

A direct product decomposition approach for symmetry exploitation in many-body methods. I. Energy calculations

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An analysis of the matrix contractions involved in many-body perturbation theory and coupled-cluster calculations leads to a convenient strategy for exploiting point group symmetry, by which the number of floating point operations can be reduced by as much as a factor of h^2 , where h is the order of the molecular point group. Contrary to a statement in the literature, the significant reduction in computation time realized in coupled-cluster calculations which exploit symmetry is not due to nonlinearities in the equations. Rather, the savings of the fully vectorizable direct product decomposition (DPD) method outlined here is associated with individual (linear) contractions, and is therefore applicable to both linear and nonlinear coupled-cluster models, as well as many body perturbation theory. In addition to the large reduction in floating point operations made possible by exploiting symmetry, core memory requirements are also reduced by a factor of $\approx h^2$. Implementation of the method for both open and closed shells is reported. Computer timings and hardware requirements are given for several representative chemical systems. Finally, the DPD method is applied to the calculation of the equilibrium geometry, totally symmetric harmonic force field and vertical ionization potentials of the cubane molecule at the coupled-cluster singles and doubles (CCSD) level.

I. INTRODUCTION

It is widely recognized that exploitation of point group symmetry in quantum chemical calculations can lead to significant savings. Algorithms for using symmetry in integral¹ and derivative integral generation,² SCF calculations,³ integral transformation,⁴ and coupled-perturbed Hartree-Fock calculations⁵ have all been presented. The first many-body perturbation theory (MBPT) and coupled-cluster (CC) programs included a passive treatment of symmetry, achieved by not processing integrals below a fixed threshold and using sparse matrix algorithms.⁶ Explicit consideration of molecular symmetry in many-body calculations of the correlation energy was reported by Carsky *et al.*,⁷ who realized that the individual components of the T_2 cluster excitation operator (t_{ij}^{ab}) vanish unless the direct product of the irreducible representations (IRs) of orbitals i, j, a , and b ($\Gamma_i \otimes \Gamma_j \otimes \Gamma_a \otimes \Gamma_b$) contains the totally symmetric representation of the molecular point group. Accordingly, the authors modified their program which implemented the coupled-cluster doubles (CCD) formalism of Bartlett *et al.*⁸ to avoid the evaluation of "symmetry forbidden" t_{ij}^{ab} amplitudes. The documented timings⁷ reflect a speedup of approximately h relative to calculations in which symmetry was ignored, as expected since this scheme corresponds to unrestricted loops over three indices (for example, i, j , and a) followed by a restricted loop over the remaining index (b) in which only those orbitals which transform as the appropriate irreducible representation are included.⁹ Neglect of symmetry forbidden integrals can lead to additional savings since the evaluation of each T amplitude element is further simplified. Such an approach was presumably used by Carsky *et al.* and is also implemented in the program of Kal-

dor,¹⁰ and passively via sparsity in the codes of Bartlett and Purvis.⁶ Unfortunately, however, the authors of Ref. 7 do not report timings for calculations in which all integrals and T amplitudes were processed, so it is not possible to determine what factor of improvement relative to such a calculation was achieved.

Somewhat later, others¹¹ reported a closed-shell implementation of the coupled-cluster singles and doubles (CCSD) model which restricted sums to exclude all symmetry forbidden integrals as well as T amplitudes. Their results demonstrate that symmetry can be used to reduce the computational time by more than the theoretical limit of h associated with the scheme of Carsky *et al.*;⁷ a calculation carried out in the D_{2h} subgroup of the full point group of N_2 ($D_{\infty h}$) ran approximately thirty times faster than the corresponding calculation in which symmetry was ignored. The authors noted that this improvement is much greater than that typically observed in configuration interaction calculations¹² and attributed it to the nonlinearity of the coupled-cluster equations.

In this paper, we outline an algorithm for exploiting symmetry in both coupled-cluster and many-body perturbation theory (MBPT) calculations, which is based on a direct product decomposition (DPD) of T amplitudes and the terms with which they are contracted [Fock matrix elements and antisymmetrized molecular orbital integrals for MBPT and linear coupled-cluster models and general one- and two-particle intermediates for nonlinear coupled-cluster approximations], and discuss its implementation for both open and closed shells. We explicitly demonstrate that the maximum possible factor of reduction in the number of floating point operations is h^2 , and show that this asymptotic limit is not associated with nonlinearities in the coupled-

cluster equations. Consequently, the significant savings which can be achieved in nonlinear CC calculations can also be realized in both linear CC models and in MBPT calculations. Although the group theoretical principles used in the DPD scheme are certainly not new to theoretical chemistry, they have not heretofore been applied to many-body calculations in the manner described below.

The principal merits of the method discussed here are computational. Unlike exploitation of matrix sparsity, implementation of the DPD method in a fully and efficiently vectorized computer code is relatively straightforward; furthermore, the approach appears to provide a suitable framework for a parallel CC and MBPT code. In the following, a cursory familiarity with the formalism of CC theory and its relationship to finite-order MBPT approximations is assumed. Readers seeking detailed explanations of these theoretical models are referred to the literature.¹³

II. FORMALISM

When the hierarchy of equations for the coupled-cluster model is appropriately factored,¹⁴ all terms involve the contraction of a cluster operator (T) with either a two- or four-index quantity. In the case of linearized coupled-cluster models, the quantities which are contracted with the amplitudes are Fock matrix elements (f_{pq}) and molecular orbital integrals ($\langle pq||rs \rangle$); for nonlinear models (such as CCD and CCSD)^{6,8} these become one- and two-particle intermediates (denoted by \mathcal{F}_{pq} and \mathcal{W}_{pqrs} , respectively) in which the corresponding f_{pq} or $\langle pq||rs \rangle$ is the leading term of an expansion which also contains contractions between Fock matrix elements and integrals with T amplitudes. [We follow the convention that i, j, k, \dots represent occupied orbitals with a, b, c, \dots unoccupied. p, q, r, \dots are generic indices which may represent either occupied or unoccupied orbitals.] Explicit equations for the CCSD model in a fully factored spin-orbital form are presented below.

T_1 equation:

$$\begin{aligned} t_i^a D_i^a = & f_{ia} + \sum_e t_i^e \mathcal{F}_{ae} - \sum_m t_m^a \mathcal{F}_{mi} + \sum_{me} t_{im}^{ae} \mathcal{F}_{me} \\ & - \sum_{nf} t_n^f \langle na||if \rangle - \frac{1}{2} \sum_{mf} t_{im}^{ef} \langle ma||ef \rangle \\ & - \frac{1}{2} \sum_{mn} t_{mn}^{ae} \langle nm||ei \rangle. \end{aligned} \quad (1)$$

T_2 equation:

$$\begin{aligned} t_{ij}^{ab} D_{ij}^{ab} = & \langle ij||ab \rangle + P_-(ab) \sum_e t_{ij}^{ae} \left(\mathcal{F}_{be} - \frac{1}{2} \sum_m t_m^b \mathcal{F}_{me} \right) \\ & - P_-(ij) \sum_m t_{im}^{ab} \left(\mathcal{F}_{mj} + \frac{1}{2} \sum_e t_j^e \mathcal{F}_{me} \right) \\ & + \frac{1}{2} \sum_{mn} \tau_{mn}^{ab} \mathcal{W}_{mnij} + \frac{1}{2} \sum_{ef} \tau_{ij}^{ef} \mathcal{W}_{abef} \\ & + P_-(ij) P_-(ab) \sum_{mc} (t_{im}^{ac} \mathcal{W}_{mbej} - t_i^e t_m^a \langle mb||ej \rangle) \\ & + P_-(ij) \sum_e t_i^e \langle ab||ej \rangle - P_-(ab) \sum_m t_m^a \langle mb||ij \rangle. \end{aligned} \quad (2)$$

Definition of \mathcal{F} and \mathcal{W} intermediates:

$$\begin{aligned} \mathcal{F}_{ae} = & (1 - \delta_{ae}) f_{ae} - \frac{1}{2} \sum_m f_{me} t_m^a \\ & + \sum_{mf} t_m^f \langle ma||fe \rangle - \frac{1}{2} \sum_{mnf} \tau_{mn}^{af} \langle mn||ef \rangle, \end{aligned} \quad (3)$$

$$\begin{aligned} \mathcal{F}_{mi} = & (1 - \delta_{mi}) f_{mi} + \frac{1}{2} \sum_e t_i^e f_{me} \\ & + \sum_{en} t_n^e \langle mn||ie \rangle + \frac{1}{2} \sum_{nef} \tau_{in}^{ef} \langle mn||ef \rangle, \end{aligned} \quad (4)$$

$$\mathcal{F}_{me} = f_{me} + \sum_{nf} t_n^f \langle mn||ef \rangle, \quad (5)$$

$$\begin{aligned} \mathcal{W}_{mnij} = & \langle mn||ij \rangle + P_-(ij) \sum_e t_j^e \langle mn||ie \rangle \\ & + \frac{1}{4} \sum_{ef} \tau_{ij}^{ef} \langle mn||ef \rangle, \end{aligned} \quad (6)$$

$$\begin{aligned} \mathcal{W}_{abef} = & \langle ab||ef \rangle - P_-(ab) \sum_m t_m^b \langle am||ef \rangle \\ & + \frac{1}{4} \sum_{mn} \tau_{mn}^{ab} \langle mn||ef \rangle, \end{aligned} \quad (7)$$

$$\begin{aligned} \mathcal{W}_{mbej} = & \langle mb||ej \rangle + \sum_f t_j^f \langle mb||ef \rangle \\ & - \sum_n t_n^b \langle mn||ej \rangle - \sum_{nf} (\frac{1}{2} t_{jn}^{fb} + t_j^f t_n^b) \langle mn||ef \rangle. \end{aligned} \quad (8)$$

Definition of effective two-particle excitation operators τ and $\tilde{\tau}$:

$$\tilde{\tau}_{ij}^{ab} = t_{ij}^{ab} + \frac{1}{2} (t_i^a t_j^b - t_i^b t_j^a), \quad (9)$$

$$\tau_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a. \quad (10)$$

In the above equations, $P_{\pm}(pq)$ is the operator

$$P_{\pm}(pq) = 1 \pm \mathcal{P}(pq), \quad (11)$$

where $\mathcal{P}(pq)$ permutes the indices of p and q , δ_{pq} is the Kronecker delta and the denominator arrays (D) are defined by

$$D_i^a = f_{ii} - f_{aa} \quad (12)$$

and

$$D_{ij}^{ab} = f_{ii} + f_{jj} - f_{aa} - f_{bb}. \quad (13)$$

Note that this places the diagonal parts of Fock matrix elements on the left-hand side of the equations; therefore, the diagonal terms of f_{ea} and f_{mi} are not included in the corresponding \mathcal{F} intermediates. For a Hartree-Fock reference function, the diagonal elements of f are simply the orbital eigenvalues.

In a spin-adapted restricted Hartree-Fock formalism, the expressions above are essentially the same as those derived by means of the unitary group approach,¹⁵ but it should be noted that they are applicable to arbitrary reference functions (including those for which the Fock operator is not diagonal) and can be readily generalized to higher coupled-cluster models such as CCSDT as well.¹⁴ The computational implementation of Eqs. (1)–(8) consists entirely of matrix-matrix products, and is therefore well suited for

modern vector computers. Elements of this intermediate-driven CC formulation were initially applied to simplification of the triple excitation amplitude (T_3) equation by Noga, Bartlett, and Urban,¹⁶ and have recently been implemented in spin-orbital form in the open-shell CCSDT model.¹⁷ A brief description of the implementation of Eqs. (1)–(8) is presented in the appendix for a variety of MBPT and CC methods. In addition, a thorough analysis is given of the number of operations required to evaluate each term for both unrestricted Hartree–Fock (UHF) and spin-adapted restricted Hartree–Fock (RHF) approaches, since there is some confusion in the literature in this area. The principal purpose of the present manuscript, however, is to describe how symmetry can be efficiently exploited in many-body calculations.

Consider a generic contraction $Z = T \times \mathcal{W}$. Clearly, the indices of T and \mathcal{W} can be grouped into two distinct categories: those which label the Z matrix (the target indices) and those which are included in the summation (the common indices). As a specific example, consider the contraction

$$Z_{ij}^{ab} = \sum_{ef} t_{ij}^{ef} \mathcal{W}_{abef}. \quad (14)$$

For linear CC models and MBPT, $\mathcal{W}_{abef} = \langle ab || ef \rangle$, and the dot product of the Z matrix of Eq. (14) with the T_2 amplitudes gives the “particle–particle ladder” (PPL) contribution to the correlation energy. For nonlinear models such as CCSD, \mathcal{W}_{abef} is the two-particle intermediate defined by Eq. (7), and the right-hand side of Eq. (14) is one of the terms in the CCSD double excitation equation. We have found that it is useful to partition the constituents of T and \mathcal{W} into two categories—the common indices and the target indices—and then analyze the simplifications made possible by symmetry in terms of the IR of the direct product of the members of each subset. This analysis, which we call the direct product decomposition (DPD), leads to a simple prescription for exploiting symmetry in *any* contraction between T amplitudes and \mathcal{W} or \mathcal{F} intermediates. For the specific example of the PPL contraction, the method proceeds as described in the following paragraph. Here we specialize to D_{2h} and its subgroups, for which $\Gamma_i \otimes \Gamma_j$ does not contain the totally symmetric representation unless $i = j$.

Define $\Gamma_{pq\cdots} = \Gamma_p \otimes \Gamma_q \otimes \Gamma_r \cdots$, and a “double direct product” as $\Gamma_{p,q,r,\cdots} \otimes \Gamma_{p,q,r,\cdots}$, where the subscript t denotes target indices and c denotes the common indices. Now, it is obvious that any amplitude, Fock matrix element, integral, or one- or two-particle intermediate must vanish unless the double direct product of the $\Gamma_{pq\cdots}$ for the target and common indices contains the totally symmetric representation of the point group. For the PPL contraction in Eq. (14), this means that the relation $\Gamma_{ij} = \Gamma_{ef} = \Gamma_{ab}$ must hold to give a nonvanishing element of the Z matrix.¹⁸ Consequently, the matrix multiplication implied by Eq. (14) can be subdivided into h distinct and independent operations *which can in principle be performed in parallel*. Neglecting symmetry, the T_2 and \mathcal{W} matrices of Eq. (14) have dimensions $n^2 \times N^2$ and $N^2 \times N^2$, respectively, where n is the number of occupied orbitals and N is the number of virtual orbitals. The dimen-

sions of the submatrices obtained within the DPD, however, depend upon the number of pq pairs which transform according to particular irreducible representations. For D_{2h} and subgroups, these values can be calculated from the simple expression

$$\mathcal{N}_r = \sum_p n(\Gamma_p) n(\Gamma_q), \quad (15)$$

where $\Gamma_p \otimes \Gamma_q = \Gamma_r$ and $n(\Gamma_p)$ is the number of occupied (or unoccupied) molecular orbitals which transform as Γ_p . In favorable cases, $n(\Gamma_p)$ approaches n/h (p occupied) or N/h (p unoccupied) and the dimensions of the T_2 and \mathcal{W} matrices become $\approx (n^2/h) \times (N^2/h)$ and $\approx (N^2/h) \times (N^2/h)$, respectively. Consequently, the number of floating point operations required to evaluate the nonzero elements of the Z matrix is reduced from $n^2 N^4$ to $\approx h^{-3} n^2 N^4$ for each submatrix. Since there are h submatrices, the total floating point count is $\approx h^{-2} n^2 N^4$. Note also that since each IR can be treated separately, the core memory requirements are also reduced by a factor of $\approx h^2$. Thus, this technique allows speedups which exceed the order of the group and can be as large as the *square* of h when the orbital population is roughly uniform by IR. It is clear that this reduction results from the nature of the (linear) contraction process, and not from nonlinearities in the coupled-cluster equation, as had been assumed.¹¹ The h^2 savings in floating point operations and memory requirements also holds for point groups with degenerate representations, although it is not as straightforward to show this as it is for D_{2h} and its subgroups.¹⁹

Although the DPD is simply a technique which eliminates the evaluation of all null contributions in the contraction process and is therefore equivalent (in principle) to complete exploitation of symmetry sparsity,²⁰ it has several attractive computational advantages. First, since the size of the symmetry submatrices is always available, the program can automatically choose a full matrix algorithm [T , \mathcal{W} (or \mathcal{F}) and Z held in core] for a specific symmetry block even when the full (unsymmetrized) matrices are far too large to fit into core, as seen in the cubane example presented in Sec. V. This should be contrasted with sparse matrix algorithms, in which sufficient core to contain all elements (zero and nonzero) of the unsymmetrized matrix must be available for a full matrix approach. Consequently, calculations using the DPD treatment of symmetry are completely vectorizable and involve no direct product checking, thereby resulting in negligible computational overhead.

In addition, the DPD approach potentially provides a suitable framework for a parallel computational implementation. Since each contraction of a given type for a specific IR is rigorously independent of all others, there is no need for communication between the h contractions and each can be carried out on a separate processor with no shared memory. In the ideal case in which $n(\Gamma_p) = n/h$ for all p , real time throughput (relative to the same calculation performed without regard to symmetry) will increase by a factor of h^3 . However, since our local computing environment does not presently involve any parallel machines, we have not made any effort in this direction to date.

Another advantage of the DPD, which is not related to

floating-point operations or memory use, lies in the efficient storage scheme for integrals and amplitudes which naturally accompanies this approach. For molecules which are not very large (less than 10–20 atoms), the symmetry packed integral, intermediate and T amplitude lists should be nearly 100% dense. When symmetry is neglected, very large lists complete with zeros must be written to disk or alternatively, information regarding the integral indices must be stored. As a result, input/output with symmetry packed lists is much less complicated and considerably more efficient than in codes which do not treat symmetry explicitly. Our strategy for integral and T amplitude storage is discussed in the following section.

Following Carsky *et al.*,⁷ the method discussed here can be generalized to all point groups by projecting out the totally symmetric component of direct products which involve degenerate representations. However, this has not yet been implemented in our program. The tremendous savings which potentially can be achieved via the DPD for highly symmetric molecules [≈ 200 for D_{4h} ; ≈ 500 for T_d ; ≈ 2000 for O_h ; $\approx 10^4$ for I_h] offer a compelling incentive for such efforts, however, and we will undoubtedly devote some attention to this in the future.

III. IMPLEMENTATION

The DPD method has been incorporated into the new quantum chemistry program package, ACES II.²¹ Correlation energy evaluation at the CCSD level as well as various MBPT approximations has been implemented for general single-determinant reference functions (RHF, UHF, and non-HF), and spin adaptation is used for RHF calculations. All contractions are evaluated by matrix multiplication, resulting in a highly vectorized computer code. In the following, we describe how the DPD approach is used in our program by means of a few examples. The algorithms discussed here are appropriate only for Abelian groups. Further details regarding the computational implementation may be found in the appendix.

A. Storage of quantities

Before discussing our implementation of the DPD method, however, it is necessary to describe how integrals ($\langle pq||rs \rangle$) and cluster amplitudes (T) are stored since this ultimately determines how the contractions are evaluated. In the ACES II code,²¹ all four-index quantities (two-electron integrals, \mathcal{W} intermediates, and T_2 amplitudes) are stored in symmetry-packed form on disk. All of the integrals are partitioned by the number of occupied and virtual indices and the specific spin case (for example, $\langle ij||kl \rangle$, $\langle ij||k\bar{l} \rangle$, $\langle \bar{a}\bar{i}||\bar{b}\bar{j} \rangle$, etc.) and are stored in separate logical files. Within each file, the specific integral types are symmetry blocked. The scheme used to pack the integrals is based on a DPD of the two left-hand indices (bra indices) and the two right-hand indices (ket indices). Each logical file of integrals is then composed of h subfiles, in which only those $\langle pq||rs \rangle$ integrals for which $\Gamma_{pq} = \Gamma_{rs} = \Gamma_{\alpha}$ are stored on the α th subfile. Each of the h subfiles containing these “symmetry subblocks” of $\langle pq||rs \rangle$ integrals is made up of a number of

logical records which consist of all unique $\langle pq||rs \rangle$ integrals for a given rs , subject to the condition that $\Gamma_{pq} = \Gamma_{rs}$.²²

Although integral storage is based on a bra-ket DPD, evaluation of individual contractions uses the common-target DPD method introduced in the previous section. Consequently, implementation of the DPD method in a many-body code is simplest when the common-target and bra-ket DPDs are identical, such as in the PPL contraction described by Eq. (14). Great simplification in both coding and computational efficiency can be achieved, however, by storing certain types of integrals in several different ways, thereby introducing redundancy. Since the number of virtual orbitals is typically much greater than the number of occupied orbitals, the largest files are those which contain the $\langle ab||cd \rangle$ and $\langle ab||ci \rangle$ integrals. It is generally unwise to store these integrals in more than one way, since these lists may occupy large amounts of disk space. We have also elected to store the $\langle ij||kl \rangle$ and $\langle ij||ka \rangle$ integrals in just one way since the permutational symmetry of the indices in the integrals are identical to that in the $\langle ab||cd \rangle$ and $\langle ab||ci \rangle$ integrals, respectively, and the same algorithms and routines are used to process both types. Integrals with two virtual and two occupied indices, however, are stored in several different ways. For example, each spin case of the $\langle ij||ab \rangle$ integrals are stored in two different logical files; the storage mode of the first follows the bra-ket DPD (all ab for each ij such that $\Gamma_{ab} = \Gamma_{ij}$), while ordering of the second set is based on the $\Gamma_{ai} = \Gamma_{bj}$ DPD. Similarly, redundant storage is also used for the T_2 amplitudes, which are equal in size and have the same permutational symmetry as the $\langle ij||ab \rangle$ integrals.

After the bra-ket DPD lists are formed and written to disk, the redundant lists are constructed by specific permutations of the bra-ket lists. This reordering is considerably more complicated than that required when symmetry is ignored, and is accomplished by means of special vectorized algorithms developed in our group.

It should be noted that the explicit use of symmetry in the DPD method does not necessitate the redundant storage of $\langle ij||ab \rangle$ and $\langle ai||bj \rangle$ integrals as well as t_{ij}^{ab} amplitudes, since multiple storage of these quantities is advantageous in any CC/MBPT program. Indeed, the redundancies in our integral lists are identical to those included in the old ACES²³ program system, which does not use symmetry explicitly. Rather, the multiple storage of these quantities is justified by the following two points: first, for a very large case (20 occupied and 150 virtual functions), the space required for the n^2N^2 lists is only ≈ 9 million words and is considerably less than this value if any elements of symmetry are present. [This value should be compared to the ≈ 125 million words needed for the $\langle ab||cd \rangle$ lists.] Second, redundant storage of these quantities allows highly efficient input/output and extensive vectorization of all steps which have a computational dependence which scales as the sixth power of the number of basis functions.

Two-index quantities such as Fock matrix elements, \mathcal{F} intermediates and T_1 amplitudes are also stored and processed as symmetry-packed lists. Each spin case of these quantities is stored on an individual logical record that contains only those elements which are allowed ($\Gamma_{ai} = \Gamma_l$,

where Γ_1 is the totally symmetric representation of the point group).

In addition, it is appropriate to discuss the amount of core memory assumed to be available by our code since this also serves to determine how contractions will be evaluated. We have chosen to follow the usual strategy used in configuration interaction programs and in certain coupled-cluster implementations,²⁴ namely, that two vectors of length n^2N^2 can be held in core simultaneously along with an additional array of length N^2 . In our case, however, we assume only that two vectors of length \mathcal{N} are stored simultaneously, where \mathcal{N} is the length of a specific symmetry subblock of a n^2N^2 quantity. If no symmetry is present, this assumption is equivalent to that of n^2N^2 storage, while the required space is reduced to $\mathcal{N} = h^{-2} n^2N^2$ when symmetry is present. With some additional work, the core requirements could be further reduced, but at the cost of significantly reduced vectorization.

B. Evaluation of contractions

In this subsection, algorithms used to evaluate two specific contractions in CC/MBPT models are described in detail. Each of the examples illustrates a general class of algorithms used to implement the DPD method in the ACES II code. The first contraction which is discussed is representative of the simplest cases—those in which the common-target DPD is the same as that used to store the integrals and amplitudes—while the second is a typical example of cases in which the storage of the quantities involved in the contraction does not follow the common-target DPD.

To help clarify the following discussion, some additional notation is desirable. Define $Q^{[\alpha|pq-rs]}$ as the α th symmetry subblock of a specific four-index quantity Q , according to a $\Gamma_{pq} = \Gamma_{rs}$ DPD. For example, $\langle ai||bj \rangle^{[\alpha|ab-ij]}$ represents the set of $\langle ai||bj \rangle$ integrals for which $\Gamma_{ab} = \Gamma_{ij} = \Gamma_\alpha$, while $[t_{ij}^{ef}]^{[\alpha|ie-f]}$ refers to the subset of T_2 amplitudes for which $\Gamma_{ie} = \Gamma_f = \Gamma_\alpha$. In addition, Γ_1 is hereafter assumed to be the totally symmetric representation of the group.

As an example of the simplest cases, consider the $\alpha\alpha$ part of the particle-particle ladder contribution to the third-order MBPT energy

$$E_3^{\text{PPL}}(\alpha\alpha) = \sum_{i < j; a < b} t_{ij}^{ab} Z_{ij}^{ab}, \quad (16)$$

where

$$Z_{ij}^{ab} = \sum_{e < f} t_{ij}^{ef} \langle ab || ef \rangle. \quad (17)$$

As seen in the above equations, evaluation of $E_3^{\text{PPL}}(\alpha\alpha)$ consists of two steps: a simple dot product between the T_2 amplitudes and a two-particle intermediate (Z), and the formation of the intermediate. The latter is simply a special case of the $t_{ij}^{ef} \mathcal{W}_{abef}$ term in the CCSD T_2 equation in which only zero and first-order terms in the correlation perturbation have been included, and has a computational dependence of n^2N^4 . The dot product between Z and T_2 requires only $O(n^2N^2)$ operations. Evaluation of the Z intermediate proceeds as follows.

1. Loop over the number of irreducible representations ($\Gamma_1, \Gamma_2, \dots, \Gamma_h$).
2. For each Γ_α , allocate memory for the $T_2^{[\alpha|ij-ef]}$ and $Z^{[\alpha|ij-ab]}$ vectors.
3. Read in the entire subfile of the $T_2^{[\alpha|ij-ef]}$ amplitudes. These are held in a two-dimensional matrix, $T(ij;ef)$.
4. Determine how many distributions of the $\langle ab || ef \rangle^{[\alpha|ef-ab]}$ integrals can be held in core (each distribution consists of all symmetry allowed $e < f$ for a given $i < j$ and is stored on a single logical record). The integrals are treated as the two-dimensional matrix $I(ab;ef)$. If the entire symmetry subblock of integrals can be held, only a single matrix multiplication will be required for each IR; otherwise the Z matrix must be constructed several columns at a time.
5. Read in the first n_{col} columns of the I matrix, where n_{col} is the value determined in step 4.
6. Perform the matrix multiplication

$$Z(ab;ij) = \sum_{e < f} I(ab;ef) T(ef;ij). \quad (18)$$

The product of this operation is the first n_{col} columns of the $Z(ab;ij)$ matrix in symmetry packed form, according to a $\Gamma_{ij} = \Gamma_{ab}$ DPD ($Z^{[\alpha|ij-ab]}$).

7. If n_{col} is not equal to the total number of columns of the $I^{[\alpha|ab-ef]}$ matrix $[\frac{1}{2} \sum_{i=1}^h N(\Gamma_i) [N(\Gamma_i) - 1] \text{ for } \alpha = 1, \sum_{i=1}^h N(\Gamma_i) N(\Gamma_i \otimes \Gamma_\alpha) \text{ otherwise}]$, then evaluate the remainder of $Z^{[\alpha|ij-ab]}$ by successive application of steps 4–6.

8. Store the complete $Z^{[\alpha|ij-ab]}$ vector on disk, and return to step 1 unless $\alpha = h$.

Once the Z vector is available, the $\alpha\alpha$ contribution to E_3^{PPL} is trivially evaluated as a dot product between symmetry packed Z and T_2 vectors

$$E_3^{\text{PPL}}(\alpha\alpha) = \sum_{n=1}^h \sum_{i < j; a < b} Z^{[\alpha|ij-ab]} T_2^{[\alpha|ij-ab]}. \quad (19)$$

Note that this n^2N^2 step contains only common indices, and the maximum simplification due to symmetry is equal to the order of the group, rather than the theoretical limit of h^2 associated with the construction of Z . Nevertheless, the cost of the T_2Z dot product is negligible in comparison with the evaluation of Z , and the theoretical factor of reduction in floating point operations is determined almost entirely by the latter operation in practical cases.

More difficult algorithms must be used when the common-target DPD for a particular contraction differs from the storage mode of the relative integrals and amplitudes. An example of this is provided by the n^2N^3 term

$$Z_{mb}^{ej} = \sum_f t_j^f \langle f\bar{e} | b\bar{m} \rangle \quad (20)$$

which contributes to the $\mathcal{W}_{\bar{m}b\bar{e}j}$ intermediate of Eq. (9). The $\langle f\bar{e} | b\bar{m} \rangle$ integrals are stored according to a bra-ket DPD ($\Gamma_{f\bar{e}} = \Gamma_{b\bar{m}}$), with each logical record of $\langle f\bar{e} | b\bar{m} \rangle^{[\alpha|f\bar{e}-b\bar{m}]}$ consisting of all $f\bar{e}$ indices for a given $b\bar{m}$ (subject of course to the condition $\Gamma_{f\bar{e}} = \Gamma_{b\bar{m}} = \Gamma_\alpha$). The appropriate common-target DPD is $\Gamma_f = \Gamma_{\bar{e}b\bar{m}}$. Evaluation of this contraction follows one of two general algorithms, both of which are included in the steps outlined below.

1. Loop over the number of irreducible representations.
2. For each Γ_α , allocate memory for $Z^{(\alpha|\bar{m}b-\bar{e}j)}$ and the symmetry-packed T_1 vector.
3. Determine if the remaining amount of available memory is sufficient to hold the full set of $\langle \bar{e}|b\bar{m} \rangle^{(\alpha|\bar{e}-b\bar{m})}$ integrals. If so, continue with step 4; otherwise proceed to step 7.
4. Reorder the $\langle \bar{e}|b\bar{m} \rangle^{(\alpha|\bar{e}-b\bar{m})}$ integrals to $\langle \bar{m}b|\bar{e}f \rangle^{(\alpha|\bar{m}b-\bar{e}f)}$ so that they may be treated as a block-diagonal two-dimensional matrix $I(\bar{m}b\bar{e};f)$. In practice, the matrix I is stored in a one-dimensional vector with appropriate offsets marking the start of each submatrix column.
5. Form $Z^{(\alpha|\bar{m}b-\bar{e}j)}$ directly by looping over Γ_f and evaluating the matrix product²⁵

$$Z(\bar{m}b\bar{e};f) = \sum_f I(\bar{m}b\bar{e};f) T_1(fj). \quad (21)$$

6. Proceed to step 13.
7. Loop over individual distributions of $\langle \bar{e}|b\bar{m} \rangle^{(\alpha|\bar{e}-b\bar{m})}$. Again, each distribution refers to all symmetry allowed \bar{e} indices for a specific $b\bar{m}$ pair.
8. Read the distribution corresponding to the particular $b\bar{m}$ pair into a matrix $I(f;\bar{e})$.
9. Loop over irreducible representations of \bar{e} . (Note that this determines the IR of index f , since Γ_f must be the same as $\Gamma_\alpha \otimes \Gamma_{\bar{e}}$.)
10. Perform the matrix product

$$T_1(jf)I'(f;\bar{e}), \quad (22)$$

where the primed matrices refer to the submatrices for which $\Gamma_f = \Gamma_\alpha \otimes \Gamma_{\bar{e}}$. In the program, this is easily done by passing specific offsets into the T_1 and I arrays to standard matrix multiply routines. The product is the corresponding submatrix of the $Z(\bar{e};mb)^{(\alpha|\bar{e}-b\bar{m})}$ target.

11. Return to step 9 if $\Gamma_{\bar{e}} \neq \Gamma_h$, and continue to fill out the target \bar{e} distribution.
12. Return to step 8 unless all $b\bar{m}$ pairs have been processed.
13. Return to step 1 unless $\Gamma_\alpha = \Gamma_h$.
14. Reorder the indices of the Z target to any specific arrangement.

The two specific algorithms outlined above are easily generalized to evaluate all contractions which appear in the CCSD amplitude equation. As mentioned previously, the simplest class of algorithms—those in which the common-target and storage DPDs are the same—can be applied to all computational steps which scale as the sixth power of the number of basis functions, while more difficult approaches such as that outlined in steps 1–14 above must be used for most of the steps with a fifth power dependence.

The most difficult obstacle to overcome in implementing the DPD approach in a computer program is that there is very little explicit consideration of integral and amplitude indices. As a result, a properly written DPD program will consist of very few loops over indices which correspond to molecular orbitals and is therefore different from essentially all existing many-body codes. With the help of practice and auxiliary routines to perform functions such as index transposition and permutation (both of which must be done differently than in a standard no symmetry approach), coding

within the DPD scheme becomes straightforward and only slightly more difficult than that required to implement traditional approaches to many-body calculations. We are currently extending the approach to include triple excitation effects in the amplitude equations. In addition, we are also working on application of the DPD approach to gradient and property calculations, using the relaxed density formalism of Salter, Trucks, and Bartlett.²⁶ The two- and four-particle intermediates which naturally arise in the fully factored CCSD equations presented in Eqs. (1)–(8) also appear in properly formulated gradient equations, so many of the strategies used in the energy code can be immediately applied to gradient calculations. Work in both of these areas will be reported in future publications.

IV. ILLUSTRATIVE CALCULATIONS

To illustrate the computational advantages of the DPD approach, we have carried out a number of calculations on small to medium sized systems. All calculations were performed on a Cray YMP supercomputer.²⁷ The choice of this machine was partially motivated by its wide availability at supercomputing centers, since this allows others to easily and unambiguously compare our timings to those of other program packages. In order to fairly assess the improvement in performance due to symmetry, calculations performed in the highest possible Abelian group and those performed in C_1 symmetry used identical algorithms. Consequently, the gains due to symmetry do not arise for spurious reasons—for example, out-of-core algorithms for C_1 and in-core for higher symmetries—but rather reflect directly the savings inherent in the DPD method.

In Table I, a number of statistics pertaining to the computational cost of CCSD calculations are presented for a number of molecules using different basis sets. Calculations have been performed in both the highest Abelian subgroup and in C_1 symmetry for all systems, and additional Abelian subgroups of O_h for the N_8 example. Documented in the table are the following categories: cpu time per CCSD iteration (these values include both the time spent doing contractions, convergence acceleration of the CCSD equations²⁸ and additional overhead such as disk i/o), and hardware performance (measured in millions of floating point operations per second) for the CCSD calculation. In addition, theoretical factors of reduction due to symmetry (FRS) were computed from the total number of floating point operations (this quantity can easily be obtained from the Cray perfrace utility) and these are compared with the cpu time ratios actually achieved.

The most notable feature of the data presented in Table I is that the theoretical values of FRS are indeed close to h^2 in most cases. Again, this asymptotic limit is only actually achieved when the symmetry blocking of the orbitals is optimum. However, values of $\approx 0.7h^2$ are achieved even in cases where the partitioning of molecular orbitals according to irreducible representation is far from regular, such as in DZP ozone which has 21, 7, 15, and 5 orbitals of a_1 , a_2 , b_1 , and b_2 symmetries, respectively. For octahedral N_8 , where ten orbitals transform as each irreducible representation of the D_{2h} point group, the value of FRS is quite close to the

TABLE I. Computation times and hardware requirements for a single iteration of the CCSD equations for a variety of chemical systems. All calculations were performed on a Cray-YMP supercomputer, using routines compiled with the CFT77 Fortran compiler. Timings are given in seconds, and the meaning of the values in each column is discussed in the main text.

Molecule and state	Reference function	No. of basis functions	Point group	cpu time per cycle	Hardware performance (megaflops)	Theoretical FRS	Achieved FRS
FOOF(1A)	RHF	64	C_1	37.0	271.4	1.0	1.0
			C_2	11.1	230.2	3.9	3.3
$B_2H_6(^1A_g)$	RHF	76	C_1	16.7	240.4	1.0	1.0
			D_{2h}	1.0	97.3	40.0	16.9
		162	D_{2h}	8.1	160.3
$O_3(^1A_1)$	RHF	48	C_1	7.3	227.8	1.0	1.0
			C_{2v}	1.0	138.5	11.6	7.1
		78	C_1	40.9	265.3	1.0	1.0
			C_{2v}	4.5	193.9	12.4	9.0
$CF_2(^3B_2)$	UHF	78	C_1	112.2	275.4	1.0	1.0
			C_{2v}	11.6	209.0	12.7	9.7
$N_8(^1A_g)$	RHF	80	C_1	213.3	269.1	1.0	1.0
			C_s	61.8	234.3	4.0	3.5
			C_{2v}	16.2	227.4	15.6	13.2
			D_{2h}	5.6	170.3	60.2	38.2

square of h , which is 64. Note however that the overall performance rate in megaflops is always largest in C_1 calculations, resulting in achieved values of FRS which are smaller than the theoretical limit. Although this may be a bit confusing to some readers, it is expected on any vector computer and is due to the fact that these machines operate optimally when the vector lengths are very long. Calculations using symmetry necessarily involve shorter vector lengths and consequently run at lower megaflop rates than those run in C_1 . For the contractions which scale as the sixth power of the number of basis functions, the vectors are long in either case and both C_1 and full symmetry runs achieve 300–310 megaflops for these terms, which is equal to the theoretical top speed of the Cray-YMP supercomputer in single processor mode. Nevertheless, in many of the fifth power steps the penalty for short vector lengths is relatively severe. On scalar machines, however, the size of matrices involved in matrix multiplies is immaterial, and the cpu ratios will be similar to the theoretical FRS. In addition, for very large calculations, all vectors will be fairly long and the actual savings will asymptotically approach the theoretical FRS as a limit. Unfortunately, C_1 calculations with large basis sets such as that used in the final diborane example in Table I and the calculations on cubane presented in the following section are not possible with the core memory and disk space available at several supercomputer centers, and no comparisons for such cases can be presented here.

It should be pointed out that the principal objective of any quantum chemical program development is to minimize the amount of cpu time needed to complete a task, rather than to increase the rate at which the floating point operations are performed. In our program, the algorithms have been designed to reduce the number of operations as much as possible by exploiting symmetry, with the vectorization of all subroutines resulting in the highest megaflop rate possible for the size of the problem. By going to lower symmetry,

somewhat more efficient floating point performance can indeed be achieved, but at the expense of increasing the number of operations by a factor of $\approx h^2$. An additional important feature is that the DPD minimizes the amount of core memory usage while still retaining a high level of simplicity in the algorithms used to compute the contractions.

V. APPLICATION TO CUBANE

As an application of the newly developed ACES II program system, we have chosen to study the cubane (C_8H_8) molecule. Since its original synthesis,²⁹ this system has attracted considerable interest because of its high (octahedral) symmetry and interesting chemical reactivity.³⁰ A number of physical studies of unsubstituted cubane have been published. A single crystal x-ray diffraction study by Fleischer³¹ confirmed the O_h symmetry of the molecule and found a carbon-carbon internuclear distance (1.55 Å) typical of that for C–C single bonds. A decade ago, the infrared and Raman spectrum of cubane was collected by Della *et al.*³² who were able to assign most of the fundamental frequencies. Later, Cole *et al.* determined reasonable values for the rotation constant using Fourier transform interferometry.³³ Some of the remaining uncertainties regarding the vibrational spectra were addressed in a high resolution laser diode study, carried out by Pine *et al.*,³⁴ who also reported a vibrationally averaged C–C distance of 1.565 Å, slightly longer than that found in Ref. 31. A year later, accurate mean internuclear distances of 1.575 ± 0.001 [(C–C)] and 1.100 ± 0.004 [(C–H)] were obtained by Almennigen *et al.* in an electron diffraction experiment.³⁵ In addition, the photoelectron spectrum of cubane has been obtained by Bischof *et al.*³⁶ and assigned with reasonable certainty.

Because of the relatively large size of the cubane molecule, theoretical calculations have mostly been limited to the SCF level. Almlöf and Jonvik determined the equilibrium

structure and totally symmetric harmonic vibrational frequencies at the SCF level with a double-zeta plus polarization (DZP) basis set, and also reported ionization potentials (IPs) obtained with Koopmans' approximation ($IP = -\epsilon_{SCF}$).³⁷ Similar calculations were reported by Schulman and Disch,³⁸ who optimized the structure at the SCF level with a similar basis set, and by Scamehorn *et al.*, who also reported Δ SCF values for the ionization potential.³⁹ While the bond lengths and harmonic frequencies determined in these studies are in satisfactory agreement with experiment, the IPs obtained from Koopmans' theorem are in relatively poor accord with those determined spectroscopically. Almlöf and Jonvik proposed an alternative assignment, but noted that their calculations were not accurate enough to confirm or disprove the experimental assignments.

In our calculations, we have determined the equilibrium geometry and totally symmetric harmonic force field of cubane at the CCSD level with the 6-31G* basis set,⁴⁰ and have calculated the first few IPs at the same level with a DZP basis which is well suited for correlated calculations.⁴¹ The geometry was optimized with the Newton-Raphson method, using numerically calculated gradients and second derivative matrices. The totally symmetric force field was calculated from the central difference formulas given in Ref. 42, and the a_{1g} harmonic vibrational frequencies were computed with the *GF* matrix formulation of Wilson, Decius, and Cross.⁴³ Configurations resulting from excitation of the electrons in the eight lowest molecular orbitals (core orbitals) were excluded from the configuration space in all calculations.

Calculated equilibrium internuclear distances, harmonic force constants and vibrational frequencies are displayed in Table II, where they may be compared to values obtained in other theoretical work and to experimental quantities. As typically observed, the bond distances obtained in correlated calculations are somewhat longer than those obtained with similar basis sets at the SCF level, with corresponding decreases in the symmetric stretching frequencies. The magnitude of the corrections due to correlation are representative

of that observed in previous studies at the CCSD⁴⁴ and SDQ-MBPT(4)⁴⁵⁻⁴⁷ levels for molecules containing single bonds. Despite the fortuitous near coincidence of 6-31G*-CCSD bond lengths and those obtained from electron diffraction, a direct comparison is inappropriate since the latter values correspond to thermally averaged internuclear distances and are expected to be somewhat longer than the true values of r_e . The overestimation of r_e in our calculations is probably due primarily to basis set effects since it is well known that expansion of the basis typically leads to a contraction of bonded distances.⁴⁸ Agreement between the CCSD harmonic vibrational frequencies and experimental results is imperfect, of course, largely because the observed frequencies are determined by the complete vibrational force field of the molecule while the theoretical values result from the harmonic approximation. Nevertheless, the difference between the two sets of values is typical of that observed in calculations carried out at comparable levels of theory.⁴⁴⁻⁴⁷ Therefore, our calculations provide support for the assignments of the a_{1g} modes in the Raman spectrum.³² Note that the diagonal CCSD harmonic force constants in Table II are higher than those obtained by an empirical fitting procedure.⁴⁹ It is probable that the theoretical values in Table II are more accurate since the results of Ref. 49 were obtained by a fit to the fundamental frequencies. The true harmonic frequencies are of course higher than the observed band positions, so this procedure includes a systematic bias which leads to a general underestimation of harmonic force constants.

Vertical ionization potentials were obtained by evaluating the CCSD energy of different states of the cation at the optimized 6-31G*-CCSD geometry of the neutral molecule. Zeroth-order functions for the different states were obtained with the UHF model, through use of different orbital occupations. Calculated IPs leading to low-lying states of the cation are presented in Table III, where they are compared with both experimental values and those obtained from Koopmans' approximation (the values of Ref. 37 are not included since they are essentially identical to the Koopmans' IPs obtained in the present work). Unlike the pre-

TABLE II. Equilibrium geometry, totally symmetric harmonic symmetric force constants and vibrational frequencies for cubane. Bond lengths in Ångstroms, force constants in mdyne/Å and frequencies in wave numbers. The symmetry coordinates follow the conventions of Ref. 53.

	r_e (CC)	r_e (CH)	F_{11}	F_{22}	F_{12}	ω_1	ω_2
DZP-SCF ^a	1.570	1.081	^b	^b	^b	3324	1074
6-31G*-SCF ^c	1.562	1.082
6-31G*-CCSD	1.575	1.099	5.46	4.20	0.12	3168	1044
X-ray ^d	1.55 ^e	1.0-1.1 ^e
Spectroscopic ^f	1.565 ^e	^b	^b	^b	^b	2995 ^f	1002 ^f
Electron Diffraction ^g	1.575 ^e	1.100 ^e
Emp. Force Field ^h	4.99	3.83	0.45	3003	999

^a From Ref. 37.

^b Not reported.

^c From Ref. 38.

^d From Ref. 31.

^e Thermally averaged internuclear distances.

^f From Refs. 32 and 34.

^g From Ref. 35.

^h From Ref. 49.

TABLE III. Vertical ionization potentials for cubane, in electron volts (eV). Koopmans' and CCSD theoretical values obtained with the DZP basis set.

Upper state	Ionization potential (eV)		
	Koopman's	CCSD	Experiment ^a
${}^2T_{2g}$	10.39	9.55	9.0–9.5
${}^2T_{2u}$	10.58	9.77	9.0–9.5
2E_g	15.72	14.41	13.7
${}^2A_{2u}$	17.35	16.02	15.6
${}^2A_{1g}$	19.23	17.79	17.6

^aFrom Ref. 36.

vious Koopmans' results that raised some doubt about the experimental interpretation, the present CCSD calculations provide strong support for the assignments of Bischof *et al.*,³⁶ with the CCSD and experimental IPs differing by less than 0.71 eV in all cases.

The CCSD calculations on cubane were performed on a Cray-YMP supercomputer. For the DZP basis (160 active orbitals), the RHF CCSD calculations required 36 s per cycle, while the open-shell UHF calculations required 93 s per cycle. Using the reduced linear equation method (RLE),²⁸ eleven cycles were required to converge the CCSD equations for the neutral molecule, and 13–16 were needed in the UHF calculations for the cations. All calculations used full matrix in-core algorithms and required only a few megawords of core memory.

VI. CONCLUDING REMARKS

In this paper, we have outlined a powerful scheme for including point group symmetry in coupled-cluster and many-body perturbation theory calculations. The method, which we term the direct product decomposition (DPD), provides an automatic means for exploiting symmetry sparsity in the cluster amplitude and Fock matrix or integral (or the corresponding intermediate) matrices and is amenable to an efficient computational implementation. Other work of three years ago showed savings which exceeded the order of the group.¹¹ Unlike the DPD method, however, the loop restriction algorithm used there is not easily parallelized nor can it be efficiently vectorized since inner loop index testing is required if symmetry sparsity is to be exploited in both T and \mathcal{W} matrices. In addition, the present paper is the first to analyze the equations in terms of symmetry and to determine the source of the improvement as well as its asymptotic limit. A clear demonstration has been given to show that the significant reduction in the number of floating point operations is an intrinsic property of the contraction process. As a result, the DPD treatment of symmetry is equally applicable to linear and nonlinear coupled-cluster models as well as to finite order many-body perturbation theory. As shown, it is also applicable to open-shell UHF and non-Hartree-Fock based CC/MBPT methods. With minor modification, our coupled-cluster code could also be used to efficiently compute correlation energies at the configuration interaction singles and doubles (CISD) level as a direct CI Brillouin-Wigner perturbation calculation.

The full incorporation of symmetry in coupled-cluster

and MBPT energy and gradient programs tremendously increases the range of problems which can be treated with these high-level techniques. For example, the calculations on cubane presented in the previous section used only modest amounts of cpu time and core memory on a Cray YMP and could easily be performed on much smaller computers. Highly symmetric molecules containing a few tens of atoms no longer represent a formidable computational obstacle since the cpu and memory requirements of calculations using the DPD approach are not limited by the total number of basis functions but rather by the maximum value of the $\mathcal{N}(p)$ defined by Eq. (14). When our implementation of CC/MBPT gradients using the DPD method is completed, we plan to apply these techniques to studies of symmetric clusters and prototype transition metal complexes.

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APPENDIX

For the most part, our computational implementation of the CCSD model strictly follows the intermediate formalism¹⁴ discussed in the main section. There are several reasons for choosing this formalism as the basis of a computational implementation. First, the algorithm is computationally efficient, since the number of required operations is minimized by grouping various terms together. Second, the clear structure of the CC equations and the relatively small number of terms in this formalism allows much simpler coding than if the unfactored CC equations are implemented in a straightforward fashion. Third, generalization to non-HF reference functions is entirely straightforward in the present approach, since only a few terms involving the appropriate Fock matrix elements need to be added and all of these involve negligible computational cost.

However, in one case our implementation differs slightly from the formalism given in the main section [Eqs. (1)–(8)]. The \mathcal{W}_{abef} intermediates defined by Eq. (7) are actually never formed and stored on disk. In most cases, the $\langle ab || cd \rangle$ integral lists are largest and thus become the bottleneck with respect to the disk space requirement of a CCSD calculation. The additional storage of \mathcal{W}_{abef} lists would severely restrict the applicability of the CCSD approach and should therefore be avoided. At the UHF level, this consideration is even more important since three different \mathcal{W}_{abef} lists would be required in addition to the three $\langle ab || cd \rangle$ lists.

An analysis of the CCSD equations shows that the contraction of $\frac{1}{4} \sum_{mn} \tau_{mn}^{ab} \langle ef || mn \rangle$ (the last term of \mathcal{W}_{abef}) with the amplitudes τ_{ij}^{ef} is identical to the contraction of $\frac{1}{4} \sum_{ef} \tau_{ij}^{ef} \langle ef || mn \rangle$ (the last term of the intermediate \mathcal{W}_{mnij}) with τ_{mn}^{ab} . Evaluation of this part of the intermediate \mathcal{W}_{abef} can therefore be avoided by simply changing the corresponding factor to $\frac{1}{2}$ in the definition of the \mathcal{W}_{mnij} intermediate. The second contribution to the intermediate is either calcu-

lated “on the fly” directly before the integrals $\langle ab || ef \rangle$ are contracted with the amplitudes or by means of an alternative algorithm as

$$Z_{ij}^{bf} = \sum_{ef} \tau_{ij}^{ef} \langle mn || ef \rangle \quad (\text{A1})$$

and

$$\Delta t_{ij}^{ab} = \sum_m t_m^a Z_{ij}^{mb} \quad (\text{A2})$$

which is however slightly more expensive. For large systems, the first approach is preferred.

Evaluation of all remaining quantities in the CCSD amplitude equations exactly follows the outline given by Eqs. (1)–(8). CCD and other approximate CC schemes⁵⁰ including the QCISD approach⁵¹ are easily obtained within our implementation of the CCSD model by skipping appropriate terms in the amplitude and energy expressions. For example, all terms involving single excitations are dropped in CCD, while all nonlinear terms involving T_1 except $T_1 \leftarrow T_1 T_2$ are omitted in QCISD. Both of these approaches and all other approximate models benefit in the same way as the CCSD approach by using the intermediate formalism.

For finite-order perturbation theory however, the intermediate formalism offers no advantage. MBPT(3) is obtained by performing one CC iteration where all nonlinear terms are skipped. All intermediates reduce in this case to

the corresponding Fock matrix elements and two-electron integrals, respectively.

For SDQ-MBPT(4), both the linear terms and the non-linear quadruple contributions have to be formed using the first-order amplitudes. Since the resulting increments from the first CC iteration and the quadruple part are used in different ways to evaluate the various pieces of the correlation energy, both contributions have to be calculated separately and cannot be combined in the same way as in the CCSD model.

For RHF reference functions, spin adaptation can be used to reduce the number of required operations significantly. Although we have implemented the CCSD equations in a spin-orbital approach, spin adaptation of most terms is easily incorporated by skipping loops and preparing the appropriate linear combination of integrals and/or amplitudes before the evaluation of a contraction. Only the ladder contributions require some additional consideration with regard to spin adaptation. By splitting integrals and amplitudes into symmetric and antisymmetric components, Pulay *et al.*,⁵² were able to show that only $\frac{1}{4}n^2N^4$ and $\frac{1}{4}n^4N^2$ operations were required to evaluate the particle–particle and hole–hole ladder contributions, respectively. We have not yet implemented this scheme in our code, however, and the ladder contributions are currently evaluated with $\frac{1}{2}n^2N^4$ and $\frac{1}{2}n^4N^2$ operations. This simplification can easily be obtained by restricting the loop for the increments to $i \leq j$ and a, b .

TABLE IV. Number of operations required for various terms of the CCSD equation for UHF and spin-adapted RHF reference functions. n_α and n_β (N_α and N_β) refer to the number of occupied (virtual) alpha and beta orbitals, respectively.

Contribution	Number of operations in UHF	Number of operations in RHF
f^0 terms:		
$\mathcal{W}_{abef} \rightarrow \Delta t_{ij}^{ab}$	$\frac{1}{8}n_\alpha^2N_\alpha^4 + \frac{1}{8}n_\beta^2N_\beta^4 + n_\alpha n_\beta N_\alpha^2 N_\beta^2$	$\frac{1}{4}n^2N^4$
$t_{ij}^{ab} \rightarrow \mathcal{W}_{mbej}$	$2 \times \left[\begin{aligned} &n_\alpha^3N_\alpha^3 + n_\beta^3N_\beta^3 + 3n_\alpha^2n_\beta N_\alpha^2N_\beta \\ &+ 3n_\beta^2n_\alpha N_\beta^2N_\alpha + n_\alpha^2n_\beta N_\alpha N_\beta^2 + n_\alpha n_\beta^2 N_\alpha^2N_\beta \end{aligned} \right]$	$2 \times 2n^3N^3$
$\mathcal{W}_{mbej} \rightarrow \Delta t_{ij}^{ab}$		
$t_{ij}^{ab} \rightarrow \mathcal{W}_{mnij}$	$2 \times \left[\frac{1}{8}n_\alpha^4N_\alpha^2 + \frac{1}{8}n_\beta^4N_\beta^2 + n_\alpha^2n_\beta^2N_\alpha N_\beta \right]$	$2 \times \frac{1}{4}n^4N^2$
$\mathcal{W}_{mnij} \rightarrow \Delta t_{ij}^{ab}$		
f^1 terms:		
$t_i^a \rightarrow \mathcal{W}_{abef}$	$n_\alpha N_\alpha^2 N_\beta^2 + n_\beta N_\alpha^2 N_\beta^2 + \frac{1}{2}n_\alpha N_\alpha^4 + \frac{1}{2}n_\beta N_\beta^4$	nN^4
$t_i^a \rightarrow \mathcal{W}_{mbej}$	$n_\alpha^2N_\alpha^3 + n_\beta^2N_\beta^3 + n_\alpha^2N_\alpha N_\beta^2 + n_\beta^2N_\alpha^2N_\beta$ $+ n_\alpha n_\beta N_\alpha^2N_\beta + n_\alpha n_\beta N_\alpha N_\beta^2$	$2n^3N^3$
$t_{ij}^{ab} \rightarrow \mathcal{F}_{ae}$	$4 \times \left[\frac{1}{2}n_\alpha^2N_\alpha^3 + \frac{1}{2}n_\beta^2N_\beta^3 + n_\alpha n_\beta N_\alpha N_\beta^2 + n_\alpha n_\beta N_\alpha^2N_\beta \right]$	$4 \times n^2N^3$
$t_{ij}^{ab} \rightarrow \Delta t_i^a$		
$\mathcal{F}_{ae} \rightarrow \Delta t_{ij}^{ab}$		
$t_i^a \rightarrow \Delta t_{ij}^{ab}$		
$t_{ij}^{ab} \rightarrow \mathcal{F}_{mi}$	$4 \times \left[\frac{1}{2}n_\alpha^3N_\alpha^2 + \frac{1}{2}n_\beta^3N_\beta^2 + n_\alpha^2n_\beta N_\alpha N_\beta + n_\alpha n_\beta^2 N_\alpha N_\beta \right]$	$4 \times n^3N^2$
$t_{ij}^{ab} \rightarrow \Delta t_i^a$		
$\mathcal{F}_{mi} \rightarrow \Delta t_{ij}^{ab}$		
$t_i^a \rightarrow \Delta t_{ij}^{ab}$		
$t_i^a t_j^b \rightarrow \Delta t_{ij}^{ab}$	$2n_\alpha^3N_\alpha^2 + 2n_\beta^3N_\beta^2 + N_\alpha^2n_\alpha n_\beta^2 + N_\beta^2n_\alpha^2n_\beta$ $+ 3N_\alpha N_\beta n_\alpha n_\beta^2 + 3N_\alpha N_\beta n_\alpha^2n_\beta$	$4n^3N^2$
$t_i^a \rightarrow \mathcal{W}_{mbej}$	$n_\alpha^3N_\alpha^2 + n_\beta^3N_\beta^2 + n_\alpha n_\beta^2 N_\alpha^2 + n_\alpha^2n_\beta N_\beta^2$ $+ n_\alpha n_\beta^2 N_\alpha N_\beta + n_\alpha^2n_\beta N_\alpha N_\beta$	$2n^3N^2$
$t_i^a \rightarrow \mathcal{W}_{mnij}$	$N_\alpha n_\alpha^2 n_\beta^2 + N_\beta n_\beta^2 n_\alpha^2 + \frac{1}{2}N_\alpha n_\alpha^4 + \frac{1}{2}N_\beta n_\beta^4$	n^4N

Since there is some confusion in the literature about the required number of operations for CCSD calculations (particularly for UHF reference functions), we present a detailed analysis of the floating point requirements for both UHF and spin-adapted RHF CCSD calculations. Table IV summarizes these results where n_α (n_β) denotes the number of occupied α (β) orbitals and N_α (N_β) the number of virtual α (β) orbitals. We consider only those terms which have a computational requirement that scales as $n^a N^b$, where $a + b \geq 5$.

With the assumption that $n_\alpha \approx n_\beta \approx n$ and $N_\alpha \approx N_\beta \approx N$, the number of operations per CCSD iteration for UHF reference functions is approximately given by

$$\frac{5}{2}n^4N^2 + \frac{3}{2}n^2N^4 + 20n^3N^3 + 3nN^4 + 18n^2N^3 + 30n^3N^2 + 3nN^4, \quad (\text{A3})$$

while for RHF with an optimal spin-adapted scheme, we obtain

$$\frac{1}{2}n^4N^2 + \frac{1}{2}n^2N^4 + 4n^3N^3 + nN^4 + 6n^2N^3 + 10n^3N^2 + n^4N. \quad (\text{A4})$$

Thus, a RHF based CCSD calculation requires roughly 4–5 times fewer operations per iteration than a corresponding UHF CCSD calculation. It should be pointed out that the number of operations for some of the fifth power terms are somewhat different than previously given in the literature.¹⁵ This is due to somewhat different factorization schemes, and the present approach is preferred when N is larger than $3n$ which is usually the case. For CCD, QCISD and finite-order perturbation theory [MBPT(3) and SDQ-MBPT(4)], the number of operations can be obtained from Table IV by skipping some contributions and doubling others to account for the separate calculation of the quadruple contribution to the energy.

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⁴See, for example, P. Carsky, B. A. Hess, and L. J. Schaad, *J. Comp. Chem.* **5**, 280 (1984), and references therein.

⁵T. Takada, M. Dupuis, and H. F. King, *J. Comp. Chem.* **4**, 234 (1983).

⁶The original CCD and CCSD programs of Bartlett and Purvis [R. J. Bartlett and G. D. Purvis, *Int. J. Quantum Chem.* **14**, 561 (1978) (CCD) and G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.* **76**, 7918 (1982) (CCSD)] included a "passive" treatment of symmetry in which those t_{ij}^{ab} found to fall below a certain threshold in the first-order wave function were not recalculated in subsequent CC iterations and no zero integrals were processed. It should be pointed out that this is in principle equivalent to the approach of Ref. 7 for D_{2h} and its subgroups.

⁷P. Carsky, L. J. Schaad, B. A. Hess, M. Urban, and J. Noga, *J. Chem. Phys.* **87**, 411 (1987).

⁸R. J. Bartlett and D. M. Silver, in *Quantum Science*, edited by J. L. Calais, O. Goscinski, J. Linderberg, and Y. Öhrn (Plenum, New York, 1976), p. 393; R. J. Bartlett and I. Shavitt, *Chem. Phys. Lett.* **50**, 190 (1977).

⁹The exact ratio of floating point operations using symmetry and those which neglect it depends on the distribution of the number of orbitals belonging to each irreducible representation and approaches h as the number of orbitals in each symmetry block becomes close to N/h , where N is the total number of orbitals.

¹⁰U. Kaldor (personal communication).

¹¹G. E. Scuseria, A. C. Scheiner, T. J. Lee, J. E. Rice, and H. F. Schaefer, *J. Chem. Phys.* **86**, 2881 (1987).

¹²The referee has pointed out that an h^2 reduction in operations is also possible for configuration interaction calculations. Consequently, potential speedups in these calculations is as great as that which can be obtained for

CC methods, despite what is said in Ref. 11.

¹³See, for example, S. A. Kucharski and R. J. Bartlett, *Adv. Quantum Chem.* **18**, 281 (1986), and references therein.

¹⁴S. A. Kucharski and R. J. Bartlett, *Theoret. Chim. Acta* (in press). See also J. Noga and R. J. Bartlett, *J. Chem. Phys.* **86**, 7041 (1987) and Ref. 16.

¹⁵G. E. Scuseria, C. L. Janssen, and H. F. Schaefer, *J. Chem. Phys.* **89**, 7382 (1988).

¹⁶J. Noga, R. J. Bartlett, and M. Urban, *Chem. Phys. Lett.* **134**, 126 (1987).

¹⁷J. D. Watts and R. J. Bartlett, *J. Chem. Phys.* **93**, 6104 (1990).

¹⁸Note that the two elements of the double direct product need not be of the form Γ_{pq} . For example, the double direct products used for the contraction $Z_{pq}^a = \sum_{ik} t_{ik}^{cd} \langle kc || da \rangle$ is $\Gamma_{kcd} \otimes \Gamma_i$ and $\Gamma_{kcd} \otimes \Gamma_a$, and $\Gamma_{kcd} = \Gamma_i = \Gamma_a$ must be satisfied.

¹⁹J. F. Stanton (unpublished notes).

²⁰This is strictly true only for D_{2h} and subgroups. In addition to symmetry zeroes, redundancies exist among amplitudes and integrals involving degenerate orbitals for groups which contain degenerate representations. Consequently, a DPD model incorporating the ideas of Carsky *et al.* will offer additional advantages over exploitation of sparsity due to symmetry since no redundant terms will be included in the summations. The term "symmetry sparsity" is used throughout this manuscript and refers to the elements of a matrix which are *rigorously* zero by symmetry. This concept should not be confused with sparsity which arises from spatial extent and small overlap of molecular orbitals in which some of the quantities involved in the calculation can become negligible in magnitude.

²¹ACES II is an entirely new program package which will replace ACES (Ref. 23). Elements of this package are the VMOL integral program written by P. R. Taylor and J. Almlöf; the GRNFC SFC program written by G. D. Purvis and R. J. Bartlett; integral transformation, correlation energy, and gradient codes written by J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett and a geometry optimization and vibrational analysis package written by J. F. Stanton and D. E. Bernholdt.

²²Throughout this paper, we follow the convention that the sequence of values corresponding to the quantity Q_{pqrs} is ordered such that the leftmost index (p) varies most rapidly, while the rightmost index (s) is the slowest to change. For example, the fifth element in a sequence of values corresponding to a $5 \times 5 \times 5 \times 5$ array Q is Q_{5111} , the 21st element is Q_{1511} , the 101st element is Q_{1151} , etc. This is the standard adopted in the FORTRAN programming language, and its use facilitates the discussion of our computational implementation of the DPD method.

²³ACES: *An ab initio Program System*, authored by R. J. Bartlett, D. E. Bernholdt, S. J. Cole, G. B. Fitzgerald, R. J. Harrison, D. H. Magers, W. D. Laidig, Y. S. Lee, R. P. Mattie, G. D. Purvis, M. Rittby, E. A. Salter, C. Sosa, J. F. Stanton, G. W. Trucks, and J. D. Watts, Quantum Theory Project, University of Florida, 1989.

²⁴T. J. Lee and J. E. Rice, *Chem. Phys. Lett.* **150**, 406 (1988).

²⁵It is important to realize that although the integrals are treated as the block-diagonal two-dimensional matrix $I(\bar{m}\bar{b}\bar{e},f)$, this does not correspond to a specific symmetry subblock of a $\Gamma_{\bar{m}\bar{b}\bar{e}} = \Gamma_f$ DPD. In this case, the $\Gamma_{\bar{m}\bar{b}} = \Gamma_f$ DPD still applies. However, for each subblock of the I matrix, $\Gamma_f = \Gamma_{\bar{m}\bar{b}\bar{e}}$, but only a specific subset of the appropriate $\bar{m}\bar{b}\bar{e}$ sets are included, namely, those for which $\Gamma_{\bar{m}\bar{e}} = \Gamma_a$. The treatment of the $I(\alpha|\bar{m}\bar{b} - \bar{e}^1)$ integrals as an $I(\bar{m}\bar{b}\bar{e},f)$ matrix as well as the process of writing $Z(\bar{m}\bar{b}\bar{e},j)$ as a $Z(\bar{m}\bar{b},\bar{e}j)$ matrix is simple only if f and j are the most slowly varying indices in the respective one-dimensional arrays which are used computationally. In this case, the sequence of values in the arrays which correspond to the two different schemes are identical and the two may be trivially interconverted by means of specific offsets marking the beginning of each matrix column. The simplicity of this exchange serves as the motivation for the manipulation performed in step 4.

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