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Configuration-interaction study of atoms. II. Electron affinities of B, C, N, O, and F

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Extensive configuration-interaction calculations have been carried out to determine electron affinities of the first-row atoms, B to F. Calculated electron affinities in eV with the observed values in parentheses are 0.15, 1.11(1.25), −0.52, 1.13(1.461), and 3.12(3.448), for B, C, N, O, and F, respectively. Our best estimates, based on an empirical extrapolation which makes use of the known C, O, and F affinities, for B and N electron affinities are 0.24 and −0.19 eV, respectively. Detailed analysis of the results in terms of contributions from various classes of configurations shows that the K-shell and KL-intershell correlation-energy contributions to these electron affinities are negligibly small, and that about 15% of the total correlation contribution comes from the triple and higher electron-excitation configurations. Symmetry-adapted pair-correlation calculations have been carried out for O, O^-, F, and F^- to study convergence patterns for the correlation energy and electron affinity with respect to the orbital basis used to construct the configurations. Such pair-correlation calculations are known to overcompute the correlation energy. The excess energies, which correspond to pair-pair interaction energies neglected in the pair-correlation calculations, were roughly constant over a range of orbital basis sizes, with magnitudes about twice the energy contributions from the configurations of triple and higher excitations omitted in the pair-correlation calculations. Accordingly, this approximation should overestimate the electron affinity if a complete orbital basis is used.

I. INTRODUCTION

In the first paper of this series,[1] hereafter referred to as I, we presented the results of extensive configuration-interaction (CI) calculations of the correlation energies of the ground states of the first-row atoms with Z from 5 to 10. In this paper we report the results of CI calculations carried out to determine the electron affinities of the atoms with Z from 5 to 9. The CI wave functions for the negative ions were determined by the same computational procedure[1] as used for the isoelectronic neutral atoms; the orbital bases used were carefully selected so that the wave functions for both negative and neutral systems would be of the same quality. Thus, if the electronic structure of a negative ion does not substantially differ from that of the isoelectronic neutral atom, we expect that reasonably accurate results for the electron affinity should be obtained. If the electronic structure does change, the results may not be accurate, but we should be able to identify the effects of the change by analyzing the results in terms of contributions from various parts of the CI expansion.

Recently, various pair-correlation approximations have been applied to calculations of electron affinities with considerable success.[2-5] Of these approximations, the symmetry-adapted pair method of Weiss[4] is of most interest because his method appears to give excellent results not only with a relatively small orbital basis but also without taking into account explicitly the effects of electron excitations higher than double. Since there seems to be no rigorous theoretical basis for this method to work well compared with other pair-correlation methods, the validity of the method must be assessed empirically. Thus, we have also carried out a series of pair-energy calculations to answer two questions pertinent in assessing the validity of the Weiss pair scheme. First, how do the results of the symmetry-adapted pair calculations depend on the orbital basis used? Second, what is the nature of cancellation of various terms which must be taking place? For example, the contributions to the electron affinity from triple and higher excitation configurations are known to be significant. This fact has been noted by others[2] and also confirmed by the present calculations.

In Sec. II we present and discuss correlation energy results of CI calculations for the first-row negative ions. The electron affinity results are then presented and discussed in terms of the contributions from various parts of the CI expansion. In Sec. III the pair-correlation approximation used in this work is described in some detail to compare with the symmetry-adapted pair method of Weiss. The results of the pair-correlation energy calculations for O, O^-, F, and F^- are then presented. Finally, the convergence patterns of correlation energies and of electron affinities that emerged from these pair-energy calculations are discussed in conjunction with cancellations of various effects inherent in pair-correlation approximations.

TABLE I. Total and correlation energies (in a.u. with sign reversed) of negative ions.

	Total energy E		Correlation energy ϵ					
				Calculated			Estimated	
Ion (state)	(HF)	(SDTQ)	(SD)	(TQ)	(SDTQ)	(SD)	(TQ)	(SDTQ)
B^- (^3P)	24.5192	24.6556	0.1317	0.0047	0.1364	0.1348	0.0075	0.1423
C^- (^4S)	37.7088	37.8802	0.1667	0.0047	0.1715	0.1714	0.0100	0.1814
N^- (^3P)	54.3219	54.5621	0.2326	0.0076	0.2402	0.2403	0.0162	0.2565
O^- (^2P)	74.7895	75.0956	0.2963	0.0098	0.3061	0.3050	0.0197	0.3247
F^- (^1S)	99.4594	99.8312	0.3602	0.0116	0.3719	0.3720	0.0249	0.3969

II. CI RESULTS AND DISCUSSION

The computational procedure for determining CI wave functions has been described in I; we give here only additional detail pertinent to the negative-ion systems. The orbital basis set of Bagus[6] with 5s and 4p Slater-type functions (STF) for F^- and the orbital basis sets of Clementi and McLean[7] with 5s and 5p STF for the other ions are used as Hartree-Fock (HF) orbital sets. For each ion appropriate types and numbers of STF were added to the HF set so that the numbers of STF for each symmetry will be the same as those used for neutral atoms (10s, 9p, 8d, 8f, 6g, 4h, 2i). Optimization of these added STF and construction of an atomic orbital set to be used in final CI calculations were performed in the same manner as described in I. The wave function for an ion was expanded in the same set of configuration state functions (CSF) used for its isoelectronic neutral atom. We shall use the same classification of CSF and the same notation adopted in I, unless stated otherwise.

The calculated results for the total energy, E(SDTQ), and total correlation energy, ϵ(SDTQ), of the negative ions treated are given in Table I. Also included are the Hartree-Fock energies and contributions to the correlation energies from the single and double excitations, ϵ(SD), and from the triple and quadruple excitations, ϵ(TQ). The calculated ϵ(TQ) are significantly larger in magnitude than those for the neutral atoms. For example, the ϵ(TQ) for F^- is -0.0116 a.u. while that for Ne is -0.0070 a.u.[1] We feel that this effect is independent of the orbital bases and will show up to the same extent in the limit of complete orbital bases. That is,

$$\left(\frac{\epsilon_{\text{limit}}(\text{SD or TQ})}{\epsilon_{\text{calc}}(\text{SD or TQ})}\right)_A \approx \left(\frac{\epsilon_{\text{limit}}(\text{SD or TQ})}{\epsilon_{\text{calc}}(\text{SD or TQ})}\right)_B ,$$

where A and B respectively designate a negative ion and its isoelectronic atom, can be used to estimate complete basis set limits. Limits for ϵ(SD) and ϵ(TQ) are thus estimated using the ratios previously determined[1] for the neutral atoms, and are presented in Table I. We note that the estimated values of ϵ(TQ) are about 5.5–6.5% of the estimated values of ϵ(SDTQ). These percentages are higher than those for neutral atoms (3–4%) but again roughly uniform.

Correlation-energy contributions from various classes of CSF for the negative ions and neutral atoms are given in Table II. It is clear from this table that the K-shell and KL-intershell correlations contribute very little to the electron affinity; the largest contribution being -0.0006 a.u. (or 0.017 eV) for B. Thus, we may neglect these con-

TABLE II. Contributions to the correlation energy from various classes of configurations. All energies are in a.u. with signs reversed.

	K shell		KL intershell			L shell	
	(SD)	(SD)	(TQ)	(SDTQ)	(SD)	(TQ)	(SDTQ)
B^- (^3P)	0.0420	0.0085	0.0020	0.0105	0.0856	0.0027	0.0883
B (^2P)	0.0420	0.0090	0.0021	0.0111	0.0703	0.0017	0.0720
C^- (^4S)	0.0417	0.0121	0.0016	0.0137	0.1168	0.0031	0.1199
C (^3P)	0.0418	0.0126	0.0015	0.0141	0.0961	0.0023	0.0984
N^- (^3P)	0.0414	0.0154	0.0017	0.0171	0.1807	0.0059	0.1866
N (^4S)	0.0414	0.0165	0.0010	0.0175	0.1225	0.0019	0.1244
O^- (^2P)	0.0410	0.0189	0.0016	0.0205	0.2409	0.0082	0.2491
O (^3P)	0.0411	0.0197	0.0011	0.0208	0.1828	0.0035	0.1863
F^- (^1S)	0.0407	0.0226	0.0012	0.0238	0.3012	0.0104	0.3114
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

tributions for the most cases. It is of interest to observe however that for the KL intershell $\epsilon(\mathrm{SD}_{KL})$ decreases slightly in magnitude when an electron is added. But this decrease is in general partially compensated by an increase in $\epsilon(\mathrm{TQ}_{KL})$. It is most likely therefore that the difference in $\epsilon(\mathrm{SDTQ}_{KL})$ of an atom and its negative ion becomes smaller if more TQ terms are added to the CI wave functions. Magnitudes of both $\epsilon(\mathrm{SD}_L)$ and $\epsilon(\mathrm{TQ}_L)$ for the L shell increase in the negative ions but the increases in $\epsilon(\mathrm{TQ}_L)$ are relatively large, in fact the magnitude is more than doubled in N, O, and F systems. This will have a significant effect on the results of electron affinity calculations, which we shall discuss in more detail below.

We write the nonrelativistic total energy E of a system as

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

where $E(\mathrm{HF})$ is the Hartree-Fock energy, and $\epsilon(\mathrm{SD})$ and $\epsilon(\mathrm{TQ})$ are correlation energy contributions [$\epsilon(\mathrm{TQ})$ here includes contributions from not only triple and quadruple but also all other higher excitation configurations.] Then, the electron affinity (EA) of an atom can also be expressed as a sum of differences in the component energies of the atom and its negative ion as

$$E_{\mathrm{EA}} = E_{\mathrm{EA}}(\mathrm{HF}) + E_{\mathrm{EA}}(\mathrm{SD}) + E_{\mathrm{EA}}(\mathrm{TQ}).$$

The electron affinity E_{EA} in the above equation is referred to simply as EA in the text.

Table III gives calculated and estimated results for the electron affinity. The calculated results were obtained by using the computed energies given in Table I for the ions and in Table IV of I for the neutral atoms. The estimated results (i) of Table III are obtained by using the estimated correlation energy limits given in Table I for the ions and in Table X of I for the atoms; the estimated results (ii) are obtained in a different manner, the details of which will be given later. We shall first discuss the results for C, O, and F where the observed values[8,9,11] are well established. The calculated results are in rather unsatisfactory agreement with the observed values, the errors being 10–20%. This indicates that the errors in the calculated energies are still too large, particularly for the negative ions. The estimated results (i) for C and F are in good agreement with the observed values while that for O(0.0469 a.u.) is still appreciably different from the observed value (0.0537 a.u.). Judging from this the reliability of the estimated values for B and N are rather questionable because, as in the case of O, EA(HF) are negative and large cancellations are taking place.

TABLE III. Calculated and estimated contributions to the electron affinity EA (in a.u.).

Atom	B	C	N	O	F
Calculated					
EA (HF) [a]	−0.0099	0.0202	−0.0790	−0.0199	0.0501
EA (SD) [b]	0.0147	0.0198	0.0552	0.0561	0.0588
EA (TQ) [c]	0.0009	0.0009	0.0047	0.0052	0.0057
EA (SDTQ) [d]	0.0156	0.0207	0.0599	0.0613	0.0645
EA	0.0057	0.0409	−0.0191	0.0414	0.1146
Estimate (i)					
EA (SD)	0.0154	0.0210	0.0579	0.0569	0.0624
EA (TQ)	0.0022	0.0039	0.0100	0.0099	0.0124
EA (SDTQ)	0.0176	0.0249	0.0679	0.0668	0.0748
EA	0.0077	0.0451	−0.0111	0.0469	0.1249
Estimate (ii)					
EA (SDTQ)	0.0188	0.0249	0.0722	0.0739	0.0777
EA	0.0089	0.0451	−0.0068	0.0540	0.1278
Observed [e]					
EA		0.0459		0.0537	0.1267

[a] Hartree-Fock contribution to EA.
[b] Single-double excitation contribution to EA.
[c] Triple-quadruple excitation contribution to EA.
[d] Total correlation contribution, EA(SDTQ) = EA(SD) + EA(TQ).
[e] References 8, 9, and 11 for C, O, and F, respectively.

In order to get more reliable estimates for B and N, the following observation was made: For C, O, and F where the observed values of the electron affinity are available, we evaluated the true correlation contributions with respect to our calculated EA(HF). It was found that our calculated EA(SDTQ) were close to 83% of these true contributions for each of the three systems. Thus, estimate (ii) of Table III is obtained by assuming that our calculated EA(SDTQ) are exactly 83% of the true EA(SDTQ) for all systems considered here. We believe that the estimated values, 0.0089 a.u. (0.24 eV) for B and −0.0068 a.u. (−0.19 eV) for N are probably correct to within 0.001 a.u. (0.03 eV). This is inferred from the fact that this estimating method gives EA for C, O, and F within 0.001 a.u. of the observed values. Whereas estimate (i) of Table III, is an extrapolation based on energy differences in isoelectronic systems, estimate (ii) is based on energy differences of systems with the same nuclear charge but different numbers of electrons. Empirically, estimate (ii) is the more reliable.

From Table III we see that our calculated results in general considerably underestimate EA(TQ) and a large part (>50%) of the error in the calculated EA is due to this underestimate. We also observe that the estimated EA(TQ) are 15 ± 2% of the estimated EA(SDTQ); these estimates of EA(TQ) should be very close to the true limits.

The previous theoretical and experimental work on electron affinities of atoms considered here has been reviewed by Moser and Nesbet,[2] McDowell,[12] and Steiner.[13] In Table IV we list some selected previous results and compare with our results. The studies of Oksuz and Sinanoglu,[14] Schaefer *et al*,[15] and Clementi and McLean[7] are semiempirical in nature and should be compared with our estimated results. Edlen[16] obtained his results by an ionization potential extrapolation method, hence his results should also be compared with our estimates. All these results are, in fact, generally comparable with our estimates (i) and (ii); in particular those of Schaefer *et al.* agree best with our estimates (ii).

The results of Weiss[4] (W), Marchetti *et al.*[7] (MKW), and Moser and Nesbet[2,3] (MN) were obtained by a nonempirical pair-correlation approximation and should be directly comparable with our calculated results. The MN I results were obtained by the orbital excitation Bethe-Goldstone calculations including three-particle terms while the MN II results were calculated in the configurational excitation form of Bethe-Goldstone equations without three-particle terms. The W/MKW results were obtained by the symmetry-adapted pair correlation method of Weiss.[4] The results of these pair-correlation calculations appear to be in general qualitatively better than our calculated results. In particular, those of W/MKW are in excellent agreement with the observed values, although only single and double excitation configurations (in our definition) are included in their calculations. As discussed earlier, the contributions to the electron affinity from triple and higher terms are substantial. Therefore, some optimum cancellations of various contributions must be taking place in these pair-correlation calculations. Furthermore, the convergence property of these approximations with respect to orbital basis used has not been firmly established. Since these pair-correlation methods can easily be adapted to larger and more complex systems than considered here, it is of interest to investigate the validity of these methods more thoroughly. We have carried out such an investigation by studying the energy convergence patterns of the symmetry-adapted pair-correlation approximation and the results will be presented in Sec. III.

III. ENERGY CONVERGENCE PATTERNS IN SYMMETRY-ADAPTED PAIR CALCULATIONS

A series of calculations of the L-shell correlation energies of the ground states of O, O^-, F, and F^- were carried out in order to study convergence patterns for the correlation energies and electron affinities in the symmetry-adapted pair approximation. In particular we are interested in the pair approximation used by Weiss. The K-shell and KL-intershell correlation effects were neglected in this study since these effects did not appear to be very important in electron affinity calculations as noted in Sec. II and also as noted by others.[2,4]

In this study we used three orbital sets of various sizes. The best set [set C] used is that of the approximate natural orbitals obtained at the end of L-shell STF optimization step (see I). The set C consists of $6s$, $6p$, $4d$, $4f$, $3g$, $2h$, and $1i$ type orbitals (these orbitals are expanded in the same numbers of STF except for the s symmetry where 7 STF are used). This set is slightly larger than the L-shell orbital set used in the full CI calculation but both sets yield essentially the same energy in the L-shell CI calculation. Two other sets of smaller size are constructed by deleting some of the least important orbitals. The set A includes $6s$, $5p$, $3d$, and $1f$ type orbitals, which has the same number of orbitals as used by Weiss[4] and Marchetti *et al.*[5] The set B consists of $6s$, $5p$, $4d$, and $4f$ type orbitals, which

TABLE IV. Electron affinities of the first-row atoms (eV).

Author (Ref.)	B	C	N	O	F
This work calculated	0.15	1.11	−0.52	1.13	3.12
Estimate (i)	0.21	1.23	−0.30	1.28	3.40
Estimate (ii)	0.24	1.23	−0.19	1.47	3.48
Oksuz and Sinanoglu (14)	···	1.17	−0.45	1.24	3.23
Schaefer, Klemm, and Harris (15)	0.187	1.242	−0.213	1.461	3.453
Clementi and McLean (7)	0.30	1.17	−0.27	1.22	3.37
Edlen (16)	0.33	1.24	0.05	1.47	3.50
Weiss, Marchetti, and Krauss (4,5)	···	···	···	1.47	3.47
Moser and Nesbet I (2)	0.223	1.29	−0.12	1.43	3.37
Moser and Nesbet II (3)	0.261	1.211	−0.582	0.963	2.898
Observed	···	1.25[a]	···	1.465[b] 1.478[c]	3.448[d]

[a] Reference 8.

[b] Reference 9.

[c] Reference 10.

[d] Reference 11.

should give energies very close to the *spdf* limit.

In generating configuration state functions (CSF) we used an *LS* coupling method of "one shell at a time" type in which the shells are coupled in a fixed order. For the systems considered here, $2s^2 2p^n$, the coupling is done as follows: The excited electron pair is coupled first to give L_1S_1; the remaining $2s$ electron(s) are coupled next with this pair to give L_2S_2; and finally the remaining $2p$ electrons which have been coupled to L_3S_3 are then coupled with others to give the total *LS* state of the atom. Thus, any configuration state function Φ that could be obtained by exciting electrons out of the orbital pair ij of the Hartree-Fock configuration (in this case, $2s^2$, $2s2p$, and $2p^2$) into the virtual orbital pair kl could be specified as

$$\Phi_{ij,kl}(L_1S_1L_2S_2L_3S_3/LS)\,.$$

The coupling of L_1S_1 is restricted to a coupling allowed for the pair of electrons which are replaced in the reference configuration (thus for $2s2p$ excitations the excited electrons can be coupled only to ^1P or ^3P). CSF involving other couplings of the excited electrons have zero matrix elements of the Hamiltonian with the reference state.

Weiss[4,5] employed a different coupling method such that a similar configuration state function could be formed as

$$\bar{\Phi}_{ij,kl}(L_1'S_1'L_2'S_2'/LS)\,,$$

where $L_1'S_1'$ represents, as before, the *LS* coupling of the excited electron pair and $L_2'S_2'$ represents the *LS* coupling of the remaining electrons. These two groups are then coupled to give a particular *LS* state.

Comparison of these two methods shows immediately that if the occupation number of the $2s$ shell is either 0 or 2 ($L_2S_2 \equiv L_1S_1$), then the two methods produce identical results; that is,

$$\Phi_{ij,kl}(L_1S_1L_2S_2L_3S_3/LS) \equiv \bar{\Phi}_{ij,kl}(L_1S_1L_3S_3/LS)\,.$$

This means that the two methods generate identical configuration state functions for $2s^2$ and $2p^2$ pairs. For the $2s2p$ the resultant CSF may differ in general but a close examination of the two methods reveals that even for this pair there are two cases where identical CSF may result. The first is when the *LS* is ^1S and the second is when the L_1S_1 is a singlet state, that is, the excited electron pair is coupled to give a singlet. Thus, the two methods yield different CSF only when *LS* is not ^1S and the excited electron pair is coupled to a triplet for the $2s2p$ orbital pair. Those CSF which Weiss called "semi-internal" are defined and grouped in the same way as he does. Since the differences between our coupling scheme and that of Weiss are small, we expect that any conclusions we may draw from the results of our pair calculations should also apply equally well to the pair-correlation approximation of Weiss.

Letting α stand for a particular coupling, $(L_1S_1L_2S_2L_3S_3/LS)$, associated with the orbital pair ij, the wave function for a symmetry-adapted pair (SAP) ij may now be written as

$$\Psi_{ij\alpha}^{\text{SAP}} = C_{\text{HF}}\Phi_{\text{HF}} + \sum_{kl} C_{ij\alpha,kl}\Phi_{ij\alpha,kl}\,,$$

where Φ_{HF} is the Hartree-Fock state function and the summation over kl represents all possible substitutions of the i and j orbitals in the HF configuration by the k and l virtual orbitals. The coefficients C_{HF} and $C_{ij\alpha,kl}$ are obtained from a variational calculation on the energy,

$$E_{ij\alpha}^{\text{SAP}} = \langle \Psi_{ij\alpha}^{\text{SAP}} | \mathcal{H} | \Psi_{ij\alpha}^{\text{SAP}} \rangle = E_{\text{HF}} + \epsilon_{ij\alpha}^{\text{SAP}}$$

where $\mathcal{H}$ represents the nonrelativistic, electronic Hamiltonian, E_{HF} the HF energy, and $\epsilon_{ij\alpha}^{\text{SAP}}$ the pair

TABLE V. *L*-shell correlation energy contributions for F^- (^1S) calculated with various orbital sets in the symmetry-adapted pair (SAP) and space orbital pair (SOP) approximations. All energies are in a.u. with signs reversed.

	Symmetry-adapted pair				Space-orbital pair			
	$2s^2$	$2s2p$	$2p^2$	Sum	$2s^2$	$2s2p$	$2p^2$	Sum
Previous calculations								
Moser and Nesbet[a]	0.0120	0.0958	0.2616	0.3694	0.0118	0.0831	0.1960	0.290 09
Weiss[b]	0.0110	0.0793	0.2315	0.3218				
This calculation[c]								
Set A	0.011 68	0.087 52	0.233 20	0.332 40	0.011 68	0.081 71	0.195 53	0.288 92
Set B	0.012 02	0.090 14	0.237 25	0.339 41	0.012 08	0.084 34	0.199 98	0.296 34
Set C	0.012 53	0.095 41	0.244 95	0.352 89	0.012 53	0.089 61	0.208 18	0.310 32

[a] These values are the results of Bethe-Goldstone calculations. The values listed under SAP and SOP are taken from Refs. 2 and 3, respectively.

[b] Reference 4.

[c] The sizes of orbital sets A, B, and C are ($6s, 5p, 3d, 1f$), ($6s, 6p, 4d, 4f$), and ($6s, 6p, 4d, 4f, 3g, 2h, 1i$), respectively.

energy for the $ij\alpha$ symmetry-adapted pair. In addition, we formed another type of pair wave functions, Ψ_{ij}^{SOP}, which we call the space orbital pair (SOP) wave functions, defined as

$$\Psi_{ij}^{\mathrm{SOP}} = C_{\mathrm{HF}}\Phi_{\mathrm{HF}} + \sum_{\alpha}\sum_{kl} C_{ij\alpha,kl}\Phi_{ij\alpha,kl} ,$$

where the summation over α is carried out over those α associated with an ij orbital pair. The coefficients are obtained as before from

$$E_{ij}^{\mathrm{SOP}} = \langle \Psi_{ij}^{\mathrm{SOP}} | \mathcal{H} | \Psi_{ij}^{\mathrm{SOP}} \rangle = E_{\mathrm{HF}} + \epsilon_{ij}^{\mathrm{SOP}} ,$$

where $\epsilon_{ij}^{\mathrm{SOP}}$ represents the pair energy for an ij space orbital pair. In this SOP approximation the contribution from all the semi-internal CSF was obtained in a single variational calculation. Finally, the full CI wave function is formed using all CSF including semi-internal CSF and the correlation energy obtained will be labeled as ϵ^{CI} or $\epsilon(\mathrm{SD})$.

Three sets of calculations described above were carried out with three orbital sets, A, B, and C. The pair energy results are given in Tables V and VI, where for SAP calculations the total pair energies representing the sum

$$\epsilon_{ij}^{\mathrm{SAP}} = \sum_{\alpha} \epsilon_{ij\alpha}^{\mathrm{SAP}}$$

are given instead of individual pair energies. In Table V all the results for F^- (^1S) are listed and earlier results of Weiss[4] and of Moser and Nesbet[2,3] are also included for comparison. As mentioned before, our SAP calculations for F^- (^1S) should be the same as those of Weiss except that a different orbital basis is used. Table V shows that his results are reasonably close to our results obtained with the set A, which is equivalent to that of Weiss in its orbital composition; the differences may be attributed to differences in the quality of orbitals since our orbitals are expanded in a larger number of STF. We note that the $2s2p$ pair energies differ most and his value is less than our SOP value obtained with the set A. This indicates that his orbital set is poor in describing the $2s2p$ pair correlation energy in spite of the fact that his set was optimized with respect to the $2s2p$ pair. Moser and Nesbet results from the Bethe-Goldstone calculations of the orbital excitation form are listed under SAP since they are most nearly comparable to this approximation. Their values are in general larger than our SAP results of the set B which should be close to the *spdf* limit. The differences here perhaps simply reflect the fact that there are more independent pairs in their calculations than in the SAP calculations and consequently the excess of the pair energy will be greater. The results of Moser and Nesbet using the configurational excitation form are listed under SOP since in this case, even though the pair definitions are similar to the SAP, the actual calculations were carried out essentially in the SOP form. Table V shows that their results are similar to our SOP results, which are in general significantly smaller in magnitude than those of the SAP calculations.

Remarks and comparisons made for F^- (^1S) results apply equally to the results for F, O^-, and O; detailed results are not given here. Only the results obtained with the set C are listed in Table VI together with those of Weiss[4] and Marchetti *et al.*[5] for these systems. As mentioned

TABLE VI. L-shell correlation energy contributions (in a.u. with signs reversed) for F (^2P), O^- (^2P), and O (^3P) calculated with our best orbital set.

System	Calculation[a]	$2s^2$	$2s2p$	$2p^2$	Semi-internal
F (^2P)	Weiss	0.0106	0.0590	0.1465	0.0280
	SAP	0.011 86	0.074 05	0.155 95	0.028 14
	SOP	0.011 86	0.069 96	0.139 56	0.029 24
O^- (^2P)	MKW	0.0107	0.059 81	0.153 34	0.025 78
	SAP	0.012 50	0.081 04	0.170 12	0.025 97
	SOP	0.012 50	0.074 58	0.140 36	0.027 39
O (^3P)	MKW	0.0103	0.041 86	0.074 89	0.048 38
	SAP	0.011 69	0.058 44	0.088 12	0.048 78
	SOP	0.011 69	0.055 53	0.079 97	0.047 69

[a] Weiss results are taken from Ref. 4, and MKW results are from Ref. 5. SAP and SOP results are calculated with the orbital set C (see Table V).

TABLE VII. Convergence patterns of the L-shell correlation energy (in a.u.) with sign reversed in pair-correlation approximations.

		L-shell correlation energy[b] (ϵ_L)			Excess energy[c] [ϵ (EE)]	
System	Orbital[a] set	CI	SAP	SOP	SAP	SOP
F^- (^1S)	Weiss		0.3218			
	A	0.280 05	0.332 40	0.288 92	0.052 35	0.008 87
	B	0.287 64	0.339 41	0.296 34	0.051 77	0.008 70
	C	0.302 09[d]	0.352 89	0.310 32	0.050 80	0.008 23
F (^2P)	Weiss		0.2441			
	A	0.225 48	0.252 96	0.232 97	0.027 48	0.007 49
	B	0.231 30	0.258 64	0.238 89	0.027 34	0.007 59
	C	0.242 80[d]	0.270 01	0.250 62	0.027 21	0.007 82
O^- (^2P)	MKW		0.249 60			
	A	0.227 97	0.274 72	0.239 25	0.046 75	0.011 28
	B	0.233 51	0.280 21	0.245 07	0.046 70	0.011 56
	C	0.242 77[d]	0.289 63	0.254 83	0.046 86	0.012 06
O (^3P)	MKW		0.175 41			
	A	0.173 66	0.195 83	0.183 58	0.022 17	0.009 92
	B	0.177 20	0.199 52	0.187 39	0.022 32	0.010 19
	C	0.184 06[d]	0.207 04	0.195 97	0.022 98	0.011 91

[a] Weiss results are from Ref. 4 and MKW results are from Ref. 5. The size of sets A, B, and C are given in Table V.

[b] See the test for definitions of approximations.

[c] $\epsilon_L^{\mathrm{SAP/SOP}}(\mathrm{EE}) = \epsilon_L^{\mathrm{SAP/SOP}} - \epsilon_L^{\mathrm{CI}}$.

[d] These values are slightly larger than those listed in Table II because of the truncation of orbitals in the full CI calculations.

earlier, our SAP definitions for the $2s2p$ pair are slightly different from those of Weiss and a direct comparison may be difficult. We mention, however, that our values obtained in the space orbital pair calculations with the set A are always larger than their SAP values for this particular pair; thus, their orbital basis sets are in general poorer than our set A. It should be noted that previous results for the semi-internal contributions agree very well with our results indicating relative insensitivity of these contributions to the orbital basis. In general, the pair energies obtained with the set C shown in Tables V and VI are believed to be within 3% or better of their respective limits. This is inferred from the results of the convergence study of Ne (^1S) in I.

In Table VII we compare total L-shell correlation energies, $\epsilon_L^{\mathrm{SAP}}$ and $\epsilon_L^{\mathrm{SOP}}$, obtained respectively by the SAP and SOP approximations with ϵ_L (SD) obtained by the CI method. Also included are excess energies ϵ_L (EE) defined as

$$\epsilon_L^{\mathrm{SAP/SOP}}(\mathrm{EE}) = \epsilon_L^{\mathrm{SAP/SOP}} - \epsilon_L(\mathrm{SD}).$$

It is clear from Table VII that both SAP and SOP excess energies are converging faster than the corresponding CI energies. The SAP excess energies appear to be roughly twice the estimated triple and higher excitation contributions given in Table I of this paper and Table X of I. On the other hand, the SOP excess energies seem to have no relation with these contributions and appear to be converging to the same value for an atom and its negative ion.

The nonrelativistic total energy E in a pair-correlation approximation may be written as

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

where the meanings of terms in the right are the same as before. Then, the electron affinity can be expressed as

$$E_{\mathrm{EA}} = E_{\mathrm{EA}}(\mathrm{HF}) + E_{\mathrm{EA}}(\mathrm{SD}) + E_{\mathrm{EA}}(\mathrm{EE})$$

by taking differences of corresponding terms in the total energies of the associated atoms and ion. In the present calculations we assumed that the correlation energies in the K shell and KL intershell do not change. Thus, the last two terms are calculated here by taking differences of the L-shell correlation energy contributions alone.

Table VIII contains the calculated correlation contributions and total electron affinities obtained by the CI, SAP, and SOP methods; the Hartree-Fock contributions, not listed, are 0.0501 and −0.0199 a.u. for F and O, respectively. Excess energy terms, EA(EE), are in general converging faster than CI terms, EA(SD), as expected. The SOP excess energy terms are very small so that the electron affinity results are essentially identical with the CI results. The SAP excess energy terms, are comparatively large and roughly half of the CI terms. Furthermore, the ratios of the contributions of the SAP excess energy term to the estimated triple and higher excitation terms shown in Table III appear to be about 2; for O this ratio is larger than 2 but the estimated EA(TQ) of O appears to be considerably underestimated

TABLE VIII. Convergence patterns of electron affinities (in a.u.) in pair-correlation approximations.

Atom	Orbital [a] set	Correlation energy contribution [b] EA(SD)	$\mathrm{EA^{SAP}(EE)}$	$\mathrm{EA^{SOP}(EE)}$	Electron affinity [c] CI(SD)	SAP	SOP
F	MN					0.1561	0.1065
	Weiss					0.1278	
	A	0.0546	0.0249	0.0014	0.1047	0.1295	0.1060
	B	0.0563	0.0244	0.0011	0.1064	0.1309	0.1076
	C	0.0593	0.0236	0.0004	0.1094	0.1330	0.1098
O	MN					0.0748	0.0354
	MKW					0.0543	
	A	0.0543	0.0246	0.0014	0.0344	0.0590	0.0358
	B	0.0563	0.0244	0.0014	0.0364	0.0608	0.0378
	C	0.0587	0.0239	0.0002	0.0388	0.0627	0.0390

[a] MN results are from Refs. 2 and 3; Weiss and MKW results are from Refs. 4 and 5, respectively. Values listed are adjusted, if necessary, to include only the L-shell pair-correlation energy contributions. For the size of sets A, B, and C, see Table V.

[b] These are given in terms of the contributions from the CI and excess energy [$\epsilon_L^{\mathrm{SAP}}(\mathrm{EE})$ or $\epsilon_L^{\mathrm{SOP}}(\mathrm{EE})$] differences. Thus, the total contribution in the SAP approximation, for example, will be the sum of EA(SD) and $\mathrm{EA^{SAP}(EE)}$.

[c] The HF contributions to the electron affinity are 0.0501 and −0.0199 a.u. for F and O, respectively.

and the actual ratio might be closer to 2. These two facts, faster convergence of EA(EE) and the constant ratio, explain the apparent success of the SAP method of Weiss with relatively poor orbital sets in predicting accurate electron affinities for O and F. That is to say that the amount of the excess energy contributions in the SAP results is such that it not only accounts for the effects of neglected triple and higher excitation terms, but also compensates for the defects in the pair energy terms. It is clear then that the SAP method would in general overestimate the electron affinity if the calculation would be carried to the limit, as indicated in our results.

The results of Moser and Nesbet are also listed under SAP and SOP in Table VIII, but it should be noted that these values are obtained, respectively, by orbital excitation and configuration excitation Bethe-Goldstone calculations. Furthermore, for the purpose of a direct comparison with our results we list here their values which include only the contributions from the L-shell correlation without the three-particle terms. As mentioned earlier, their configurational excitation calculations are similar to our SOP calculations and as expected, their EA results (listed under SOP) are very close to our SOP and CI(SD) results, which significantly underestimate the electron affinities. On the other hand, their orbital excitation EA results without three-particle terms (listed under SAP) are appreciably larger than our SAP results. This indicates that in general their orbital excitation calculations would always give EA(EE) very much greater than EA(TQ).

IV. SUMMARY AND CONCLUSIONS

From the results and discussion given it appears that we have obtained the wave functions for the first-row negative ions which yield 94–95% of the true correlation energy. It was found, however, that these wave functions were still not quite accurate enough so that our calculated correlation energy contributions to the electron affinity turned out to be only about 83% of the true contributions. Furthermore, the errors in our calculated electron affinities are about 0.1 eV for B and C, and 0.3 eV for N, O, and F; these errors are essentially the same in magnitude as those in the calculated correlation energy for atoms. This implies that the method used in the present work would not give reliable results for electron affinity of larger atoms because the magnitude of the error in calculated correlation energy would inevitably increase.

The detailed analysis of the results in terms of various classes of configurations revealed, however, two important facts concerning correlation contributions to the electron affinity. The first is that the K-shell and KL-intershell contributions should be less than 10^{-2} eV, which are small enough to be neglected. The second is that the contributions from the triple and higher excitation configurations are significantly large, namely about 15% of the total correlation energy contribution. It is clear then that we should get better results by considering the L-shell correlation energy alone because we would be able to use a larger and better orbital basis than used in the present calculations, and further we would be able to include more triple and higher excitation configurations. This approach has an additional advantage in that it could be applied to larger atomic systems, particularly the second-row atoms, with essentially the same amount of computational effort. It is most likely that a similar situation prevails in the second-row atom systems in that the main correlation contributions come from the M shell.

It has been definitely proved at least for O and F systems that the symmetry-adapted pair-correlation method of Weiss does overestimate the electron affinity if the calculation is carried out to the orbital basis limit. However, this fact should not diminish the utility of this method. It was found from the energy convergence study that the variation of the excess energy (due to the neglect of pair-pair interaction) with respect to orbital basis was very small. Further, the magnitude of the excess energy turned out to be approximately proportional to the estimated contribution from the triple and higher excitation configurations, namely, $\mathrm{EA(EE)} \approx 2 \times \mathrm{EA(TQ)}$. It is most likely that a similar convergence pattern also exists in other systems. Therefore, this method should give good estimates of electron affinity provided that an adequate (but not necessarily complete) orbital set is used.

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