

Complete-active-space self-consistent-field and contracted configuration-interaction study of the electron correlation in Ne, F⁻, Ne⁺, and F

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(Received 16 April 1982)

The complete-active-space self-consistent-field (SCF) and externally contracted multireference configuration-interaction (CI) methods are employed for the calculation of the electron correlation contribution to the electron affinity of F and ionization potential of Ne. The calculations are performed in the truncated Gaussian-type orbital (GTO) basis set approximation. The results of the complete-active-space (CAS) SCF approach are lower by about 0.6 eV than the experimental values. The most elaborate contracted CI calculations yield the fluorine atom electron affinity equal to 3.09 eV (expt. 3.400 eV) and the neon atom ionization potential equal to 21.25 eV (expt. 21.63 eV).

I. INTRODUCTION

Considerable progress has been achieved over the past few years in the development of powerful computational strategies for the calculation of accurate wave functions for many-electron systems.^{1,2} The multiconfiguration (MC) self-consistent field (SCF) approach³ has been generalized to what is known as the complete-active-space (CAS) SCF method.⁴⁻⁶ With the appropriate choice of the active orbital space^{4,5} the CAS SCF method is able to account for the most important correlation effects in a given many-electron system.⁶⁻⁸ The remaining correlation contributions can be treated by using the multireference configuration-interaction methods (MC-CI).⁹⁻¹⁴ The problem of the rapid increase of the length of the corresponding CI expansion has recently been given computationally feasible solution in the form referred to as the externally contracted configuration-interaction (CCI) method.¹⁵⁻¹⁷ Currently the MC-CCI scheme based of the CAS SCF eigenvectors determined in the selected active orbital space represents one of the most promising and accurate computational methods for the calculation of energies and properties of many-electron systems.

In most cases the quantity of primary interest is the change in the correlation energy upon physical or chemical processes rather than its absolute value. It is generally believed that computing the corresponding differences should be much easier

than obtaining accurate values of the total correlation energy. Both the CAS SCF and the MC-CCI method appear to be perfectly suited for the calculation of relative values of the correlation energy. Atomic electron affinities and ionization potentials represent the area where the two methods can undergo a severe test. The fluorine atom electron affinity and the ionization potential of Ne are very convenient for this purpose and their calculation has frequently been utilized to verify different methods.¹⁸⁻²⁷ Moreover, highly reliable experimental data are available for both these quantities.²⁸⁻³⁰

In contrast to several semiempirical treatments^{18,19,25} the present calculations are performed with the use of highly sophisticated *ab initio* methods and they are carried out for all systems with the same numerical accuracy. Obviously, the results obtained in this study must suffer from some unavoidable approximations. The accuracy of our results is certainly affected by the use of the truncated Gaussian-type orbital (GTO) expansions for CAS SCF orbitals. Though the error introduced by the contraction of external pairs in the MC-CCI method is rather negligible,^{16,31} the MC-CCI energies may suffer from the erratic treatment of unlinked clusters.^{15,32,33} All these factors limit the accuracy of the calculated electron affinities and ionization potentials and shooting right at the corresponding experimental values would mean a rather unexpected cancellation of different errors.^{20,24,26,27}

Furthermore, we do not aim at either reproducing or predicting the most accurate values of electron affinities and ionization potentials. The main purpose of this study is to investigate how much of the pertinent correlation contribution can be recovered by using the most elaborate computational methods applicable for many-electron systems and relatively standard truncated basis sets. This may give some idea concerning the expected accuracy of molecular calculations.

II. CALCULATIONS

A. Basis sets

All calculations reported in this paper have been performed in the truncated basis set approximation. The optimized (11s 7p) GTO basis sets for F and Ne determined by Huzinaga³⁴ have been augmented with two diffuse *s*-type functions and two sets of diffuse *p*-type Gaussians. Then five sets of *d*-type functions have been added leading to the (13s 9p 5d) GTO basis set which has been contracted to the (10s 9p 5d) contracted GTO (CGTO) set. The complete description of the (13s 9p 5d / 10s 9p 5d) GTO/CGTO basis sets for all systems investigated in this paper has been given elsewhere.³⁵

It follows from the second-order perturbation calculations of Egarter and Egarter²⁶ and Jankowski *et al.*²⁷ that the contribution of higher than *d*-type orbitals to the electron affinity of F and ionization potential of Ne can be quite significant. To study the effect of *f*-type functions the calculations have been repeated with the (13s 9p 5d 1f / 10s 9p 5d 1f) GTO/CGTO basis sets and the *f*-orbital exponent has been varied and optimized with respect to the total energy of each system. Though including the *f*-type GTO results in the lowering of the total energy for each system, it has a diverse effect on the calculated energy differences. The latter have been found almost independent of the *f*-orbital exponent variation.

B. CAS SCF calculations

The basic principles and the strategy of the CAS SCF method have been described in detail elsewhere.⁴⁻⁶ The method is based on the partition of the orbital space into subspaces of inactive, active, and external orbitals. The occupancy of each inactive orbital is kept frozen though its form is varied. The group of active orbitals may have nonzero frac-

tional occupancies, while all external orbitals are assumed to be empty. The full CI is performed in the active orbital space with all "active" electrons distributed among all active orbitals in all possible ways. The orbitals entering the full CI wave function are optimized by using the super-CI approach.^{4,5,36}

It is convenient to introduce some symbolic notation which would define the inactive-active space partition and simultaneously the CAS SCF CI wave function. In what follows we shall use the symbol ($i_1, i_2, \dots / a_1, a_2, \dots$) where i_k denote the inactive orbitals and a_k are the symbols for active orbitals. In the present paper we have tried different partitions of the space of one-electron functions. Obviously, the choice of the number of active orbitals is limited by the size of the full CI problem in the active subspace. Hence, only the most occupied active orbitals should be included in the active subspace. It can be concluded from accurate second-order perturbation calculations^{26,27} for the systems considered in the present paper that the correlation contribution to 1s pairs is negligible for both the electron affinity of the fluorine atom and the ionization potential of Ne. Thus, in all calculations the 1s orbital has been considered as inactive.

The main part of the CAS SCF calculations carried out within this study refers to the following partition scheme: (1s / 2s 2p 3s 3p). We have also performed some calculations with the 2s orbital moved to the inactive subspace and the 3s orbital removed from the active subspace, i.e., the calculations which correspond to the (1s 2s / 2p 3p) CAS SCF wave function with six electrons distributed among four orbitals. Including the 3d orbital in the active space results in a considerable increase of the length of the CAS SCF CI wave function. Hence, we have decided to take into account the corresponding contributions to the correlation energy *a posteriori* within the MC-CCI scheme. The same applies also to the study of the correlation contribution due to the presence of the *f*-type orbital.

The CAS SCF orbitals calculated for the (1s / 2s 2p 3s 3p) CAS SCF wave functions have then been employed in constructing the multireference wave function for the MC-CCI scheme.

C. MC-CCI calculations.

The externally contracted multireference CI method has been described in recent papers by one of the present authors.¹⁵⁻¹⁷ In the MC-CCI approach the space of one-electron functions is parti-

tioned into frozen, inactive, active, and external orbitals. The first group of orbitals (f_1, f_2, \dots) is kept frozen in all configurations. The inactive orbitals (i_k) are doubly occupied in all configurations contributing to the reference space, while the active orbitals (a_k) are allowed to have fractional occupancies in this space. Finally all single and double substitutions of active and inactive orbitals are allowed and the so-called contraction over the external orbital indices is performed.¹⁵⁻¹⁷ This procedure significantly reduces the dimension of the actual CI problem with rather negligible loss in the accuracy of the calculated correlation energies.^{15,32} According to the definition of different orbital subspaces the MC-CCI wave function can be completely defined by the symbol ($f_1, f_2, \dots / i_1, i_2, \dots / a_1, a_2, \dots$) and the specification of reference configurations. It is also worth while to mention that the orbitals which have been considered as active in the CAS SCF approach may become inactive or frozen in the MC-CCI scheme. Moreover, the dimension of the external orbital subspace can be reduced by neglecting some orbitals, or equivalently, by neglecting the corresponding single and double substitutions. In practice, the unwanted external orbitals are neglected in the integral transformation step.

The one-particle functions employed in the present MC-CCI studies have been obtained from ($1s/2s\ 2p\ 3s\ 3p$) CAS SCF calculations. Only a few pilot calculations for Ne and Ne^+ have been performed by using the ($1s\ 2s/2p\ 3p$) CAS SCF eigenvectors. According to the arguments presented in Sec. II B the $1s$ orbital is kept frozen for all systems studied in this paper. In order to reduce the size of the final CI problem the $2s$ orbital has been considered as being inactive within the MC-CCI approach. The active space in all cases comprises $2p$ and $3p$ orbitals and the MC-CCI wave function can be given the symbol ($1s/2s/2p\ 3p$). To complete its definition one needs to specify the set of reference configurations. For all atomic systems investigated in this study the reference configurations comprise the Hartree-Fock- (HF-) type ground state configuration and all configurations obtained from it by single and double replacements within the active space.

In order to reduce the dimension of the contracted pair functions some of the external orbitals have been removed during the transformation of integrals from the CGTO basis set to the set of one-particle CAS SCF functions. The neglected CAS SCF eigenvectors involve primarily the s part of the d -type GTO's and the p part of the f -type GTO. For the ($13s\ 9p\ 5d/10s\ 9p\ 5d$) CGTO basis set we

have removed four s -type functions and two sets of p -type orbitals reducing the final basis set dimension to 57 functions. The dimension of the final set of one-electron functions for the ($13s\ 9p\ 5d\ 1f/10s\ 9p\ 5d\ 1f$) CGTO set has been reduced to 63 functions by neglecting five s -type orbitals and three sets of p -type orbitals. In all cases these are the highest energy CAS SCF eigenvectors.

More details concerning the computational aspects of the MC-CCI approach can be found in recent papers by one of the present authors.¹⁵⁻¹⁷ The computational scheme is based on the earlier general CI approach.⁹ In the first step the CI wave function involving single and double substitutions in the reference configurations and limited to the active orbital space, is generated. The corresponding CI energy is nearly the same as the CAS SCF energy obtained for the same active space, since with the present choice of reference configurations the difference between the two energies is predominantly due to higher than quadrupole excitations. For the same reason the unlinked cluster effects in the reference space CI energy should be negligible.

Finally, of some interest is also the first-order MC-CCI wave function generated for the given reference space and the associated second-order corrected total energy,^{15,17} which is size consistent.^{33,37-39}

III. RESULTS AND DISCUSSION

The calculated total CAS SCF and MC-CCI energies of F, F^- , Ne^+ , and Ne are shown in Table I. In the same table also the restricted Hartree-Fock (RHF) energies and the second-order estimates^{15,17} of the MC-CCI energy are presented. The data of Table I are used mainly for the illustration of the basis set extension effect.

Extending the (spd) basis set (basis A) to the ($spdf$) set (basis B) by addition of a single set of f -type GTO's has obviously a negligible effect on the RHF energies, since only the p -type component of the f -type GTO may contribute to the RHF energy. With the present choice of the active space in the CAS SCF calculations the same should also apply to the CAS SCF energy data. Some change in the ($1s/2s\ 2p\ 3s\ 3p$) CAS SCF energies of $\text{F}(^2P)$ and $\text{Ne}^+(^2P)$, though relatively small, indicates that the $9p$ subset is still not saturated enough from the point of view of the correlation effects.

It has been found that both the RHF and CAS SCF energies calculated with basis B are almost in-

TABLE I. Total energies (in a.u.) of F, F⁻, Ne⁺, and Ne according to different methods.

Method	Basis set ^a	Orbital subspaces ^b	Total energy			
			F(² P)	F ⁻ (¹ S)	Ne ⁺ (² P)	Ne(¹ S)
RHF SCF	<i>A</i>	(/1s 2s 2p)	-99.408 01	-99.457 89	-127.815 97	-128.544 98
	<i>B</i>	(/1s 2s 2p)	-99.408 03	-99.457 90	-127.815 99	-128.545 00
CAS SCF	<i>A</i>	(1s 2s /2p 3p)	-99.469 95	-99.565 67	-127.871 26	-128.635 01
	<i>A</i>	(1s /2s 2p 3s 3p)	-99.507 83	-99.610 22	-127.907 00	-128.677 89
	<i>B</i>	(1s /2s 2p 3s 3p)	-99.508 53	-99.610 23	-127.907 74	-128.677 89
Second-order MC-CCI	<i>A</i>	(1s /2s /2p 3p)	-99.627 44	-99.747 14	-128.014 39	-128.812 22
	<i>B</i>	(1s /2s /2p 3p)	-99.642 21	-99.766 21	-128.042 98	-128.833 03
MC-CCI	<i>A</i>	(1s /2s /2p 3p)	-99.603 52	-99.718 21	-128.002 16	-128.786 25
	<i>B</i>	(1s /2s /2p 3p)	-99.623 50	-99.737 22	-128.026 63	-128.807 44

^a*A* refers to the (13s 9p 5d /10s 9p 5d) CGTO basis set while *B* denotes the optimized (13s 9p 5d 1f /10s 9p 5d 1f) CGTO bases. For F and F⁻ the *f*-orbital exponent is equal to 1.5. For Ne⁺ and Ne its value equals 3.0.

^bPartition into inactive-active orbital subspaces for the CAS SCF method and frozen-inactive-active subspaces for the MC-CCI method. For the RHF SCF method all occupied orbitals are considered as active. See text for details.

dependent of the value of the *f*-orbital exponent (α_f). The MC-CCI energies are a little more sensitive to its variation and the corresponding data are shown in Table II. Surprisingly enough the α_f values which minimize the total MC-CCI energy are nearly the same for the given neutral system and its ion. Since the energy differences for the atom-ion pairs are hardly affected by the α_f value, we have not attempted more sophisticated optimization of the *f*-orbital exponents for each system. The values $\alpha_f=1.5$ and $\alpha_f=3.0$ treated as the optimal ones for the F-F⁻ and Ne⁺-Ne pairs, respectively, are very close to those corresponding to the MC-CCI energy minima for these systems. All results reported in this paper for what is called the optimized basis *B* refer to those values of the *f*-orbital exponent.

The quantity of primary interest is the difference between the correlation energy for the neutral and

the ionic system. The majority of present results refers to the *L*-shell correlation effects and the correlation energy contributions recovered in different calculations are given in Table III. They are compared with the *L*-shell correlation energy data obtained by other authors. Though the present *L*-shell correlation energies are considerably smaller than the values calculated by other authors, the correlation contribution to the electron affinity of F, EA(F) and the ionization potential of Ne IP(Ne) is fairly close to the results of accurate calculations reported so far. Of the reference results compiled in Table III the correlation energy data obtained for the F-F⁻ pair by Sasaki and Yoshimine²³ are presumably the most accurate ones. They have been obtained by using the CI method with single, double, triple, and quadrupole excitations, and a very large basis set of Slater-type orbitals (STO's) (10s 9p 8d 8f 6g 4h 2i).⁴⁰ Including the higher angu-

TABLE II. Total (1s/2s/2p 3p) MC-CCI energies of F, F⁻, Ne⁺, and Ne and their dependence of the *f*-orbital exponent (α_f) for the (13s 9p 5d 1f /10s 9p 5d 1f) CGTO basis set.

α_f	Total energy (in a.u.)			
	F(² P)	F ⁻ (¹ S)	Ne ⁺ (² P)	Ne(¹ S)
0.5	-99.607 42	-99.721 79		
1.0	-99.617 40	-99.731 60	-128.012 75	-128.794 53
1.5	-99.623 50	-99.737 03	-128.019 23	-128.802 54
2.0	-99.623 42	-99.736 53	-128.023 63	-128.806 51
2.5	-99.623 17	-99.736 06	-128.025 94	-128.807 01
3.0	-99.621 89	-99.734 66	-128.026 63	-128.807 44
3.5			-128.026 18	-128.806 76
4.0			-128.025 19	-128.805 61

TABLE III. *L*-shell correlation energies of F, F⁻, Ne⁺, and Ne and *L*-shell correlation contributions to the electron affinity (EA) of F and ionization potential (IP) of Ne. All energies in a.u.

		Correlation energy		EA(F)	Correlation energy		IP(Ne)
		F(² P)	F ⁻ (¹ S)		Ne ⁺ (² P)	Ne(¹ S)	
This work ^a							
(1s/2s 2p 3s 3p) CAS SCF	basis A	-0.0998	-0.1523	0.0525	-0.0910	-0.1329	0.0419
	basis B	-0.1005	-0.1523	0.0518	-0.0918	-0.1329	0.0411
(1s/2s/2p 3p) second-order MC-CCI							
	basis A	-0.2194	-0.2893	0.0699	-0.1984	-0.2672	0.0688
	basis B	-0.2342	-0.3083	0.0741	-0.2270	-0.2880	0.0610
(1s/2s/2p 3p) MC-CCI							
	basis A	-0.1955	-0.2603	0.0648	-0.1862	-0.2413	0.0550
	basis B	-0.2155	-0.2793	0.0638	-0.2106	-0.2624	0.0518
Reference results							
Sasaki and Yoshimine ^b		-0.2458	-0.3114	0.0656		0.3052	
Weiss ^c		-0.2441	-0.3218	0.0777	-0.2369	-0.2987	0.0618
Moser and Nesbet ^d		-0.2345	-0.2909	0.0564	-0.2332	-0.2851	0.0519
Jankowski <i>et al.</i> ^e			-0.3357	(0.0820) ^f		-0.3200	

^aSee footnotes a and b to Table I.

^bCI results including excitations through quadruples (Ref. 23).

^cSymmetry-adapted atomic Bethe-Goldstone calculations (Ref. 21).

^dAtomic Bethe-Goldstone calculations (Ref. 22).

^eSecond-order correlation energies (Ref. 27).

^fEstimated by using the data for F from Ref. 26.

lar momentum functions is obviously important from the point of view of the total *L*-shell correlation energy. However, in spite of using a much smaller GTO basis the *L*-shell correlation energy difference calculated in the present paper in the MC-CCI approximation is very close to the result reported by Sasaki and Yoshimine.

The results of atomic Bethe-Goldstone calculations of Weiss²¹ and Moser and Nesbet²² are also considered to be of high accuracy, though the computed correlation energies are nonvariational.⁴¹ They also depend on the assumed form of the pair functions.²¹ Nonetheless, the atomic Bethe-Goldstone approach⁴¹ appears to be quite successful in predicting rather small correlation energy differences. The empirical estimates of the correlation contribution to the EA(F) and IP(Ne) values based on the experimental data²⁸⁻³⁰ and the HF calculations¹⁸ are equal to 0.075 a.u. and 0.066 a.u., respectively. Hence, the results obtained by Weiss²¹ within the symmetry-adapted Bethe-Goldstone approach can be considered as highly successful. However, they seem to indicate a rather nonsystematic character of the method, for they overestimate the correlation contribution to EA(F) and simultaneously underestimate the corresponding result for IP(Ne). Similar observations can be made with regard to the calculations by Moser and Nesbet²² based on spin-orbital pairs.⁴¹ The missing part

of the correlation contribution to EA(F) is much larger than than for IP(Ne). On the contrary, the present MC-CCI values are systematically lower than the empirical estimates by about 0.01 a.u. in both cases. Also the CAS SCF results exhibit a very systematic behavior, though in this case the missing part of correlation effects is as much as about 0.02 a.u.

It is interesting to follow the changes in the correlation contribution to EA and IP due to differences in the amount of correlation effects accounted for by a given method. For the CAS SCF approach with the active space involving only 2*p* and 3*p* orbitals the correlation contributions to EA (F) and IP (Ne) amount to 0.0458 and 0.0347 a.u., respectively, and they are by about 0.03 a.u. lower than the corresponding empirical estimates. On increasing the active space to (2*s* 2*p* 3*s* 3*p*) the error in the correlation contribution is uniformly reduced by about 0.01 a.u. Additionally, the MC-CCI approach based on the (1*s*/2*s* 2*p* 3*s* 3*p*) CAS SCF eigenvectors corrects the calculated correlation contributions by ca. 0.01 a.u. The difference between the basis A and basis B results is very small. However, including a single set of *f*-type GTO's worsens the final results a little. This is presumably due to the effects of the *p* part of the *f*-type GTO set on the correlation energy of F and Ne⁺. Increasing the basis set size and including the higher angular momentum func-

tions should in fact lower the energy of F^- and Ne a little more than those of F and Ne^+ . The effect of higher than d -type orbitals on the second-order correlation contribution to $IP(Ne)$ can be estimated from the results of Egarter and Egarter²⁶ and amounts to about 0.009 a.u. Hence, quite a part of the missing correlation contribution to $EA(F)$ and $IP(Ne)$ calculated within the MC-CCI scheme is due to the incompleteness of the GTO-CGTO basis sets employed in the present study.

Another source of the small inaccuracy of our results can be related to the limitations of the MC-CCI approach. One of the major deficiencies of this method is that it does not account appropriate-

ly for the unlinked cluster effects. Though they should be rather small for large enough active spaces, their contribution can be still important when computing the correlation energy differences. Some part of the unlinked cluster contribution is neglected in the second-order MC-CCI approach and this could be the reason that our second-order estimates of the MC-CCI energy give quite remarkable results for the correlation contribution to both $EA(F)$ and $IP(Ne)$. However, the second-order MC-CCI approach should be considered with some care, for it may exhibit a rather nonsystematic behavior. Its performance is based on subtle cancellation effects between the higher-order linked and

TABLE IV. Comparison of different results for the electron affinity of F and ionization potential of Ne (in eV).^a

		EA(F)	IP(Ne)
This work ^b			
(1s 2s / 2p 3p) CAS SCF	basis A	2.60	20.78
(1s / 2s 2p 3s 3p) CAS SCF	basis A	2.79	20.98
	basis B	2.77	20.96
(1s / 2s / 2p 3p) second-order MC-CCI	basis A	3.26	21.71
	basis B	3.37	21.50
(1s / 2s / 2p 3p) MC-CCI	basis A	3.12	21.34
	basis B	3.09	21.25
Reference <i>ab initio</i> results			
Weiss ^c		3.47	21.52
Moser and Nesbet ^d		3.37	
Moser and Nesbet ^e		2.90	21.25
Sasaki and Yoshimine ^f		3.12	
Staemmler and Jungen ^g		3.62, 3.70	21.52, 21.60
Egarter and Egarter ^h			21.59
Jankowski <i>et al.</i> ⁱ		3.53	
Semiempirical estimates ^j			
Clementi and McLean ^k		3.37	
Ösüz and Sinanoglu ^l		3.23	
Schaefer <i>et al.</i> ^m		3.45	
Sasaki and Yoshimine ^f		3.40, 3.48	
Experimental		3.400 ⁿ	21.63 ^o

^a1 a.u. = 27.21 eV.

^bBased on the data of Table I.

^cReference 21.

^dReference 42.

^eReference 22.

^fReference 23.

^gReference 24.

^hCalculated from the second-order correlation energy data (Ref. 26).

ⁱCalculated from the second-order energy data (Ref. 27).

^jResults obtained by combining different, *ab initio* results and empirical estimates of the correlation contribution.

^kReference 18.

^lReference 19.

^mReference 20.

ⁿReferences 28 and 29.

^oReference 30.

unlinked contributions.^{32,33,38,39}

Our final results for EA(F) and IP(Ne) obtained according to different approximations are shown in Table IV. They are compared with *ab initio* calculations of other authors, with semiempirical estimates based partly on the calculated values and with the experimental data. The present results follow from highly systematic *ab initio* calculations. The methods employed in this study have a very wide range of applicability in atomic and molecular calculations and the results obtained in this paper set up to some extent the corresponding accuracy limits. With truncated basis sets of moderate size which are used in molecular *ab initio* studies one can hardly expect to have a better accuracy for the calculated energy differences than that for the present values of the electron affinity and ionization potential. The performance of the CAS SCF method is fairly good provided the active orbital space is large enough to account for the most important correlation effects. According to the present results half of the missing portion of the correlation effects is then accounted for by the MC-CCI method based on the CAS SCF eigenvectors. The final results, however, are still by about 0.3 eV lower than the corresponding experimental data. This error is presumably the right estimate of the accuracy which can be achieved in similar molecular calculations.

It follows from the data of Table IV that several methods which appear to be less sophisticated than those employed in the present investigations have yielded much better results for both EA(F) and IP(Ne). However, in most cases these methods do not exhibit the same accuracy with respect to the two electronic processes. Nonetheless, the methods which are primarily based on the ordinary second-order correlation energy data are quite successful. This is presumably due to some interplay between the higher-order linked and unlinked contributions

to the correlation energy whose mutual cancelation can be to some extent expected. Hence, correcting the MC-CCI correlation energies for the erratic treatment of unlinked clusters may lead to some improvement of the final results. However, this improvement is of the order of magnitude of the basis set truncations effects and in principle both these factor should be carefully considered. The higher-order excitations that are not accounted for within the MC-CCI approach based on the CAS SCF solution seem to be of little importance.

Another factor which makes some contribution to the difference between the present results and the experimental data is the limitation of the active orbital subspace to *s*- and *p*-type shells. This excludes certain classes of excitations which may significantly contribute to the missing part of the correlation energy differences.⁴³ However, increasing the dimension of the active space makes the corresponding calculations rather difficult, if not impossible, at the molecular level.

Finally, let us mention that much higher accuracy can be expected for atomic and molecular properties which are expressible in terms of the energy derivatives.⁴⁴ The correlation contribution involves then differences of the correlation energy differences. It follows from our recent studies of molecular polarizabilities^{7,8} that the electron correlation effects recovered within the CAS SCF scheme can be sufficient for calculating highly accurate property values. Since in most cases the main attention is paid to the accurate prediction of electric and magnetic properties of many-electron systems, the inaccuracy problems encountered in the present study should be less important. However, predicting the energies of electronic processes in many-electron systems with uniformly better accuracy than that achieved in the present paper represents a rather difficult task.

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¹The basic formal concepts underlying the methods considered in the present paper are well covered by the articles published in, *The Unitary Group for the Evaluation of Electronic Energy Matrix Elements*, Vol. 22 of *Lecture Notes in Chemistry*, edited by J. Hinze (Springer, Berlin, 1981).

²The state of the art of computational methods is well represented by the papers included in the *Proceedings*

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