

The Direct-Product Decomposition Approach for Symmetry Exploitation in Many-Body Methods in Case of Non-Abelian Point Groups

Published as part of *The Journal of Physical Chemistry A* special issue "John F. Stanton Memorial Issue".

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Cite This: *J. Phys. Chem. A* 2026, 130, 2918–2928



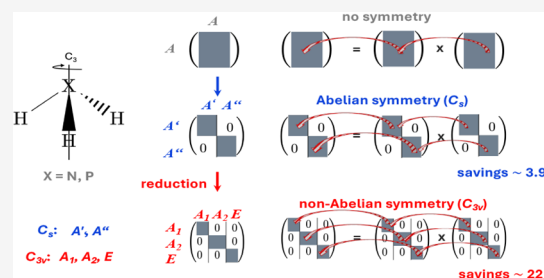
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ABSTRACT: We demonstrate, for the specific case of C_{3v} , how the direct-product decomposition scheme for the treatment of symmetry in coupled-cluster (CC) calculations can be extended to non-Abelian point groups. We show that for the two-electron integrals and CC amplitudes, a block structure can be obtained by resolving the reducible products of two irreducible representations into their irreducible representations. To deal with the necessary re-sorts of the ordering of the two-electron integrals and amplitudes, spin adaptation, and the $O(M^5)$ contractions (with M as the number of basis functions) of a CC calculation, we suggest a strategy that uses both the reduced and nonreduced representations of the corresponding quantities and switches back and forth between them. While the reduced representations are the ones used in the $O(M^6)$ contractions, the other steps are better carried out in the nonreduced representation. Our pilot implementation of the CC singles and doubles method confirms in test calculations for NH_3 and PH_3 using different basis sets that significant savings (of more than 20 compared to treatments without symmetry and about 5 compared to treatments using C_s symmetry) are possible and these findings suggest that the exploitation of non-Abelian symmetry would render CC computations on large, highly symmetric molecules possible.



1. INTRODUCTION

Symmetry is a very important concept in all areas of natural science.¹ For chemistry, symmetry is useful for the explanation of chemical bonding (within molecular-orbital theory² or ligand-field theory³), the interpretation of spectra via selection rules,⁴ the explanation of chemical reactivity via the Woodward–Hoffmann rules,⁵ etc. However, symmetry can be also exploited to facilitate and speed up computational simulations of all kinds. The main point is then that the use of symmetry can lead to a reduction in the computational cost and thus make simulations faster or even feasible in the first place. This aspect of symmetry has turned out particularly useful in quantum chemistry, where computations often are very costly in terms of both computing time and memory requirement. Symmetry has been thus considered straight from the beginning⁶ and since then many publications have dealt with the use of symmetry in quantum-chemical computations.^{7–26}

The key in the exploitation of symmetry in quantum chemistry lies in the fact that the solutions of the electronic Schrödinger equation (and also of the Hartree–Fock (HF) equations, etc.) are required to have symmetry properties imposed by the underlying symmetry of the molecule. The solutions of the electronic Schrödinger equation, etc. thus have

to transform as one of the irreducible representations of the corresponding point group of the atom or molecule. Symmetry considerations furthermore lead to selection rules that render certain quantities (e.g., one- and two-electron integrals, amplitudes in perturbation and coupled-cluster (CC) theory, etc.) to vanish which can be exploited in quantum-chemical computations. The literature documents many examples for the usage of symmetry in quantum-chemical computations and impressive savings due to the exploitation of symmetry have been reported.

To be more specific, symmetry can be exploited in quantum-chemical computations in (a) the integral evaluation^{7,9,10,13,22} and the self-consistent-field (SCF) step,^{9,16,22} (b) the transformation of the integrals from the atomic-orbital (AO) to the molecular-orbital (MO) representation,^{11,20} and (c) within the

Received: January 15, 2026

Revised: March 10, 2026

Accepted: March 11, 2026

Published: March 26, 2026



ACS Publications

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American Chemical Society

2918

<https://doi.org/10.1021/acs.jpca.6c00311>
J. Phys. Chem. A 2026, 130, 2918–2928

electron-correlation treatment.^{18,19,23,25,26} In the first of the three tasks the challenge is to exploit symmetry in the evaluation and handling of quantities that are not necessarily symmetry-adapted (i.e., that do not transform as one of the irreducible representations of the point group of the molecule). This is due to the fact that the underlying AOs are not necessarily symmetry-adapted. On the other side, electron-correlation treatments are most often formulated in terms of MOs and all involved quantities (integrals and amplitudes in the case of CC computations, for example) are symmetry-adapted. For the treatment of the latter in CC computations, Stanton et al.¹⁸ devised an elegant and efficient scheme for the exploitation of symmetry in case of Abelian point groups (i.e., in order to be more precise D_{2h} and its subgroups). Their direct-product decomposition (DPD) scheme enables a symmetry blocking of all quantities and can be implemented without a significant overhead. However, the scheme in its original version is restricted to Abelian point groups, as it relies on the fact that the direct product of two irreducible representations is another irreducible representation, something which does no longer hold for non-Abelian point groups. Attempts to extend the DPD scheme to non-Abelian point groups can be traced back to the 90ies (unpublished work by Stanton and Gauss), but those attempts were never pushed to a working code.

In this paper, we resume this issue and reinvestigate the possibility to fully exploit non-Abelian point-group symmetry in electron-correlated calculations. We will report a pilot implementation of the CC singles and doubles (CCSD) method²⁷ and will demonstrate that the exploitation of non-Abelian point-group symmetry can lead to significant savings and, thus, is worthwhile to be considered.

We start our discussion in the next section (Section 2) by briefly reviewing the DPD scheme for exploiting symmetry in case of Abelian point groups. This is followed by a description of our proposed extension of the DPD scheme to the special case of C_{3v} symmetry, i.e., one of the simplest non-Abelian point groups. Details about our pilot program are given in Section 3, and in the result section (Section 4) we report and discuss the operation counts for CCSD computations on NH_3 and PH_3 using different basis sets. We conclude with a summary and an outlook (Section 5) and there in particular discuss the perspectives for a general implementation for arbitrary non-Abelian point groups.

2. SYMMETRY IN QUANTUM-CHEMICAL CALCULATIONS

2.1. General Concepts

Symmetry selection rules generally can be used to decide which quantities need to be computed, stored, and processed. For example, a quantity

$$A_{pqr\dots} = \int a_p a_q a_r \dots d\tau \quad (1)$$

where the functions $a_p, a_q, a_r, \dots$ can be classified according to the irreducible representations of the given point group and integration is over all variables (collectively referred to as τ), can only have a nonzero value if the direct product of the irreducible representations of the functions $a_p, a_q, a_r, \dots$ contains the totally symmetric representation.

In quantum chemistry, the molecular orbitals (MOs) ϕ_p are often obtained as solutions of the canonical HF equations and accordingly transform as the irreducible representations of the point group of the considered molecule. It is of advantage to

order them, occupied orbitals (indices $i, j, k, \dots$) and virtual orbitals (indices $a, b, c, \dots$) separately, so that those of the same irreducible representation are grouped together, i.e.,

$$\{\phi_1^{\text{irrep1}}, \phi_2^{\text{irrep1}} \dots \phi_{n_{\text{irrep1}}}^{\text{irrep1}}, \phi_1^{\text{irrep2}}, \phi_2^{\text{irrep2}} \dots \} \quad (2)$$

with $n_{\text{irrep1}}, n_{\text{irrep2}}, \dots$ as the number of occupied/virtual orbitals per irreducible representation. Using this ordering, two-dimensional objects such as, for example, the one-electron integrals (here and in the following we always assume that the operator that appears in the integrals transforms as the totally symmetric representation) acquire a block structure in the following referred to as block matrix (see Scheme 1).

Scheme 1. Block Structure of a Two-Dimensional Matrix in Case of C_{2v} Symmetry with Four Irreducible Representations

$$\begin{matrix} & A_1 & B_1 & B_2 & A_2 \\ \begin{matrix} A_1 \\ B_1 \\ B_2 \\ A_2 \end{matrix} & \begin{pmatrix} \blacksquare & 0 & 0 & 0 \\ 0 & \blacksquare & 0 & 0 \\ 0 & 0 & \blacksquare & 0 \\ 0 & 0 & 0 & \blacksquare \end{pmatrix} \end{matrix}$$

This block structure turns out to be useful also for matrix products, as the product of two block matrices is easily obtained by just multiplying the individual blocks with each other (see Scheme 2).

Scheme 2. Block-by-Block Multiplication of Two Block Matrices

For higher-dimensional quantities such as the two-electron integrals, amplitudes from CC computations, etc., the discussion is more involved, as a convenient block structure is not automatically obtained like in the case of the two-dimensional matrices.

2.2. Direct-Product Decomposition in the Case of Abelian Point Groups

In the case of Abelian point groups, all irreducible representations are one-dimensional and the direct product of two irreducible representations is again a one-dimensional irreducible representation. This property of Abelian point groups can be, as shown in ref 18, used to establish a block structure even for higher-dimensional matrices. Focusing on four-dimensional matrices (two-electron integrals, double-excitation amplitudes in CC computations, etc.) a block structure can be obtained by considering those matrices as two-dimensional objects with super indices formed from the original indices. The irreducible representation of the super index is then just the direct product of the indices that define the super index. For a two-electron integral (and in the same way for the double-excitation amplitudes t_{ij}^{ab})

$$\langle pq|rs\rangle = \int d^3r_1 \int d^3r_2 \varphi_p(\mathbf{r}_1) \varphi_q(\mathbf{r}_2) \frac{1}{r_{12}} \varphi_r(\mathbf{r}_1) \varphi_s(\mathbf{r}_2) \quad (3)$$

a two-dimensional quantity $I_{(pq);(rs)}$ can be defined with super indices formed from the indices p and q as well from r and s , respectively. Note that this is just one way to define a two-dimensional quantity, as other ordering such as $I(pr, qs)$, $I(ps, qr)$ are also possible. The actual choice depends on the targeted contraction and, for example, is different for the ladder and ring terms in CC treatments. For $I_{(pq);(rs)}$ a block structure is then obtained in the same way as for simple two-dimensional matrices (see Scheme 3).

Scheme 3. Block Structure of a Four-Dimensional Matrix in Case of C_{2v} Symmetry with Four Irreducible Representations^a

	A_1	B_1	B_2	A_2	
A_1					$A_1: A_1 \otimes A_1; B_1 \otimes B_1; B_2 \otimes B_2; A_2 \otimes A_2$
B_1					$B_1: B_1 \otimes A_1; A_1 \otimes B_1; A_2 \otimes B_2; B_2 \otimes A_2$
B_2					$B_2: B_2 \otimes A_1; A_2 \otimes B_1; A_1 \otimes B_2; B_1 \otimes A_2$
A_2					$A_2: A_2 \otimes A_1; B_2 \otimes B_1; B_1 \otimes B_2; A_1 \otimes A_2$

^aThe information on the right gives all products of two irreducible representations that correspond to a super index of given symmetry.

As this procedure results in a decomposition of the direct product of four irreducible representations in the direct product of two direct products of two irreducible representations, it has been coined direct-product decomposition (DPD) approach. The resulting block structure for four and higher-dimensional quantities significantly simplifies the exploitation of symmetry in electron-correlated computations, as a contraction like the

particle particle ladder (PPL) term in CC computations can now be performed in a block-wise manner. Figure 1 explains the procedure. The resulting savings are in the ideal case of the square of the order of the group and actual computations indeed show savings (in the operation count) close to the optimal value.¹⁸ The actual savings in the computation times, however, are somewhat lower, as the symmetry blocking reduces the size of the matrices and thus slows down (for example, when optimized BLAS routines are used for the multiplication) the speed of the calculations. Even more importantly, the DPD scheme enables the exploitation of symmetry with a minimum of overhead, as no extensive symmetry checks are needed after the used quantities have been “symmetry blocked”.

2.3. Extension of the Direct-Product Decomposition Scheme to C_{3v} Symmetry

The challenge when dealing with non-Abelian point group symmetries is that the direct product of two irreducible representations is generally no longer given by one irreducible representation but rather as a direct sum of several irreducible representations. For that reason a simple DPD as in the Abelian case does not lead to a useful block structure for higher-dimensional matrices. We will discuss this issue in the following for the specific case of C_{3v} . This point group contains 6 symmetry operations, namely E , C_3 , C_3^2 , σ_{v1} , σ_{v2} , and σ_{v3} . It has 3 irreducible representations (A_1 , A_2 , and E), i.e., two one-dimensional ones and a two-dimensional one. Its character table is given in Table 1 and the direct product of E with E , thus, is

$$E \otimes E = A_1 \oplus A_2 \oplus E \quad (4)$$

We will use in the following a particular choice for the E representation in the way that one component transforms in C_s (the largest Abelian subgroup of C_{3v}) as A' and the other as A'' . Accordingly, we denote these components as $E(A')$ and $E(A'')$. Note that the different components of higher-dimensional

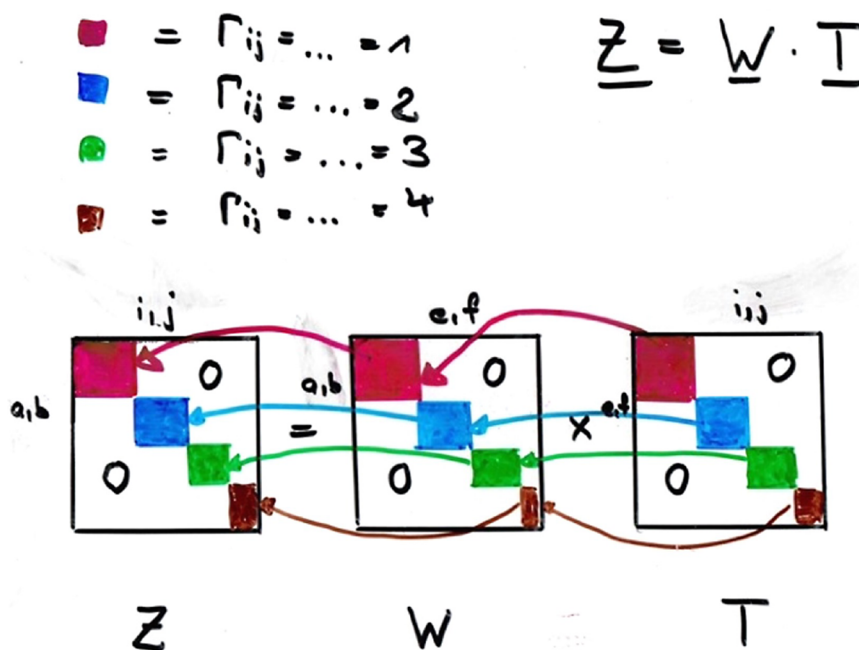


Figure 1. Slide from one of the author's talk (J.G. together with John F. Stanton, John D. Watts, and Rodney J. Bartlett) at the 31st Sanibel Symposium 1991 in St. Augustine, (Florida, USA) explaining the block-by-block multiplication in the PPL terms of CCSD within the DPD scheme.

Table 1. Character Table of the Non-Abelian Point Group C_{3v}

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

irreducible representations always can be chosen in such a manner and that in this way the discussion of C_{3v} suffices to illustrate our suggested adaption of the DPD scheme to non-Abelian symmetries. In addition, the phases of the different components of a degenerate irreducible representation need to be fixed such that the phase relations between them are consistent (can be done in the SCF procedure after the diagonalization of the Fock matrix).¹⁵ However, our discussion does not apply to complex Abelian point groups (e.g., C_3) which in a real representation also have higher-dimensional irreducible representations. The reason is that we exploit that the different components of a degenerate irreducible representation belong in the largest real Abelian subgroup to different irreducible representations and this, for example, clearly is not the case for C_3 . For a treatment of complex Abelian point-group symmetry in the framework of quantum-chemistry codes that can deal with complex wave function parameters, see ref 28.

A straightforward application of the DPD scheme would yield for four-index quantities such as the two-electron integrals to the block structure shown in Scheme 4 which apparently contains off-diagonal blocks and thus is not particularly useful for performing contractions in electron-correlated computations. Another problem of this block structure is the redundancy of information, i.e., integrals with the same value appear twice which is caused by the two-dimensional E representation. A diagonal block structure, however, is recovered if the direct product $E \otimes E$ is reduced, which can be done using projection operators²⁴ and leads to

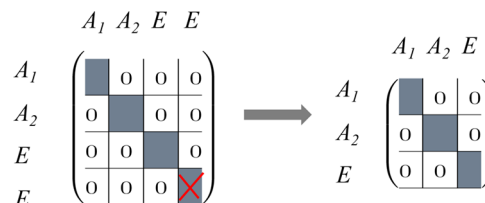
$$E \otimes E(A_1) = \frac{1}{\sqrt{2}}E(A') \cdot E(A') + \frac{1}{\sqrt{2}}E(A'') \cdot E(A'') \quad (5)$$

$$E \otimes E(A_2) = \frac{1}{\sqrt{2}}E(A') \cdot E(A'') - \frac{1}{\sqrt{2}}E(A'') \cdot E(A') \quad (6)$$

$$E \otimes E(E, \text{first component}) = \frac{1}{\sqrt{2}}E(A') \cdot E(A') - \frac{1}{\sqrt{2}}E(A'') \cdot E(A'') \quad (7)$$

$$E \otimes E(E, \text{second component}) = -\frac{1}{\sqrt{2}}E(A') \cdot E(A'') - \frac{1}{\sqrt{2}}E(A'') \cdot E(A') \quad (8)$$

With the reduction carried out, a diagonal block structure as shown in Scheme 5 can be recovered and the redundancy in the E blocks can be eliminated by simply dropping the second E block.

Scheme 5. Block Structure of a Four-Dimensional Matrix in Case of C_{3v} Symmetry after Reduction with Three Irreducible Representations; the Block That Has Been Crossed Out Is Redundant and Can Be Skipped^a

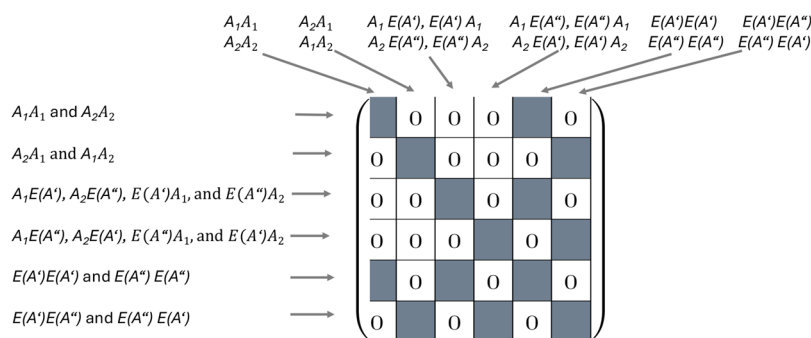
^aThe two E blocks in the first matrix corresponds to the blocks containing the first and second component of the E representation, respectively.

The reduced DPD representation is obtained by first sorting the nonreduced quantities (in case of the two-electron integrals the integrals obtained in an integral transformation using the largest Abelian subgroup, i.e., in our case C_v symmetry) in such a manner that the $I(E(A')E(A'), E(A')E(A'))$ elements are in the A_1 block, the $I(E(A')E(A''), E(A')E(A''))$ elements in the A_2 block and the $I(E(A')EA'), E(A'')E(A''))$ elements in the E block (see Scheme 6). Note that we already at this point do not need all elements of (EE, EE) type and in this way eliminate redundancies. Redundancies are also avoided by just storing those of $I(E(A')A_1, E(A')A_1)$ and $I(E(A')A_2, E(A')A_2)$ type and not the redundant $I(E(A'')A_1, E(A'')A_1)$ and $I(E(A'')A_2, E(A'')A_2)$ elements.

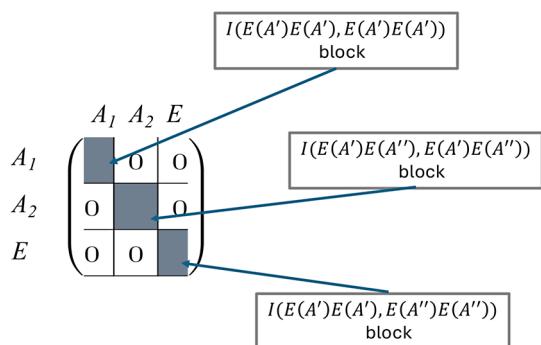
From this nonreduced representation the reduced one is easily obtained via

$$(E \times E)(A_1) \cdot (E \times E)(A_1) = (E(A') \times E(A')) \cdot (E(A') \times E(A')) + (E(A') \times E(A'')) \cdot (E(A'') \times E(A'')) \quad (9)$$

$$(E \times E)(E) \cdot (E \times E)(E) = (E(A') \times E(A')) \cdot (E(A') \times E(A')) - (E(A') \times E(A'')) \cdot (E(A'') \times E(A'')) \quad (10)$$

Scheme 4. Block Structure of a Four-Dimensional Matrix in Case of C_{3v} Symmetry without Reduction of the $E \otimes E$ Blocks

Scheme 6. Sorting of a Four-Dimensional Quantity (e.g., Two-Electron Integrals or Double-Excitation Amplitudes) in a Non-Reduced Block Matrix^a



^aNote that the designation of the blocks are only meant to indicate the subblock in which the corresponding non-reduced elements are incorporated.

$$\begin{aligned} (E \times E)(A_2) \cdot (E \times E)(A_2) &= 2(E(A') \times E(A'')) \cdot (E(A') \times E(A'')) \\ &\quad - E(A') \times E(A'') \cdot (E(A') \times E(A'')) \\ &\quad + (E(A') \times E(A')) \cdot (E(A'') \times E(A'')) \end{aligned} \quad (11)$$

Note that the given expressions account for the fact that reduction is necessary for both the right and left side of the four-index quantity. In addition, reduction requires that all elements of the four-index quantity that possess either on the right or left side $E \times E$ symmetry (except those with all four orbitals belonging to the E representation) are scaled by $\sqrt{2}$.

Using the block structure of the reduced matrices contractions like the one required for the PPL term can be carried out in the same manner as for the Abelian case, i.e., block by block (see Scheme 7).

Scheme 7. Block-by-Block Multiplication of Two Reduced Four-Dimensional Block Matrices as Required for the $O(M^6)$ Terms in MP3, CCD, and CCSD Computations

The discussion so far enables an efficient handling of non-Abelian symmetry of the $O(M^6)$ terms in third-order Møller-Plesset (MP3) perturbation theory,²⁹ CC doubles (CCD)^{30–32} as well as CCSD computations²⁷ provided the required two-electron integrals and double-excitation amplitudes are ordered properly. For actual CCD/CCSD computations, however, additional issues need to be discussed, as there are (a) necessary re-sorting steps required for the four-index quantities (for different contractions involving the same four-index quantity different orderings of its elements are needed and those are subject to different DPDs), (b) formation of spin-adapted quantities needed for an efficient closed-shell treatment, and (c) handling of the additional $O(M^5)$ terms in CCD and CCSD calculations. These issues are trivially dealt with in the case of Abelian point-group symmetry, but require some additional thoughts in case of non-Abelian symmetry.

2.4. Non-Reduced and Reduced Representations

The key idea to resolve the raised issues is to use both a reduced and a nonreduced representation for the four-index quantities of interest (see Figure 2). The reason for doing this is simply that

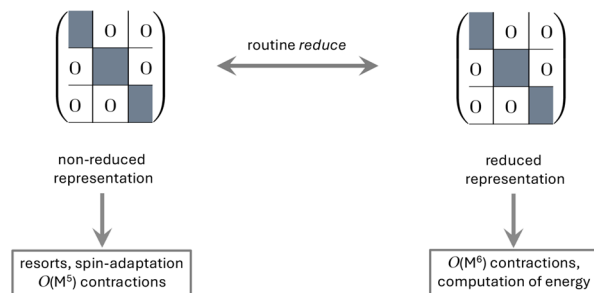


Figure 2. Simultaneous usage of nonreduced and reduced representations in CC computations exploiting non-Abelian symmetry.

re-sorts are straightforward in the nonreduced representation (as all entries there represent quantities with four specific indices assigned unlike for the reduced representation where the entries are actually linear combinations of such quantities), while the $O(M^6)$ contractions are efficiently done using the reduced representation. However, it is not necessary to keep simultaneously both representations in memory or on disk, as it is very simple to switch back and forth (see eqs 9 to 101). A key element of our implementation is therefore a routine (in our implementation called *reduce*) that does exactly that as shown in Figure 2.

2.5. Re-sort of Reduced Representations of Four-Index Quantities

For the re-sort of a four-index quantity we suggest to first revert back to the nonreduced representation, then do the re-sort, and finally reduce the re-sorted quantity, as shown in Figure 2. A complication arises here due to the fact that the nonreduced representation does not involve all elements of the four-dimensional quantity (the “missing integral/amplitude” issue) that are needed for the sort. For example, for a re-sort $(12,34) \rightarrow (14,23)$, one has in the original nonreduced representation all quantities of type $E(A')E(A'')E(A')E(A'')$, $E(A')E(A'')E(A'')E(A')$, and $E(A')E(A'')E(A')E(A')$, but misses those of $E(A')E(A'')E(A'')E(A')$. However, the missing quantity is given by

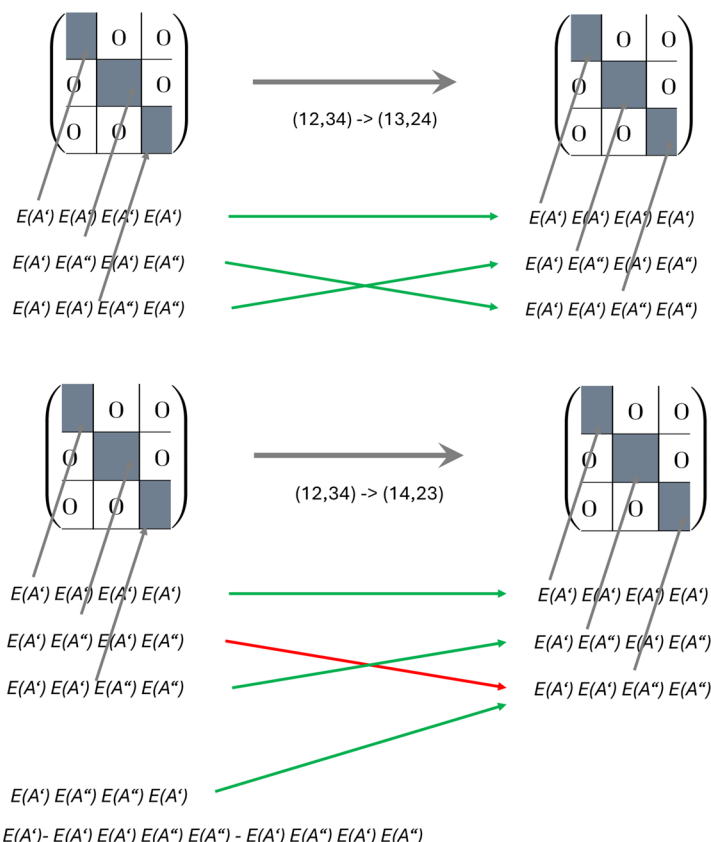
$$\begin{aligned} I(E(A')E(A''), E(A'')E(A')) &= I(E(A')E(A'), E(A'')E(A')) \\ &\quad - I(E(A')E(A'), E(A'')E(A'')) \\ &\quad - I(E(A')E(A''), E(A')E(A'')) \end{aligned} \quad (12)$$

and, thus, a re-sort of the nonreduced quantity is possible, though the corresponding routine is more involved than in the Abelian case. Two examples of re-sorts (i.e., $(1234) \rightarrow (1324)$, where no problem due to “missing integrals/amplitudes” appears, and $(1234) \rightarrow (1423)$, where the “missing integral/amplitude” issue has to be dealt with) are explained in Scheme 8.

2.6. Spin-Adaptation of Reduced Representations of Four-Index Quantities

The efficient formulation of MP and CC models in case of a closed-shell reference (i.e., a restricted HF reference determinant) involves so-called spin-adapted quantities. For example, in case of the double-excitation amplitudes they are given by

Scheme 8. $(1234) \rightarrow (1324)$ and $(1234) \rightarrow (1423)$ Re-sorts for Non-Reduced Block Matrices^a



^aThe red arrow shows the part of the re-sort affected by the “missing integral/amplitude” issue.

$$\widetilde{t}_{ij}^{ab} = 2t_{ij}^{ab} - t_{ij}^{ba} \quad (13)$$

However, the reduced amplitudes cannot be “spin-adapted” using [eq 13](#), as the reduced spin-adapted amplitudes are actually defined by applying the reduction to the nonreduced spin-adapted amplitudes. Again, the solution is to switch back to the nonreduced representation, spin-adapt, and to obtain the reduced spin-adapted quantity by reduction of the nonreduced spin-adapted quantity. The corresponding routine is straightforward to set up, but again more involved than in the Abelian case, as we again have to deal with the “missing integral/amplitude” issue. In order to obtain the spin-adapted $I(E(A')E(A''), E(A')E(A''))$ elements, we need the $I(E(A')E(A''), E(A'')E(A'))$ elements that are not present in the corresponding block matrix, but the required missing elements can be again reconstructed using [eq 12](#).

2.7. $O(M^5)$ Contractions in CCD and CCSD Computations

Besides the time-determining $O(M^6)$ terms, CCD and CCSD computations involve additional $O(M^5)$ terms. There are two types of them, one which contracts two four-index quantities into a two-index quantity

$$I_1(p, q) = \sum_{r,s,t} I_2(rs, tp) I_3(rs, tq) \quad (14)$$

and one that contracts a four-index quantity with a two-index quantity to yield a four-index quantity

$$I_1(pq, rs) = \sum_t I_2(pq, rt) I_3(t, s) \quad (15)$$

While both contractions in principle require new DPDs, where the four irreducible representations of the four-index quantities are decomposed into a product of three irreducible representations and a remaining one, it is in the Abelian case more convenient to perform these contractions using the given DPDs. The same is also true in the case of non-Abelian point-group symmetry except that these contractions then need to be carried out using the corresponding nonreduced representations. The contraction in [eq 15](#) is straightforward to carry out in the nonreduced representation (thereby assuming that the two-index quantity is given as a two-dimensional block matrix), while for the first contraction, i.e., the one of [eq 14](#), one has to deal again with the “missing integral/amplitude” issue. In addition, one has to account for the two-dimensionality of the E representation by including in some terms an additional factor of 2 and 4, respectively.

With this, the required tools for handling non-Abelian point-group symmetry have been identified and set up. These tools will make it possible to perform MP3, CCD, and CCSD computations with exploitation of non-Abelian point-group symmetry. Our implementation is described in the next section, before we demonstrate the potential savings that result from the exploitation of non-Abelian point group symmetry (in comparison to just Abelian point-group symmetry).

3. IMPLEMENTATION AND COMPUTATIONAL DETAILS

We implemented our proposed strategy for exploiting non-Abelian point-group symmetry in a pilot program termed “Quantum Chemistry with Exploitation of Non-Abelian

Symmetry" (QUENA) for performing MP3, CCD, and CCSD computations for closed-shell molecules with C_{3v} symmetry. The CCSD equations used in this implementation are modified versions of those reported in refs 33, 18 and exploit spin-symmetry (apart from the use of the symmetric/antisymmetric algorithm^{34,35} in the ladder terms), thus ensuring (apart from a factor of 2 in the ladder terms due to the symmetric/antisymmetric algorithm) minimal cost. For completeness as well as for the discussion in the next section, we summarize in the following our equations:

a) energy

$$E = \sum_{m,n} \sum_{e,f} \langle mnlef \rangle \widetilde{\tau}_{mn}^{ef} \quad (16)$$

b) singles equations

$$\begin{aligned} D_{ij}^a t_i^a = & \sum_e \left\{ \mathcal{F}_{ae} + \frac{1}{2} \sum_m \mathcal{F}_{me} t_m^a \right\} t_i^e \\ & - \sum_m \left\{ \mathcal{F}_{mi} - \frac{1}{2} \sum_e \mathcal{F}_{me} t_i^e \right\} t_m^a + \sum_e \sum_m \mathcal{F}_{me} \widetilde{\tau}_{im}^{ae} \\ & + \sum_e \sum_m \langle amlie \rangle t_m^e - \sum_{m,n} \sum_e \langle mnlie \rangle \widetilde{\tau}_{mn}^{ae} \\ & + \sum_m \sum_{e,f} \langle amlef \rangle \widetilde{\tau}_{im}^{ef} \end{aligned} \quad (17)$$

c) doubles equations

$$\begin{aligned} D_{ij}^{ab} t_{ij}^{ab} = & \langle ablij \rangle + P_+(ai, bj) \sum_e \mathcal{F}_{ae} t_{ij}^{eb} - P_+(ai, bj) \\ & \sum_m \mathcal{F}_{mi} t_{mj}^{ab} \\ & + \sum_{m,n} \mathcal{W}_{mnij} \tau_{mn}^{ab} + \sum_{e,f} \mathcal{W}_{abef} \tau_{ij}^{ef} \\ & + \frac{1}{2} P_+(ia, jb) \sum_m \sum_e \left[\mathcal{W}_{mbej} \widetilde{\tau}_{im}^{ae} - \mathcal{W}_{mbje} t_{im}^{ea} \right. \\ & \left. - 2 \mathcal{W}_{mbie} t_{jm}^{ea} - 2 \langle mblej \rangle t_i^e t_m^a + 2 \langle mblie \rangle t_j^e t_m^a \right] \\ & - P_+(ia, jb) \sum_m \langle mblij \rangle t_m^a + P_+(ia, jb) \sum_e \langle ablej \rangle t_i^e \end{aligned} \quad (18)$$

In the given equations the two-electron integrals, in Dirac notation, are denoted by $\langle pq|rs \rangle$ and the single- and double-excitation amplitudes are given by t_i^a and t_{ij}^{ab} , respectively. The double-excitation amplitudes here correspond to the $\alpha\beta\alpha\beta$ amplitudes within a spin-orbital formulation.¹⁸ In addition, the so-called τ amplitudes

$$\tau_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b \quad (19)$$

are used as well as the corresponding spin-adapted t and τ amplitudes defined by

$$\widetilde{t}_{ij}^{ab} = 2t_{ij}^{ab} - t_{ij}^{ba} \quad (20)$$

and

$$\widetilde{\tau}_{ij}^{ab} = 2\tau_{ij}^{ab} - \tau_{ij}^{ba} \quad (21)$$

Spin-adapted two-electron integrals are denoted in the given equations by

$$\langle \overline{pq|rs} \rangle = 2\langle pq|rs \rangle - \langle pq|sr \rangle \quad (22)$$

and the orbital-energy denominators are given by

$$D_i^a = \frac{1}{\varepsilon_i - \varepsilon_a} \quad (23)$$

and

$$D_{ij}^{ab} = \frac{1}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \quad (24)$$

with orbital energies ε_p , respectively. Furthermore, the intermediates $\mathcal{F}$ and $\mathcal{W}$ are defined by

$$\mathcal{F}_{mi} = \sum_n \sum_e \langle \overline{mnlie} \rangle t_n^e + \sum_n \sum_{e,f} \langle mnlef \rangle \widetilde{\tau}_{in}^{ef} \quad (25)$$

$$\mathcal{F}_{ae} = \sum_m \sum_f \langle \overline{amlef} \rangle t_m^f - \sum_{m,n} \sum_f \langle mnlef \rangle \widetilde{\tau}_{mn}^{af} \quad (26)$$

$$\mathcal{F}_{me} = \sum_n \sum_f \langle \overline{mnlef} \rangle t_n^f \quad (27)$$

$$\mathcal{W}_{abef} = \langle ablef \rangle - P_+(ae, bf) \sum_m \langle mblef \rangle t_m^a \quad (29)$$

$$\begin{aligned} \mathcal{W}_{mbej} = & \langle mblej \rangle + \sum_f \langle mblef \rangle t_j^f - \sum_n \langle mnlej \rangle t_n^b \\ & + \frac{1}{2} \sum_n \sum_f \langle \overline{mnlef} \rangle \left\{ \frac{1}{2} \widetilde{t}_{jn}^{bf} - t_j^f t_n^b \right\} - \frac{1}{2} \sum_n \\ & \sum_f \langle mnlf e \rangle \left\{ \frac{1}{2} t_{jn}^{fb} - t_j^f t_n^b \right\} \end{aligned} \quad (30)$$

and

$$\begin{aligned} \mathcal{W}_{mbje} = & \langle mblje \rangle + \sum_f \langle mblfe \rangle t_j^f - \sum_n \langle mnlje \rangle t_n^b \\ & + \sum_n \sum_f \langle mnlf e \rangle \left\{ \frac{1}{2} t_{jn}^{fb} - t_j^f t_n^b \right\} \end{aligned} \quad (31)$$

and

$$\widetilde{\mathcal{W}}_{mbej} = 2\mathcal{W}_{mbej} + \mathcal{W}_{mbje} \quad (32)$$

Finally, the symmetric permutation operator $P_+(pq, rs)$ is defined by

$$P_+(pq, rs)Z(pq, rs) = Z(pq, rs) + Z(qp, sr) \quad (33)$$

with $Z(pq, rs)$ as an arbitrary four-index quantity. The calculations with QUENA use orbital energies and two-electron integrals (in the MO representation) from a preceding CFOUR calculation^{36,37} which for the QUENA computations in C_{3v} were run in the largest Abelian subgroup of C_{3v} , namely C_s . This also means that the orbitals in the two-dimensional E representation are chosen such that they transform either as A' or A'' . The results obtained with QUENA have been validated such that the results (i.e., energies) agree for the C_s and C_{3v} computations carried out with QUENA and also with those performed with CFOUR using no symmetry or only C_s .

Table 2. Number of Operations with Savings Due to Symmetry Given in Parentheses for the $O(M^5)$ and $O(M^6)$ Steps of a CCSD Computation for NH_3 Using the cc-pVQZ Basis

term	C_1	C_5	C_{3p}
formation of intermediates			
$\mathcal{F}_{mi}$	2,450,000	843,890 (2.9)	188,338 (13.0)
$\mathcal{F}_{ae}$	68,600,000	17,878,420 (3.8)	3,481,788 (19.7)
$\mathcal{W}_{mij}$	12,250,000 + 87,500	3,513,850 + 27,515 (3.5)	674,094 + 5679 (18.1)
$\mathcal{W}_{abef}$	1,920,800,000	526,886,860 (3.6)	90,653,844 (21.2)
$\mathcal{W}_{mikej}$ and $\mathcal{W}_{mijke}$	$2 \times 343,000,000 + 2 \times 68,600,000 + 2 \times 2,450,000$	$2 \times 88,036,900 + 2 \times 18,959,390 + 2 \times 696,485$ (3.8)	$2 \times 16,544,244 + 2 \times 3,294,054 + 2 \times 125,469$ (20.7)
contractions in singles equations			
t_2 terms	68,600,000 + 2,450,000	18,959,390 + 696,485 (3.6)	3,391,390 + 127,585 (20.2)
contractions in doubles equations			
$\sum_m \mathcal{F}_{mi}^{ab}$	2,450,000	843,890 (2.9)	186,222 (13.2)
$\sum_e \mathcal{F}_{ae}^{db}$	68,600,000	17,878,420 (3.8)	3,384,452 (20.3)
$\sum_{m,n} \mathcal{W}_{mnij}^{ab}$	12,250,000	3,513,850 (3.5)	674,094 (18.2)
$\sum_{e,f} \mathcal{W}_{abef}^{cd}$	9,604,000,000	2,445,152,900 (3.9)	43,102,6844 (22.3)
$\sum_m \sum_e \mathcal{W}_{mij}^{ab} \widetilde{t}_{am}^{cd}$ and $\sum_m \sum_e \mathcal{W}_{mij}^{ca} \widetilde{t}_{im}^{ab}$	$2 \times 343,000,000$	$2 \times 88,036,900$ (3.9)	$2 \times 16,544,244$ (20.7)
t_1^2 terms	$4 \times 2,450,000$	$4 \times 696,485$ (3.5)	$4 \times 125,469$ (19.5)
t_1 terms	68,600,000 + 2,450,000	18,959,390 + 696,485 (3.6)	3,294,054 + 125,469 (20.8)
total	13,357,487,500	3,450,096,635 (3.9)	610,731,751 (21.9)

Table 3. Number of Operations with Savings Due to Symmetry Given in Parentheses for the $O(M^5)$ and $O(M^6)$ Steps of a CCSD Computation for PH_3 Using the cc-pVQZ Basis

term	C_1	C_5	C_{3p}
formation of intermediates			
$\mathcal{F}_{mi}$	14,288,400	4,729,050 (3.0)	1,017,462 (14.0)
$\mathcal{F}_{ae}$	222,264,000	5,7785,140 (3.8)	11,308,552 (19.7)
$\mathcal{W}_{mij}$	128,595,600 + 918,540	35,701,450 + 277,745 (3.6)	6,762,758 + 55,303 (19.0)
$\mathcal{W}_{def}$	3,457,440 000	942,210,476 (3.7)	165,114 588 (20.9)
$\mathcal{W}_{mij}$ and $\mathcal{W}_{mij}^{oe}$	$2 \times 2,000,376,000 + 2 \times 14,288,400 + 2 \times 222,264,000$	$2 \times 511,528,500 + 2 \times 60,960,290 + 2 \times 4,007,425$ (3.9)	$2 \times 95,938,688 + 2 \times 10,766,682 + 2 \times 727,133$ (20.8)
contractions in singles equations			
t_2 terms	222,264,000 + 14,288,400	60,960,290 + 4,007,425 (3.6)	11,156,026 + 744,061 (19.9)
contractions in doubles equations			
$\sum_m \mathcal{F}_{mi} f_{mj}^{ab}$	14,288,400	4,729,050 (3.0)	1,000,534 (14.3)
$\sum_e \mathcal{F}_{ae} f_{ij}^{ab}$	222,264,000	5,7785,140 (3.8)	10,919,208 (20.4)
$\sum_{m,n} \mathcal{W}_{mij} f_{nm}^{ab}$	128,595,600	35,701,450 (3.6)	6,762,758 (19.0)
$\sum_{e,f} \mathcal{W}_{def} f_{ij}^{ef}$	31,116,960,000	7,902,563,684 (3.9)	1,417,918,180 (21.9)
$\sum_m \sum_e \mathcal{W}_{mij} f_{em}^{oe}$ and $\sum_m \sum_e \mathcal{W}_{mij} f_{em}^{oe}$	$2 \times 2,000,376,000$	$2 \times 511,528,500$ (3.9)	$2 \times 95,938,688$ (20.9)
t_1^s terms	$4 \times 14,288 400$	$4 \times 4,007,425$ (3.6)	$4 \times 727,133$ (19.7)
t_1 terms	$222,264,000 + 14,288,400$	$60,960,290 + 4,007,425$ (3.6)	$10,766,682 + 727,133$ (20.6)
total	44,310,481,740	11,363,497,745 (3.9)	2,053,904,159 (21.6)

4. EXPLORATORY COMPUTATIONS ON NH₃ AND PH₃

To demonstrate the potential computational savings due to the exploitation of the full molecular point-group symmetry, we report in Tables 2 and 3 the operation counts (of the $O(M^5)$ and $O(M^6)$ steps only) for CCSD computations on NH₃ ($r(\text{NH}) = 1.1 \text{ \AA}$, $\angle(\text{HNH}) = 103.42^\circ$) and PH₃ ($r(\text{PH}) = 1.42 \text{ \AA}$, $\angle(\text{HPH}) = 119.63^\circ$) when performed with C_1 , C_s , and C_{3v} symmetry using the cc-pVQZ basis set.^{38,39} The operation counts are given for the relevant terms (see previous section) individually together with the saving factor compared to the corresponding computations performed with lower symmetry. We refrain from reporting timings, as our pilot code has yet not been optimized. On the other side, the reported number of operations should provide information about potential savings that can be obtained with an optimal code, although the real savings will (due to the reduced size of the matrices in the matrix–matrix operations) remain somewhat smaller.

From the operation counts in both tables, we see that the calculations run with C_{3v} symmetry require much fewer operations per iteration than the corresponding calculations run with C_s or even C_1 . While the savings of about 3.9 for both NH₃ and PH₃ in the calculations using C_s compared to the calculation using no symmetry is in line with what was already observed in ref 18, the calculation using C_{3v} reduce the operation count by another factor of 5.5, resulting in overall savings compared to calculations using no symmetry of about 21.6 to 21.9. We note that the saving factors are the largest for the terms involving many virtual orbitals. Thus, while for the hole–hole ladder term the saving is only 18.2 for NH₃ (19.0 for PH₃), the savings are for the ring and particle–particle ladder term with 20.7 and 20.9 (ring terms) and 22.3 and 21.9 (particle–particle ladder) larger. The savings are very similar for NH₃ and PH₃ and similar results are also obtained for computations using the smaller cc-pVDZ and cc-pVTZ basis sets.^{38,39} The overall savings are here for all steps of a CCSD iteration: 19.5 (NH₃/cc-pVDZ), 21.1 (NH₃/cc-pVTZ), 19.5 (PH₃/cc-pVDZ), and 20.9 (PH₃/cc-pVTZ), respectively. We thus conclude that exploitation of the full symmetry in cases with non-Abelian point-group symmetry can lead to additional significant savings (compared to treatments just using the largest Abelian subgroup) and that a general implementation would open the possibility of CC calculations on large and highly symmetric molecules [such as for example C_{60} which so far are not possible with a standard CC code, (CCSD calculation on C_{60} , however, are already possible using CC schemes that use Cholesky decomposition of two-electron integrals, see ref 25)].

We also like to comment on the maximal (or optimal) savings that in principle can be reached in the treatment of non-Abelian symmetry. Assuming an equal distribution of the orbitals among the different irreducible representations (thereby taking into account the degeneracy and attributing twice as many orbitals to the E representation), one can expect savings of about 22.9 for the $O(M^6)$ steps; we obtain in our examples savings of about 22.0. This is less than the square of the order of the group (which one obtains in the case of Abelian point groups and would be 36 for C_{3v}), but significant.

5. CONCLUSIONS AND OUTLOOK

In the present work, we demonstrate how the direct-product decomposition approach by Stanton et al.¹⁸ for the treatment of Abelian point-group symmetry in CC calculations can be extended to non-Abelian point groups. The key findings are here

that a block structure for higher-dimensional quantities such as the two-electron integrals and the amplitudes can be obtained by resolving the reducible products of two irreducible representations (in the case of C_{3v} of the $E \otimes E$ product) into its irreducible representations. This also allows to eliminate redundancies (i.e., by just keeping one of the E blocks) and enables to perform the $O(M^6)$ contractions in the same way as in the Abelian case without a significant overhead for symmetry exploitation. However, complications arise (a) in the re-sorts of these higher-dimensional quantities, (b) when carrying out spin-adaptation, and (c) in case of the $O(M^5)$ contractions. To overcome these complications we propose a strategy which employs both the reduced and the nonreduced representations of the involved higher-dimensional quantities, as all the problematic steps are rather straightforwardly carried out in the nonreduced representation (apart from the fact that one has to deal with the “missing integral/amplitude” issue which is due to the fact that not all integrals in the calculation are available but when needed can be reconstructed from the available ones). It is not necessary to store both representations, as one can easily switch back and forth between them, a strategy which we use in our implementation within the new program package QUENA. This program features a pilot implementation for the case of C_{3v} symmetry and parts of the symmetry treatment so far are hard coded for that point group. Exploratory computations for NH₃ and PH₃ showed that the full exploitation of C_{3v} point-group symmetry leads to significant savings compared to corresponding computations in C_1 (savings of the order of 21.0 to 22.0) and C_s symmetry (savings of the order of 5.5 to 6.0), respectively. We expect that generalization of our concepts to other non-Abelian point groups is straightforward. Work along these lines is in progress, as also work concerning the extension of the current concepts of symmetry exploitation to the perturbative treatment of triple excitations in the framework of CCSD(T).⁴⁰

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work has been supported through regular funds provided by the Johannes Gutenberg-Universität Mainz. The unexpected death of John F. Stanton in March 2025 was a great shock and a great loss for many of us. John was one of my (J.G.) best friends and with about 90 joint publications certainly by far my most important collaborator. Doing science with John was always fun. He was a great source of inspiration and he was always willing to take new challenges. The present work is in some way a reminiscence to our first joint paper (i.e., the one introducing the direct-product decomposition approach for CC calculations) and, thus, its dedication to his memory is more than appropriate.

The authors thank Simon Blaschke and Jonas Greiner for discussions as well as Sophia Burger, Magdalena Büchner, and Stella Stopkowicz for helpful comments on the manuscript.

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