383
Total	(SD)	672	735	740	644	520	649	1493	1571	741
Triple and quadruple										
KL intershell	(TQ_{KL})	115	199	154	93	72	134	423	351	100
L shell	(TQ_L)	10	58	58	18	14	67	510	726	226
Total	(TQ)	125	257	212	111	86	201	933	1077	326
Total	(SDTQ)	798	993	953	756	607	851	2427	2649	1068

for atoms considered here are given in Table II. They range from 520 to 1571.

It is clear from the size of the atomic orbital set (35 orbitals) that all CSF of triple-quadruple excitations could not be included. Thus, we selected these CSF by a procedure described below. This procedure avoids a rather tedious and time consuming configuration search but, we hoped, selects most of the important CSF. First, some important excitation processes were selected from the results of preliminary calculations, namely separate K-shell and L-shell CI calculations. These processes are given in Table III, where $1s$, $2s$, $2p$ designate the HF orbitals while s_1, p_1, d_1, and s_1', p_1', d_1', f_1' designate the leading ANO for the K shell and L shell, repectively. Basis configurations to be considered were then generated by combining two of these processes. Thus, processes 1–3 (K-shell processes) were combined with processes 4–14 (L-shell processes) producing basic configurations for the KL-intershell excitation; processes 4–14 were combined with themselves to produce basic configurations for the L-shell excitations. We did not use KL-intershell processes since these were less important than the K- or L-shell processes selected. Except for some CSF generated by very high intermediate angular momentum coupling, all possible CSF for a given state of an atom that could be generated from these basic configurations were used in the full CI calculations. The numbers of these CSF are given in Table II and range from 86 to 1077.

Computational Detail

All calculations were carried out with the ALCHEMY computer programs written by the theoretical chemistry group at IBM San Jose. Important additions to ALCHEMY made by one of us (F.S.) specifically for atomic CI calculations include:

TABLE III. Excitation processes used in selecting triply and quadruply excited configurations.

Index	Process
	K shell
1	$1s1s \rightarrow s_1 s_1$
2	$1s1s \rightarrow p_1 p_1$
3	$1s1s \rightarrow d_1 d_1$
	L shell
4	$2s2s \rightarrow 2p2p$
5	$2s2p \rightarrow 2p d_1'$
6	$2s2p \rightarrow s_1' p_1'$
7	$2s2p \rightarrow p_1' d_1'$
8	$2s2p \rightarrow d_1' f_1'$
9	$2p2p \rightarrow p_1' p_1'$
10	$2p2p \rightarrow d_1' d_1'$
11	$2p2p \rightarrow 2p f_1'$
12	$2p d_1' \rightarrow d_1' f_1'$
13	$2s p_1' \rightarrow s_1' p_1'$
14	$2p p_1' \rightarrow p_1' p_1'$

(a) A program to evaluate Hamiltonian matrix elements in terms of various integrals over orbitals. This is an implementation of the method for atomic systems mentioned in Sec. I.[12] With this program we were able to carry out the large-scale CI calculations reported here. We also believe that this program makes it possible to carry out sophisticated CI calculations for the second and the third row atoms, especially for the third row where the complexity of the wave function is enhanced by the presence of occupied d orbitals.

(b) A program to carry out automatic orbital optimization. Because of the accuracy we are aiming at, orbital optimization is a vital part of the whole calculation. This program handles two aspects of the optimization, variation of orbital exponents and natural orbital iterations. This program was used to determine HF orbitals for the ^5S state of carbon by an iterative natural orbital method.

The following four-step procedure was used to calculate CI wave functions for all atoms considered here: (i) evaluation of expressions (or formulas) for the Hamiltonian matrix elements, (ii) optimization of the K-shell orbitals, (iii) optimization of the L-shell orbitals, and (iv) a final full CI calculation followed by a series of partial energy calculations. These calculations were carried out on an IBM 360/195 computer. Computation times for the first step are still by far the longest and ranged from 20 min for B to 120 min for F. It should be noted, however, that these expressions for an atom could also be used for isoelectronic ions. The second and the third steps took 3–5 minutes and 4–15 minutes, respectively (the times quoted here are for the entire steps including up to 30 CI calculations). The last step took 2–5 minutes.

III. RESULTS AND DISCUSSIONS

Using a whole set and subsets of configuration state functions described in Sec. II, we have calculated the following energies:

$$E(\mathrm{HF+SDTQ}),\quad E(\mathrm{HF}),$$

$$E(\mathrm{HF+SD}),\quad E(\mathrm{HF+SD}_K),$$

$$E(\mathrm{HF+SD}_{KL}),\quad E(\mathrm{HF+SD}_L),$$

$$E(\mathrm{HF+SD+TQ}_{KL}),$$

where terms in parentheses represent the classes of CSF used in the CI calculation. From these

TABLE IV. Calculated total energies, correlation energies, and empirical correlation energies. (SD) and TQ) refer to contributions of single-double and triple-quadruple excitations, respectively; (SDTQ) refers to the results of full CI calculations. Energies are in a.u. with signs reversed.

Atom	Total energy		Correlation energy				Remainder			
							Magnitude		Percentage	
(state)	(HF)	(SDTQ)	(SD)	(TQ)	(SDTQ)	(empirical)[a]	(SD)	(SDTQ)	(SD)	(SDTQ)
B(^2P)	24.5291	24.6500	0.1171	0.0038	0.1209	0.1247	0.0076	0.0038	6.1	3.1
C(^3P)	37.6886	37.8393	0.1469	0.0038	0.1507	0.1565	0.0097	0.0058	6.2	3.7
C(^1D)	37.6313	37.7924	0.1565	0.0046	0.1611	0.1675	0.0109	0.0064	6.5	3.8
C(^1S)	37.5496	37.7385	0.1837	0.0052	0.1889	0.1970	0.0133	0.0081	6.8	4.1
C(^5S)	37.5992	37.6893	0.0894	0.0006	0.0900	0.0924[b]	0.0030	0.0024	3.2	2.6
N(^4S)	54.4009	54.5812	0.1774	0.0029	0.1803	0.1886	0.0112	0.0083	6.0	4.4
O(^3P)	74.8094	75.0542	0.2402	0.0046	0.2448	0.2579	0.0177	0.0131	6.9	5.1
F(^2P)	99.4093	99.7166	0.3014	0.0059	0.3073	0.3220	0.0206	0.0148	6.4	4.6
Ne(^1S)	128.5471	128.9168	0.3627	0.0070	0.3697	0.3896	0.0269	0.0199	6.9	5.1

[a] Values from Ref. 14 with the Lamb shift correction included.

[b] Evaluated assuming the same relativistic and Lamb shift corrections as those for C(^3P).

energies the total correlation energy and contributions to the correlation energy from various classes of CSF are computed as follows:

$$\epsilon\,(\mathrm{SDTQ}) = E\,(\mathrm{HF}+\mathrm{SDTQ}) - E\,(\mathrm{HF}),$$

$$\epsilon\,(\mathrm{SD}) = E\,(\mathrm{HF}+\mathrm{SD}) - E\,(\mathrm{HF}),$$

$$\epsilon\,(\mathrm{TQ}) = \epsilon\,(\mathrm{SDTQ}) - \epsilon\,(\mathrm{SD}),$$

$$\epsilon\,(\mathrm{SD}_\alpha) = E\,(\mathrm{HF}+\mathrm{SD}_\alpha) - E\,(\mathrm{HF}), \quad \text{for } \alpha = K, KL, L,$$

$$\epsilon\,(\mathrm{TQ}_L) = E\,(\mathrm{HF}+\mathrm{SDTQ}) - E\,(\mathrm{HF}+\mathrm{SD}+\mathrm{TQ}_{KL}),$$

$$\epsilon\,(\mathrm{TQ}_{KL}) = \epsilon\,(\mathrm{TQ}) - \epsilon\,(\mathrm{TQ}_L).$$

The main results of the full CI calculations are presented in Table IV and calculated correlation energies are compared with the empirical values.[14] The errors of the calculated correlation energy, with respect to the empirical values, are given for both the SD and SDTQ CI results. Although the magnitudes of correlation errors for ground state atoms increase from B to Ne as expected, the percentage errors are uniformly within 1% in the SD results and within 2% in the SDTQ results. On the whole we are able to determine wave functions for all atoms considered here that give 95% or more of the empirical correlation energy in the framework of the configuration-interaction method.

Although there have been many studies of the correlation energy of the first row atoms by the pair-correlation approximation, only few variational full CI calculations that include configurations of higher than double excitation have been reported. These include calculations on B(^2P)[2], C(^3P)[3], and Ne(^1S)[4,5]; Table V gives comparison of these results with ours. Our total energy results for these atoms show significant improvement over previous results, and our calculated contributions of triple-quadruple excitations either exceed or are very close to previous estimates. We include also in this table our estimates for the TQ contributions for B and Ne. These estimates are substantially larger than those estimated by previous authors. We describe later how we have obtained these estimates. Since our CI wave functions include only limited number of triple and quadruple excitation terms, the true contributions of these excitations are expected to be greater than the calculated values. Thus, we believe that the contributions of these higher excitations should be of the order of 3-4% of the total correlation energy for the ground-state atoms of the first row. A more detailed discussion will be given later in this section in conjunction with the analysis of the errors.

Table VI summarizes the results of the partial energy calculations in terms of shell correlation energies which may be more directly comparable with those calculated by the pair-correlation approximations. It is of interest to note that, for the ground-state atoms, the K-shell correlation energies are nearly constant while the KL-intershell correlation energies increase in magnitude

TABLE V. Comparison with previous CI results. Energies are in a.u.

Atom		Total	Correlation	Triple-quadruple contribution	
(state)	Ref.	energy	energy	(calc.)	(estimate)
B(^2P)	2	− 24.6392	−0.1101	−0.0025	−0.0038
	This work	− 24.6500	−0.1209	−0.0038	−0.0053
C(^3P)	3	− 37.8338	−0.1452	−0.0018	
	This work	− 37.8393	−0.1507	−0.0038	
Ne(^1S)	5	−128.8868	−0.3403	−0.0037	−0.0040
	4	−128.8800	−0.3333	−0.0057	−0.0078
	This work	−128.9168	−0.3697	−0.0070	−0.0150

linearly by an amount of about 0.0034 a.u. from B to Ne. The L-shell correlation energies increase in magnitude linearly by 0.026 a.u. from B to N and by 0.060 a.u. from N to Ne. Another observation is that the magnitude of the KL-intershell (TQ) contribution is largest for B, decreases as the atomic number increases and is constant for N to Ne, indicating that this is not very important for the total correlation energy of these atoms.

Previous work on the atoms considered here has been reviewed by Nesbet[7]; more recent reviews were given by Dutta and Dutta[11] on N and by Lee, Dutta, and Das[10] on Ne. For the purpose of comparing the calculated shell correlation energies with those of previous work we selected the ground state of the carbon atom as a typical example, and a comparison is given in Table VII. The first column of Table VII gives the Miller and Kelly[15] results calculated using many-body perturbation theory. The shell correlation energies quoted here are taken from their modified pair-correlation energy results that include three-body interaction effects. The second column is results of Nesbet[7] obtained from orbital-excitation Bethe-Goldstone calculations, also including the three-body interaction effects. Both calculated and estimated energies of Bunge and Bunge,[3] obtained in the CI framework including triple and quadruple excitations are given next. Considering that orbitals of only up to f symmetry are employed in other works whereas those of up to i symmetry are used in our calculations, these results shown in Table VII are generally in good agreement. The estimated energies of Bunge appear to be quite accurate except the KL-intershell energy of -0.0123 a.u. This energy is probably underestimated by as much as -0.002 a.u. With this revised value of -0.0143 a.u. the sum of their estimated shell correlation energies becomes -0.1592, which is more reasonable considering the lack of additivity of -0.0036 a.u. in our calculated results. This underestimate of the KL-intershell correlation energy also appears in previous work on other atoms, even when the estimate is made by the sum of independently calculated pair energies. This discrepancy is mainly due to the neglect of triple and higher excitations of the KL-intershell. For example, we computed this effect to be -0.0015 a.u. for $C(^3P)$, which should be compared with the underestimate of -0.002 a.u. mentioned above. However, as shown in Table VI, this effect is not very important for larger atoms, Ne for example.

TABLE VI. Contributions to the correlation energies by shells and by classes of excitations. Energies are in a.u. with all signs reversed.

Atom (state)	K shell (SD)	KL intershell (SD)	KL intershell (TQ)	KL intershell (SDTQ)	L shell (SD)	L shell (TQ)	L shell (SDTQ)
$B(^2P)$	0.0420	0.0090	0.0021	0.0111	0.0703	0.0017	0.0720
$C(^3P)$	0.0418	0.0126	0.0015	0.0141	0.0961	0.0023	0.0984
$C(^1D)$	0.0418	0.0125	0.0017	0.0142	0.1060	0.0029	0.1089
$C(^1S)$	0.0418	0.0122	0.0028	0.0150	0.1352	0.0025	0.1377
$C(^5S)$	0.0423	0.0124	0.0004	0.0128	0.0357	0.0002	0.0359
$N(^4S)$	0.0414	0.0165	0.0010	0.0175	0.1225	0.0019	0.1244
$O(^3P)$	0.0411	0.0197	0.0011	0.0208	0.1828	0.0035	0.1863
$F(^2P)$	0.0407	0.0231	0.0010	0.0241	0.2409	0.0049	0.2458
$Ne(^1S)$	0.0402	0.0266	0.0010	0.0276	0.2992	0.0060	0.3052

TABLE VII. Comparison of shell correlation energies of $C(^3P)$ computed in various approximations. Energies are in a.u. with signs reversed.

Author	Miller and Kelly (Ref. 15)	Nesbet (Ref. 7)	Bunge and Bunge (Ref. 3) (calc.)	Bunge and Bunge (Ref. 3) (estimate)	This work
K shell	0.0423	0.0409	0.0409	0.0425	0.0418
KL intershell	0.0129	0.0125	0.0115	0.0123	0.0141
L shell	0.1007	0.0962	0.0970	0.1024	0.0984
Sum	0.1559	0.1496	0.1494	0.1572	0.1543
Full CI			0.1452	0.1550	0.1507

In order to assess the validity of our approach in calculating CI wave functions for excited states, we carried out similar calculations for three low-lying excited states of carbon atom, the ^1D and ^1S states of the configuration $1s^22s^22p^2$ and ^5S state of the configuration $1s^22s2p^3$. The energy results of these calculations are already given in Tables V and VI. Term energies of these states, relative to the ground state of ^3P, calculated in various approximations, are given in Table VIII, together with those of previous work[7, 16] and the observed values. Our results are in reasonable agreement with the observed values, the errors being 2% or less. The contributions of triple-quadruple excitations to the term energies are in general small but in the right direction. These contributions appear to be relatively large for states of different

TABLE VIII. Term energies (in a.u.) relative to the ^3P state for neutral carbon. (SD) indicates that only single and double excitations are considered; (SDTQ) indicates that triple and quadruple excitations are also included.

Configuration State		$1s^22s^22p^2$ ^1D	$1s^22s^22p^2$ ^1S	$1s^22s2p^3$ ^5S
Hartree-Fock		0.0573	0.1390	0.0894
L-shell CI				
This work	(SD)	0.0474	0.0999	0.1498
This work	(SDTQ)	0.0468	0.0999	0.1519
Weiss (Ref. 16)	(SD)	0.0478	0.0996	
Nesbet I (Ref. 7)	(SD)	0.0485		
Nesbet II (Ref. 7)	(SDTQ)	0.0465		
Full CI				
This work	(SD)	0.0476	0.1022	0.1469
This work	(SDTQ)	0.0469	0.1008	0.1501
Experimental (Ref. 17)		0.0463	0.0985	0.1536

orbital configurations. The L-CI and full-CI calculations give essentially the same results. In this connection it is instructive to compare the K-shell and KL-intershell correlation energies for these states. The K-shell correlation energies are the same within figures quoted in Table VI for the ^3P, ^1D, and ^1S states while a slight increase in magnitude is indicated for the ^5S state. However, this increase is compensated by a decrease in the KL-intershell energy for the ^5S state, particularly in the (TQ) contribution yielding the sum of these energies in line with others. This indicates that L-shell CI calculations should give reasonably accurate term energies for states resulting from L-shell electron excitations.

As indicated in Table IV, there still exist the remaining errors of 3–5% assuming the empirical correlation energies to be exact. There are two sources for these errors, namely incompleteness of the orbital set and truncation of triple and higher excitations. Bunge[3] noted that it is possible to find convergence patterns for the energy permitting the estimate of the saturation remainders. Using a similar method we analyzed the errors and made estimates for the effects of the triple and higher excitations.

For this purpose a detailed study of the L-shell correlation energy of Ne(^1S) was carried out. In this study an enlarged STF set consisting of 10s, 9p, 8d, 7f, 6g, 5h, 4i, 3k, and 2l STF, which includes the Hartree-Fock set, was employed and the same number of atomic orbitals are constructed by orthonormalizing individual STF to the HF orbitals. Using all of these atomic orbitals a single and double CI calculations was carried out to generate a set of L-shell approximate natural orbitals, ϕ_{nl} (n and l designate the principal and angular-momentum quantum number). The energy contribution $\Delta E(nl)$ of each ϕ_{nl} was calculated in a series of CI calculations in which ϕ_{nl}'s were successively deleted one at a time starting with the second ANO of l symmetry ($l = 8$) and ending with the first s ANO. The results are shown in Fig. 1, where $\log_{10}\Delta E(nl)$ is plotted against $\log_{10} n$. We find a convergence pattern in Fig. 1 such that the energy contributions $\Delta E(nl)$ are approximately proportional to some power of n, that is, $\Delta E(nl) \approx a_l n^{b_l}$, where a_l and b_l are constants for a given l value. We also see that variation of b_l with l is small. The irregularities at high n values are probably due to the fact that ϕ_{nl} of high n are no longer proper ANO, because of linear dependency and their small occupation numbers (less than 10^{-6}).

The saturation remainder for each l value could thus be estimated by extrapolating each line to the limit and also taking into account the irregularity at high n values. The estimated remainder and the sum of calculated $\Delta E(nl)$ for each l value are given in Table IX and also plotted in Fig. 2 as a function of l in log-log scales. In Fig. 2 we again find a convergence pattern which enables us to estimate, in a similar manner, the remaining contribution from the orbitals of higher angular momenta ($l > 8$). Thus, the single and double limit for the L-shell correlation energy was estimated to be −0.3091 a.u. This value is 103.3% of the computed L-shell correlation energy of −0.2992 a.u. described earlier (Table VI). Assuming that this percentage holds also for the K-shell and KL-

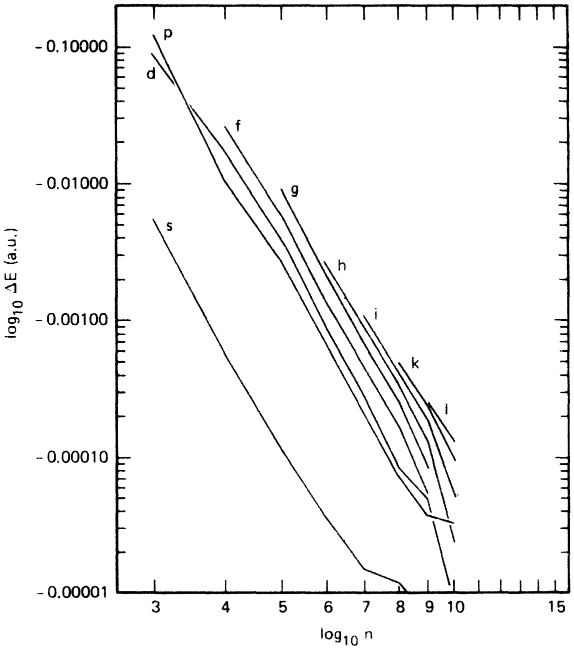

FIG. 1. Partial energy contributions ΔE_{nl} of the L-shell natural orbitals, ϕ_{nl}, of Ne(^1S).

TABLE IX. Computed and estimated contributions to the L-shell correlation energy of Ne(^1S) from different l values. Energies are in units of 10^{-5} a.u. with signs reversed.

l	Calculated	Estimated remainder	Total estimate
s	621	0	621
p	13 560	3	13 563
d	11 086	7	11 093
f	3414	9	3423
g	1245	13	1258
h	407	17	424
i	171	19	190
k	81	34	115
l	38	18	56
$\geqslant m$		170	170
Total	30 623	290	30 913

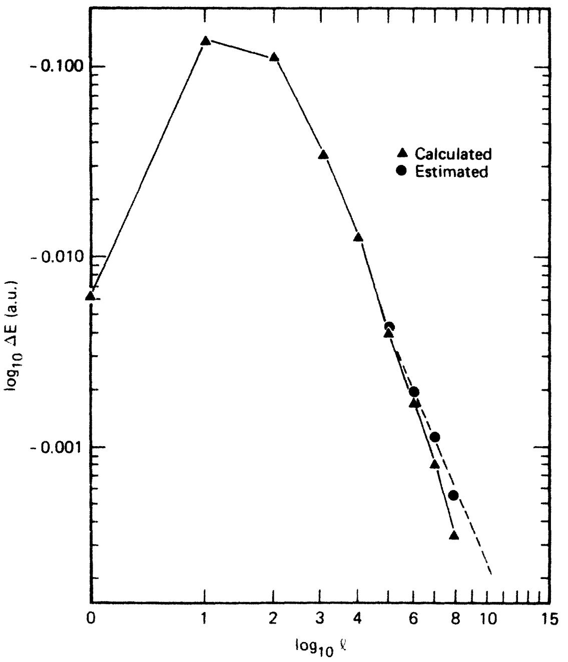

FIG. 2. Computed and estimated contributions to the L-shell correlation energy of Ne(^1S) from different l values.

intershell correlation, the single and double limit for the total correlation energy of Ne(^1S) was estimated to be −0.3747 a.u. This means that −0.0120 a.u. or 60% of the error shown in Table IV, −0.0199 a.u., is due to the orbital basis limitation while the truncation error of higher excitations is −0.0079 a.u. or 40% of the error.

Based on a similar analysis of the energy convergence pattern Bunge and Peixoto[5] reported an estimate of −0.321 ± 0.006 a.u. for the L-shell correlation energy of Ne(^1S), which is in excellent agreement with our estimate of −0.322 a.u. including the effect of triple and higher excitations. However, a detailed comparison of components of this energy shows significant differences, in particular, the contribution from the L-shell triple and higher excitations. They predicted an upper bound of −0.0037 ± 0.0005 a.u. for this effect while we found an upper bound of −0.0130 a.u., −0.0060 a.u. of which is obtained by a direct calculation. Using a perturbation technique, Barr and Davidson[4] calculated the total triple and quadruple excitation contribution for Ne(^1S) to be −0.0057 a.u. and from this they estimated the true contribution to be −0.0078 a.u. These values are substantially different from our calculated value of −0.0070 a.u. and the estimated value of −0.0150 a.u. Furthermore, their calculated value was obtained by using 60 natural orbitals and including nearly all of possible triple and quadruple excitations which could be generated from simultaneous excitations of different pairs while our calculated value was obtained by using 35 natural orbitals with a severely truncated set of 326 configurations. This indicates that our method of selecting important triple and quadruple excitation configurations is reasonably effective.

The energy limits of higher excitations for other atoms were estimated by assuming that 40% of the SDTQ errors listed in Table IV were due to the truncation of CSF of triple and higher excitations. The results are given in Table X together with the SD limits. The TQ limits of the ground state

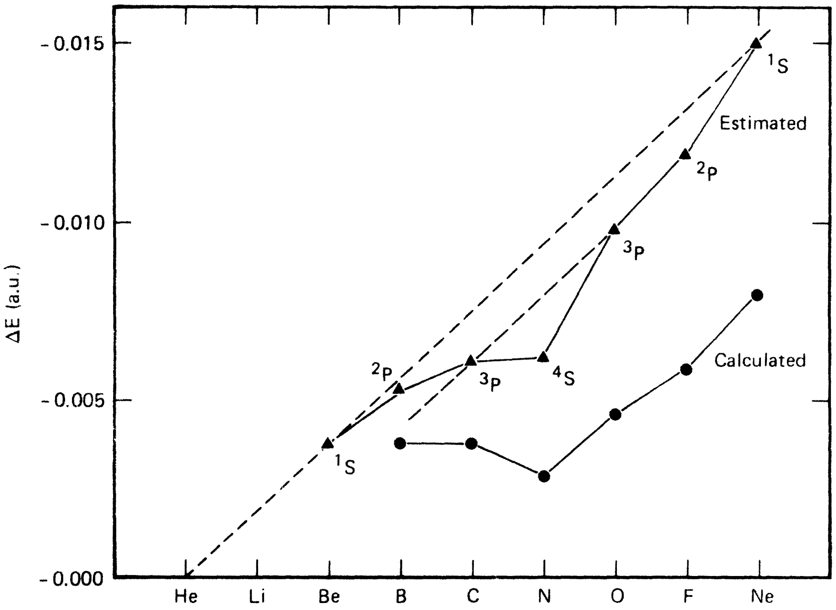

FIG. 3. Computed and estimated energy contributions ΔE of triple and higher excitations.

TABLE X. Estimated limits of contributions to the correlation energy from single-double and higher excitation configurations. All energies are in a.u. with sign reversed.

Atom (state)	Single and double	Triple and higher
B(^2P)	0.1194	0.0053
C(^3P)	0.1504	0.0061
C(^1D)	0.1605	0.0070
C(^1S)	0.1886	0.0084
C(^5S)	0.0908	0.0016
N(^4S)	0.1824	0.0062
O(^3P)	0.2481	0.0098
F(^2P)	0.3101	0.0119
Ne(^1S)	0.3746	0.0150

atoms are also plotted in Fig. 3, where the Bunge results of −0.0038 a.u. for Be(^1S)[1] is also included for comparison. Our estimated limits are in general higher than those of previous work (see Table V), but we believe our estimates to be reasonable upper bounds based on the observation that direct calculations with a relatively small number of TQ configurations already yielded 50–70% of the estimated values.

Figure 3 exhibits interesting features that may be interpreted as some regularity in the triple and higher excitation effects on the correlation energies of the first-row ground-state atoms. The first feature is that a line connecting the estimated values for Be(^1S) and Ne(^1S) intersects the zero line at $Z=2$; the other is that a line connecting the values for $C(^3P)$ and $O(^3P)$ is almost parallel to the ^1S line. The estimated ^2P line is not parallel to the ^1S line but it lies at least between the ^1S and ^3P lines, and the value for $N(^4S)$ lies below the ^3P line. Relative positions of these lines or points indicate a general dependence of the higher excitation effect on the symmetry of the states.

IV. CONCLUSION

The results of the present calculations demonstrate that a wave function of high accuracy can be determined in the framework of the CI method with a reasonable amount of computational effort for the first-row atoms. It is also demonstrated that wave functions of similar quality could be obtained for excited states, thereby making possible the prediction of term energies to within a few percent or better. We expect that CI calculations of similar accuracy for larger atoms, the second-row atoms for example, could also be carried out. The computational effort required would necessarily increase but not by a prohibitingly large amount.

The energy effects of triple and higher excitations are estimated to be of the order of 3–4% of the total correlation energy for the ground state of the first-row atoms. These estimates are significantly larger than previous estimates but a near uniformity of the percentage effects among different atoms is rather gratifying, and it is most likely that a similar uniformity should also hold in the second-row atoms.

The electron affinities of atoms considered here have also been calculated and will be reported in the following paper, together with a detail comparison with those calculated in the pair-correlation approximations.

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