

A parallel vectorized implementation of triple excitations in CCSD(T): application to the binding energies of the AlH₃, AlH₂F, AlHF₂ and AlF₃ dimers

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Received 29 December 1990; in final form 15 January 1991

An efficient method for evaluating various non-iterative estimates of connected triple excitations in coupled-cluster theory is outlined and related to a similar expression occurring in Møller-Plesset perturbation theory. The method is highly vectorized and capable of utilizing multiple processors on a shared-memory machine, leading to computational rates in excess of one billion floating-point operations per second on four processors of a CRAY Y-MP. Using the new procedure, the binding energies of the D_{2h} diborane-type dimers of AlH₃, AlH₂F, AlHF₂ and AlF₃ have been determined to be 32, 40, 20 and 47 kcal/mol, respectively. For Al₂F₆, the correlation procedure includes 232 molecular orbitals and over 1.5×10^6 single and double coupled-cluster amplitudes, effectively accounting for over 2×10^9 connected triple excitations.

1. Introduction

The electron-correlation energy was defined by Löwdin [1] as the difference between the exact non-relativistic energy and the Hartree-Fock (HF) self-consistent-field (SCF) energy. Although the correlation energy is a small percentage of the total energy, it can profoundly affect calculated molecular properties. Hence, if quantum chemistry is to be capable of evaluating properties to within "chemical accuracy", an increased effort must be given to the development of efficient methods and algorithms that account for the correlation energy. One such procedure, which looks increasingly more promising, and which will be considered here, is a coupled-cluster (CC) expansion of the wavefunction [2-4]. The

coupled-cluster method is founded upon an exponential ansatz,

$$|\Psi\rangle = \exp(T)|\Psi_0\rangle, \quad (1)$$

where $|\Psi\rangle$ is the exact wavefunction, $|\Psi_0\rangle$ is a reference wavefunction and T is an excitation operator expressed as

$$T = T_1 + T_2 + T_3 + T_4 + \dots \quad (2)$$

In eq. (2), T_1 and T_2 are, for example, cluster operators generating singly- and doubly-excited configurations Ψ_i^a and Ψ_{ij}^{ab} multiplied by cluster amplitudes t_i^a and t_{ij}^{ab} .

To date, the majority of coupled-cluster wavefunctions have been based on a closed-shell HF determinant and the excitation operator T has been truncated at the single and double excitation level. While the resulting single and double excitation coupled-cluster wavefunction (CCSD) contains essentially the same number of unknowns as a single and double excitation configuration-interaction wave-

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function (CISD), its determination is considerably more complicated. Despite the additional complexity, a number of very efficient programs have been developed [5,6] to determine the CCSD wavefunction at little extra cost than that required for a CISD treatment. More importantly, the CCSD wavefunction, in contrast to the CISD wavefunction, has the very attractive property of being exactly size-extensive [2]; a property which becomes increasingly important as the number of electrons to be correlated increases.

Recently, considerable attention has been given to the role of triple and higher excitations in the coupled-cluster wavefunction, as inclusion of these higher excitations can substantially increase the range of applicability of a single-reference-based method. However, full account of triple excitations in a single, double and triple excitation CC treatment (CCSDT) is computationally very expensive [7,8], scaling as n^8 , where n is nominally the number of molecular orbitals in the correlation procedure (in comparison, the CCSD method scales as n^6). As a result of this significant increase in computational cost, a number of alternative procedures which partially account for triple excitations have been explored [9]. Of the variety of schemes proposed, the most computationally practical appear to be those based on including the effects of triple excitations using perturbation theory. In this case, a non-iterative evaluation of the triples energy is performed after the CCSD wavefunction has been determined using the converged CCSD amplitudes. Although there are a variety of perturbation schemes available, a recent comparative study [10] indicated that the CCSD(T) method of Raghavachari et al. [11] consistently gives the best agreement with the energy obtained from a full CCSDT treatment. Furthermore, this method has also been shown to perform very well on a variety of "difficult" problems [12–14].

In this paper, we explore the computational requirements for evaluating the triples contribution to the CCSD(T) energy, outline an efficiently vectorized and parallelized algorithm, and provide sample timings obtained on a CRAY Y-MP computer. Although the methodology is developed specifically for the triples contribution to the CCSD(T) energy, the applicability of the algorithm to fourth-order Møller-Plesset perturbation theory (MP4) is also consid-

ered. To illustrate the viability of performing very large CCSD(T) calculations, we have applied the new procedure to the evaluation of the binding energies of the D_{2h} diborane-type dimers of AlH_3 , AlH_2F , AlHF_2 and AlF_3 . The usefulness of this approach lies in the fact that we are able to apply a very accurate size-extensive electron-correlation treatment even for the largest system considered here, where we have correlated 48 electrons.

2. Theory

Indices i, j, k and l denote occupied orbitals and a, b, c and d denote unoccupied orbitals. Assuming a closed-shell reference determinant and canonical orbitals, we can write $E_{(T)}$ as

$$E_{(T)} = \frac{1}{3} \sum_{ijk}^{\text{occ}} \sum_{abc}^{\text{vir}} (4W_{ijk}^{abc} + W_{ijk}^{bca} + W_{ijk}^{cab}) \\ \times (V_{ijk}^{abc} - V_{ijk}^{cba}) / D_{ijk}^{abc}, \quad (3)$$

where W_{ijk}^{abc} , V_{ijk}^{abc} and D_{ijk}^{abc} are given by

$$W_{ijk}^{abc} = P_{ijk}^{abc} \left(\sum_d^{\text{vir}} (bd|ai)t_{kj}^{cd} - \sum_l^{\text{occ}} (ck|jl)t_l^{ab} \right), \quad (4)$$

$$V_{ijk}^{abc} = W_{ijk}^{abc} + (bj|ck)t_i^a + (ai|ck)t_i^b \\ + (ai|bj)t_k^c, \quad (5)$$

$$D_{ijk}^{abc} = f_{ii} + f_{jj} + f_{kk} - f_{aa} - f_{bb} - f_{cc}. \quad (6)$$

In eqs. (4)–(6), $(ab|cd)$ are the two-electron integrals in charge-density notation, t_i^a and t_{ij}^{ab} are the CCSD amplitudes, f_{ii} , etc. are the eigenvalues of the closed-shell Fock operator and P_{ijk}^{abc} is a permutation operator defined by

$$P_{ijk}^{abc}(ijk) = (ijk)^{abc} + (ikj)^{abc} + (kji)^{abc} \\ + (kji)^{cba} + (jki)^{bca} + (jik)^{bac}. \quad (7)$$

We note that the expression for $E_{(T)}$, in a slightly different form, has been given previously for a closed-shell spin-adapted reference by Lee et al. [15]. It was first derived in a spin-orbital formulation by Raghavachari et al. [11].

Given the formation of the intermediates \mathbf{W} , \mathbf{V} and \mathbf{D} , the evaluation of $E_{(T)}$ is a process of order $n_o^3 n_v^3$, where n_o and n_v are the numbers of occupied and virtual orbitals, respectively. However, since the

formation of \mathbf{W} requires two contractions of order n_0 and n_v , the ultimate computational cost of $E_{(T)}$ is of order $n_0^4 n_v^3 + n_0^3 n_v^4$ or nominally n^7 . In designing an algorithm to evaluate $E_{(T)}$ it is convenient to compute and store in memory either all $W(abc)$ for a given (ijk) index, denoted $W^{ijk}(abc)$, or all $W(ijk)$ for a given (abc) index, i.e. $W^{abc}(ijk)$. The former of these two options exhibits considerably better vectorization in the formation of the intermediates, although it requires significantly more memory. As it is becoming evident that the memory available on even small workstations is increasing at a rapid rate, we have chosen to compute $W^{ijk}(abc)$.

Considering only the \mathbf{W} intermediate and expanding the first three terms in the permutation operator, we can write the contributions to $W^{ijk}(abc)$ as

$$W^{ijk}(abc) \leftarrow \sum_d^{\text{vir}} (bd|ai)t_{kj}^{cd} - \sum_l^{\text{occ}} (ck|jl)t_{li}^{ba}, \quad (8)$$

$$W^{ijk}(abc) \leftarrow \sum_d^{\text{vir}} (cd|ai)t_{jk}^{bd} - \sum_l^{\text{occ}} (bj|kl)t_{hi}^{ca}, \quad (9)$$

$$W^{ijk}(abc) \leftarrow \sum_d^{\text{vir}} (ad|ck)t_{ji}^{bd} - \sum_l^{\text{occ}} (bj|il)t_{ik}^{ac}. \quad (10)$$

The two contributions appearing in eq. (8) can be conveniently formulated as a pair of matrix multiplications,

$$\sum_d^{\text{vir}} (bd|ai)t_{kj}^{cd} \equiv \sum_d^{\text{vir}} A1^i(ba, d)t^{jk}(d, c), \quad (11)$$

$$\sum_l^{\text{occ}} (ck|jl)t_{li}^{ba} \equiv \sum_l^{\text{occ}} A2^{kj}(c, l)t^i(l, ba), \quad (12)$$

which, on a CRAY Y-MP, are best vectorized over the compound virtual index ba . The computation of the two terms in eqs. (9) or (10) is analogous to those in eq. (8); however, the intermediate \mathbf{W} should first be sorted such that the compound vector index is now ca or ac , respectively. Both sorts, although at the n^6 level, can be vectorized over n_v^2 by using an index array of the same length, which is defined outside the evaluation of $E_{(T)}$. Fully expanding the permutation operator to include all six terms will result in six pairs of matrix multiplications and six corresponding sorts. Given the formation of \mathbf{W} , the contributions necessary to form intermediate \mathbf{V} (eq. (5)) can be added trivially.

For optimal performance, with no input/output operations, the t_1 and t_2 amplitudes, the $(vv|vo)$, $(vo|vo)$ and $(vo|oo)$ integrals, and two arrays of length n_v^3 (for \mathbf{W}) are required to be held in main memory. The largest memory requirement obviously occurs for the $(vv|vo)$ integrals which increase in size very quickly. To overcome this limitation, we have designed various "out-of-core" options which require the $(vv|vo)$ integrals to be presorted to a random access device so that for a given occupied index, i , the complete n_v^3 $(vv|vi)$ integrals can be read. Algorithms can be derived which require between two and five arrays of length n_v^3 . Without symmetry reductions, this transforms into a minimum memory requirement of 16 megawords for a calculation containing 200 virtual orbitals. We note, however, that such an "out-of-core" option will naively require on the order of n_0^3 reads of the integrals of length n_v^3 . As will now be discussed, this can be reduced by limiting the range of the occupied indices in eq. (3).

After the intermediates \mathbf{W} and \mathbf{V} have been obtained, the triples energy can be evaluated. In this step, considerable savings can be achieved by limiting the summations so that $i \geq j \geq k$ and $a \geq b \geq c$. The former will significantly reduce the number of \mathbf{W} and \mathbf{V} intermediates which need to be computed, and also the input/output requirements for the "out-of-core" option. Using these restrictions, eq. (3) can be arranged to yield

$$E_{(T)} = \sum_{i \geq j \geq k}^{\text{occ}} \sum_{a \geq b \geq c}^{\text{vir}} [(Y_{ijk}^{abc} - 2Z_{ijk}^{abc}) \\ \times (W_{ijk}^{abc} + W_{ijk}^{bca} + W_{ijk}^{cab}) + (Z_{ijk}^{abc} - 2Y_{ijk}^{abc}) \\ \times (W_{ijk}^{acb} + W_{ijk}^{bac} + W_{ijk}^{cba}) + 3X_{ijk}^{abc}] \\ \times (2 - \delta_{jk}) / D_{ijk}^{abc}, \quad (13)$$

where

$$X_{ijk}^{abc} = (W_{ijk}^{abc} \tilde{V}_{ijk}^{abc} + W_{ijk}^{acb} \tilde{V}_{ijk}^{acb} \\ + W_{ijk}^{bac} \tilde{V}_{ijk}^{bac} + W_{ijk}^{bca} \tilde{V}_{ijk}^{bca} \\ + W_{ijk}^{cab} \tilde{V}_{ijk}^{cab} + W_{ijk}^{cba} \tilde{V}_{ijk}^{cba}), \quad (14)$$

$$Y_{ijk}^{abc} = \tilde{V}_{ijk}^{abc} + \tilde{V}_{ijk}^{bca} + \tilde{V}_{ijk}^{cab}, \quad (15)$$

$$Z_{ijk}^{abc} = \tilde{V}_{ijk}^{acb} + \tilde{V}_{ijk}^{bac} + \tilde{V}_{ijk}^{cba}, \quad (16)$$

$$\tilde{V}_{ijk}^{acb} = V_{ijk}^{acb} / (1 + \delta_{abc}), \quad (17)$$

$$\delta_{ijk} = \delta_{ij} + \delta_{jk}. \quad (18)$$

The above algorithm for the computation of $E_{(T)}$ has been fully implemented, using point-group symmetry of D_{2h} and subgroups. Adapting the procedure to use multiple processors on a shared-memory computer can be easily achieved by using a multitasked matrix-multiply routine and parallelizing the sorts and final energy summation over the n_v orbitals. On the CRAY Y-MP, we have used the library BLAS 3 matrix-multiply routine and have passed the relevant triples energy routines through the FPP and FMP FORTRAN preprocessors.

As noted in section 1 and also elsewhere [16], the triples contribution to the CCSD(T) energy is closely related to the triples contribution to fourth-order perturbation theory. However, it also contains an additional term which arises in fifth-order of perturbation theory [17,18]. Evaluation of only the fourth-order contribution to the triples energy, which has been termed CCSD+T [19], can be achieved by neglecting any contribution from the t_1 amplitudes, or in essence setting \mathbf{V} equal to \mathbf{W} in eq. (5). With this simplification and the use of "t₂ amplitudes" obtained from perturbation theory, the above algorithm may be directly used to evaluate the triples contribution to the MP4 energy. In this respect, it is of interest to note that our treatment of triple excitations is similar to that reported by Dupuis et al. [20], but they choose to compute $W^{abc}(ijk)$ rather than $W^{ijk}(abc)$. More recently, Baker et al. [21] have investigated various strategies for computing the triples component of the MP4 energy on vector and parallel processors. Their formulation and implementation are substantially different from that given here, but although no chemical application of the method has yet been reported, it appears likely that the computational cost should be similar to ours.

3. Binding energies of the AlH_3 , AlH_2F , AlHF_2 and AlF_3 dimers

From a theoretical perspective, the study of electron-deficient bonding in aluminum compounds has, until recently, received very little attention; in part, this can be attributed to the fact that saturated aluminum compounds tend to form larger oligomers.

The major exceptions are the experimental structural determination of the hexamethyl [22] and hexahalogen [23] analogs of dialane (Al_2H_6). The prototype electron-deficient aluminum compound dialane has eluded detection to date. This is in sharp contrast to the study of electron-deficient boron clusters, where diborane (B_2H_6) has received considerable theoretical attention [24] and is very well characterized experimentally [25]. The recent synthesis of digallane (Ga_2H_6) [26] extends our experimental knowledge in this valence isoelectronic sequence. In light of these recent developments in gallium chemistry, there might be some concern as to the inherent stability of dialane. This question was indirectly addressed by Liang et al. [27], who recently undertook a theoretical study of the structural and vibrational spectrum of dialane. The energetics of dialane have since been considered directly by Lamertsma and Leszczyński [28] who theoretically evaluated the dimerization energy of AlH_3 , using a basis set of double-zeta-plus-polarization quality and fourth-order Møller-Plesset perturbation theory. In this study, we use our newly developed CCSD(T) implementation and large one-particle basis sets to extend the work of Lamertsma and Leszczyński on dialane and also to study the fluorinated derivatives. For the monomers containing both H and F, we limit our study of the dimers to the D_{2h} isomer only. For $(\text{AlF}_3)_2$, the computed binding energy can be compared with the experimental value obtained from mass spectroscopic studies [23], and the structure compared with one which has been proposed [23] based on parallels with the experimentally characterized chlorinated compounds, AlCl_3 and $(\text{AlCl}_3)_2$.

Two different one-particle basis sets have been employed in this study. The first is a segmented basis of triple-zeta-plus-polarization (TZP) quality, while the second is a more extensive basis contracted using the atomic-natural-orbital (ANO) method [29]. The TZP basis set for aluminum is the McLean and Chandler [6s4p] contracted basis [30], while for hydrogen and fluorine, respectively, the [3s] and [5s3p] contracted sets of Dunning [31] have been used. A single p polarization function ($\alpha = 1.0$) was added to the hydrogen basis, while the aluminum and fluorine basis sets were augmented with a two-term d-orbital which had an effective Slater exponent of 1.6 and 2.2, respectively. The ANO basis for Al is

based on the (18s13p) primitive set of Partridge [32] augmented with a (6d4f) even-tempered polarization set. The exponents for the polarization set are given by $\alpha=2.5\alpha_0$; $n=0, k$, with $\alpha_0(d)=0.0315$ and $\alpha_0(f)=0.0944$. The resulting (18s13p6d4f) set was contracted to [5s4p2d1f]. For fluorine, the (13s8p) primitive set of van Duijneveldt [33] was used, augmented by a (6d4f) polarization set ($\alpha_0(d)=0.16$, $\alpha_0(f)=0.49$) and contracted to [4s3p2d1f]. The hydrogen basis is a (8s6p4d)/[4s2p1d] set developed by Almlöf and Taylor [29] for the ground state of H₂. For the ANO basis set, only the spherical harmonic components of the functions were used.

The SCF optimizations and vibrational frequency calculations have been performed using GRADSCF^{#1}. The coupled-cluster energies have been evaluated using the TITAN^{#2} program package interfaced with MOLECULE-SWEDELEN^{#3} and suitably modified to utilize multiple processors. All correlated calculations were performed at Cray Research, Inc. on a CRAY Y-MP/8128, while some of the SCF structure optimizations were carried out at NASA Ames.

4. Results and discussion

The structures of the monomers and dimers have been fully optimized at the SCF level of theory with the TZP basis set. Each of the monomers is planar with either D_{3h} or C_{2v} symmetry, while the dimers adopt a D_{2h} bridged conformation similar to that of diborane (see figs. 1 and 2, for example). To verify that each of the computed stationary points was a minimum on the potential energy surface, a harmonic vibrational analysis has been performed using analytic energy second derivatives. These optimized

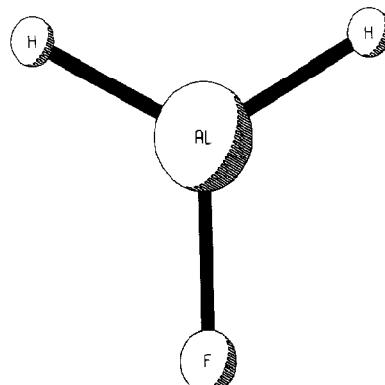


Fig. 1. The planar C_{2v} AlH₂F monomer unit.

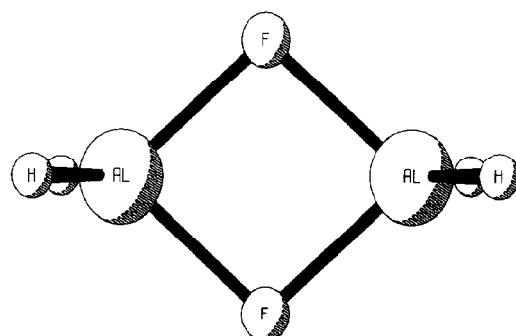


Fig. 2. The D_{2h} dimer (AlH₂F)₂. The Al and H atoms all lie in one reflection plane while the Al and F atoms lie in another reflection plane. The Al atoms lie along the principal rotation axis.

structures, given in table 1, have been used in all calculations. For dialane the structures are found to be in good agreement with the recent theoretical studies of Liang et al. [27] and Lammertsma and Leszczyński [28]. For (AlF₃)₂, the terminal Al-F bond distance is in good agreement with the proposed value of 1.63 Å [23]; however, the proposed Al-Al bond distance (2.54 Å) is considerably shorter than the calculated value. This latter discrepancy probably arises from the assumption that the bridge \angle AlFA is 90°, which although true for (AlCl₃)₂ is unlikely to be the case here due to the smaller Al-F distance.

The binding energies for the various dimers are presented in table 2. In addition, we also report the zero-point energy vibrational corrections (ZPE) to the binding energies and the values of the \mathcal{T}_1 diagnostic [34]. The \mathcal{T}_1 diagnostic has been shown to be a good indicator of the applicability of a single-ref-

^{#1} GRADSCF, an ab initio gradient program system designed and written by A. Komornicki at Polyatomics Research Institute.

^{#2} TITAN is a set of electronic structure programs, written by T.J. Lee, A.P. Rendell and J.E. Rice.

^{#3} MOLECULE-SWEDELEN is an electronic structure program system written by J. Almlöf, C.W. Bauschlicher Jr., M.R.A. Blomberg, D.P. Chong, A. Heiberg, S.R. Langhoff, P.-Å. Malmqvist, A.P. Rendell, B.O. Roos, P.E.M. Siegbahn and P.R. Taylor.

Table 1
SCF optimized structures^{a)} obtained with the TZP basis

Monomer	Symmetry	<i>R</i> (Al-H)	<i>R</i> (Al-F)	\angle (F-Al-H)
AlH ₃	D _{3h}	1.573	—	—
AlFH ₂	C _{2v}	1.563	1.634	117.4
AlF ₂ H	C _{2v}	1.548	1.623	121.3
AlF ₃	D _{3h}	—	1.612	—
Dimer	Symmetry	<i>R</i> (Al-Al)	<i>R</i> (Al-X) ^{b)}	<i>R</i> (Al-Y) ^{c)}
(AlH ₃) ₂	D _{2h}	2.615	1.730	1.566
(AlFH ₂) ₂	D _{2h}	2.785	1.809	1.561
(AlF ₂ H) ₂	D _{2h}	2.551	1.712	1.617
(AlF ₃) ₂	D _{2h}	2.730	1.781	1.612

^{a)} Bond lengths in Å, angles in deg. ^{b)} X is the bridging atom. ^{c)} Y is the terminal atom.

Table 2
Binding energies and zero-point vibrational corrections^{a)}

Dimer	SCF ^{b)}	MP2 ^{b)}	CCSD	CCSD(T)	ZPE ^{c)}	\mathcal{I}_1^d
(AlH ₃) ₂	28.6(27.7)	37.1(35.1)	36.0	37.2	-4.2	0.008/0.010
(AlFH ₂) ₂	42.5(41.9)	45.7(44.2)	45.7	46.1	-2.5	0.012/0.010
(AlF ₂ H) ₂	16.7(15.1)	22.7(19.6)	22.1	22.9	-2.8	0.012/0.012
(AlF ₃) ₂	48.9(47.5)	50.1(52.8)	51.3	51.5	-1.6	0.012/0.011

^{a)} All energies in kcal/mol. ^{b)} Values in parentheses are obtained using the TZP basis.

^{c)} Zero-point vibrational correction using TZP SCF harmonic frequencies scaled by 0.89.

^{d)} Monomer/dimer \mathcal{I}_1 diagnostic (see footnote 2).

erence based method that is limited to the treatment of single and double excitation operators [34]. Comparison of the SCF and MP2 results obtained in the TZP basis with those obtained in the ANO basis indicates that the binding energies are close to convergence with respect to further improvement in the one-particle space. For the MP2 results, this finding is somewhat surprising given that the ANO basis set dramatically lowers the total energies relative to the TZP basis (e.g. approximately 0.22 E_h for AlF₃) and also that at the correlated level, f functions have been found to be important for a variety of fluorine-containing compounds [35,36]. The good agreement between the MP2 and CCSD results indicates that infinite-order effects are of little importance in the determination of the dimer binding energies. Furthermore, the inclusion of triple excitations produces a very minor change in the binding energies; the largest effect, 1.2 kcal/mol, is found for (AlH₃)₂, whereas for all the fluorinated dimers, the change is

less than 1.0 kcal/mol. The small effect of triple excitations is in accord with expectations based on the value of the \mathcal{I}_1 diagnostic. Specifically, the value of \mathcal{I}_1 shows virtually no change from the monomer to the dimer and is well below the empirically suggested value of 0.02 at which connected triple and higher excitations may become important [34].

The BSSE has been computed by using a counterpoise correction scheme [37]. It should be noted that the relevant monomer energies in the presence of the ghost orbitals are significantly higher than those of the isolated monomers (e.g. 11 kcal/mol for AlH₃). This results from the large structural distortion which accompanies the formation of the dimer, and necessitates that the BSSE be computed by comparing the monomer energies obtained in the presence of the ghost orbitals with monomer energies obtained without ghost orbitals at the distorted geometries appropriate for the dimer.

Using this procedure, the total BSSE (i.e. twice the

correction from one monomer unit) for $(\text{AlH}_3)_2$ in the ANO basis set at the SCF and CCSD(T) levels is 0.2 and 0.6 kcal/mol, respectively. For $(\text{AlFH}_2)_2$, the SCF value is 0.6 kcal/mol and the CCSD(T) value is 3.4 kcal/mol. The BSSE for $(\text{AlF}_3)_2$ and $(\text{AlF}_2\text{H})_2$ has not been computed but is expected to be similar to either $(\text{AlFH}_2)_2$ or $(\text{AlH}_3)_2$, depending on whether the fluorine atoms are bridging or not. Interestingly, the majority of the correlation contribution to the dimerization energy in $(\text{AlFH}_2)_2$ is found to be BSSE, which is not the case for $(\text{AlH}_3)_2$. Since the presence of ghost orbitals in the monomer BSSE calculations will partially compensate for the large distortion of the monomer from planarity, these estimates of the BBSEs are expected to be a conservative upper bound to the real values.

The BSSE is somewhat larger with the TZP basis set than with the ANO basis, though the dimerization energies still agree to within 4 kcal/mol. Thus, the small change in the dimerization energies that accompanies the expansion of the basis from TZP to the large ANO set, and the consistency in the values obtained with the various correlated methods suggests that the binding energies are nearly converged with respect to expansion of both the one- and n -particle spaces. The remaining sources of error in our computed binding energies are, therefore, due to the use of an equilibrium geometry taken from an SCF rather than correlated calculation, and the neglect of core-valence correlation, which may be important for aluminum. Both of these effects are likely to be more important for the dimer than for the monomer; hence, our calculated binding energies are probably slight underestimates. Our best dimerization energies, including corrections for BSSE and ZPE, are 32,

40, 20, and 47 kcal/mol for AlH_3 , AlH_2F , AlHF_2 and AlF_3 , respectively. For AlF_3 , this is in very good agreement with the experimental value of 51 ± 4 kcal/mol [23].

5. Computational timings

In table 3, we report the timings required for the CCSD and CCSD(T) calculations on the various dimers. In addition, the "speed" of the calculations, as measured by millions of floating-point operations (megaflop) per second (megaflops), is also given. All calculations were performed on a single processor of a CRAY Y-MP computer and performance was measured using the Cray hardware performance monitor. The largest calculation, on the AlF_3 dimer, contained 232 molecular orbitals in the CCSD(T) procedure and over 1.5×10^6 t_1 and t_2 amplitudes, and effectively treated over 2×10^9 t_3 amplitudes. The timings for all four dimers indicate that these calculations are well within the capabilities of modern computer systems. For the triples component of the CCSD(T) energy, we find that very high performance is obtained even for the smallest of the dimers. Furthermore, for all the dimers the computation of the triples energy is found to be less expensive than the determination of the CCSD wavefunction, although with a less stringent convergence criterion this would not be the case for the AlF_3 dimer.

To assess the potential for multitasking the triples component of the CCSD(T) energy, we have used the BSSE evaluation for the AlFH_2 dimer. This system contains 182 basis functions, which in C_s symmetry comprises 111 a' functions and 71 a'' func-

Table 3
CPU time and megaflops^{a)} rates obtained on a single processor of a CRAY Y-MP

Dimer	Amplitudes			CCSD			CCSD(T) ^{b)}	
	t_1	t_2	t_3	iter ^{c)}	s/iter	megaflops	s	megaflops
$(\text{AlH}_3)_2$	139	47824	9582119	18	9	54	20	243
$(\text{AlFH}_2)_2$	290	246032	125046740	20	29	129	233	249
$(\text{AlF}_2\text{H})_2$	476	711002	627940356	21	88	179	1203	257
$(\text{AlF}_3)_2$	693	1569684	2099444324	21	221	214	4194	265

^{a)} Megaflops rate obtained on a single CRAY Y-MP processor using the hardware performance monitor.

^{b)} The triples component of the CCSD(T) energy.

^{c)} The CCSD wavefunction was converged to a threshold of 10^{-10} in the root-mean-square error in the t_1 and t_2 amplitudes.

Table 4

Timings and megaflops rates obtained on a CRAY Y-MP for multitasking the triples part of the CCSD(T) energy^{a)}

	Number of processors				
	1	2	4	6	8
timings (s)					
matrix multiply	495.6	514.9	515.6	516.2	517.4
sorts	8.3	8.4	8.8	9.3	9.6
formation of V	3.8	4.0	4.3	5.1	5.4
energy summation	9.9	10.0	10.4	10.6	11.0
total time	517.6	537.3	539.1	541.2	543.4
megaflops rates					
megaflops (CPU) ^{b)}	297.4	291.0	289.8	288.8	287.7
megaflops (wall) ^{c)}	240.3	543.6	1007.7	1345.4	1299.2
megaflops rates					
megaflops (CPU) ^{b)}	299.5	290.5	286.8	285.2	277.4
megaflops (wall) ^{d)}	299.2	577.3	1129.5	1669.9	2138.8

^{a)} This is for the BSSE calculation of $(\text{AlFH}_2)_2$; see text for details of calculation.^{b)} Megaflops rate obtained from the Cray hardware performance monitor using the total CPU time.^{c)} Megaflops rate obtained from the Cray hardware performance monitor using the wall clock time and running in a multiuser environment (UNICOS 6.0).^{d)} Megaflops rate obtained from the Cray hardware performance monitor using the wall clock time and running in a dedicated environment (UNICOS 5.1).

tions. In table 4, we present the times required for the various steps in the formation of the triples energy, obtained using between one and eight processors of a CRAY Y-MP running UNICOS 6.0 in a multiuser environment. The matrix-multiply time represents the time spent in performing the matrix operations required to form the intermediate \mathbf{W} quantities (for example eqs. (11) and (12)). The sort time is that required to rearrange the \mathbf{W} intermediate between successive matrix multiplications (for example between eq. (8) and eq. (9)). The total time for the formation of intermediate \mathbf{W} is, therefore, the sum of the matrix-multiply time and the sort time. The time for the formation of intermediate \mathbf{V} is the time required to compute \mathbf{V} given \mathbf{W} (see eq. (5)). The final energy summation is the time required to compute the triples energy according to eq. (13). The results from table 4 show that the most significant overhead associated with multitasking is encountered on going from one to two processors, and that this is primarily incurred in the matrix-multiply routine. The addition of processors beyond two has only a minor effect on the total CPU time.

In table 4, we also present the megaflops which have been obtained from both the total CPU time and the wall clock time. These rates are presented for a multiuser environment running UNICOS 6.0 and for a dedicated environment running UNICOS 5.1. It is noteworthy that due to the lower symmetry of this calculation, the megaflops rate (CPU) is significantly higher than any of those reported in table 3 for the aluminum dimers. Indeed, for large systems with little or no symmetry, we might expect to observe performance close to the Y-MP asymptotic value (approximately 330 megaflops). The results obtained using four processors show a degradation of less than 5% relative to the performance seen using only one processor. The megaflops as obtained using the wall clock time on a lightly loaded multiuser machine show that performance levels of beyond one gigaflop per second are readily obtained, and in a dedicated environment (with eight processors), performance levels of more than two gigaflops per second are sustained.

6. Conclusions

A highly vectorized algorithm for the perturbative inclusion of triple excitations in coupled-cluster calculations has been outlined. The methodology, although developed within the CCSD(T) formulation is applicable to a variety of other similar methods which incorporate triple excitations, such as CCSD+T and MP4. Furthermore, on a shared-memory computer architecture, the method can be readily parallelized, leading to gigaflops performance on a CRAY Y-MP.

Using the new methodology, very large calculations have been performed to determine the binding energies of the D_{2h} diborane-type dimers of AlH_3 , AlH_2F , $AlHF_2$ and AlF_3 . Formation of all four dimers is predicted to be exothermic with the fully fluorinated dimer being the most stable.

Acknowledgement

The implementation of the parallel versions for these calculations is the result of numerous discussions with some of our colleagues at Cray Research, Inc., especially Jeffrey Nicholson. The authors gratefully acknowledge the support of Cray Research, especially Robert Eades; without the access to their computer facilities, most of these calculations would not have been possible. APR was supported by a National Research Council Post-Doctoral Research Fellowship and AK was supported by NASA Grant No. NCC2-499.

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