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REGULAR ARTICLE

The symmetrized random matrix approach, an efficient method to obtain relativistic molecular symmetry adapted functions

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Abstract In relativistic quantum chemical calculation of molecules, where the spin-orbit interaction is included, the electron orbitals possess both the double point group symmetry and the time-reversal symmetry. If symmetry adapted functions are employed as the basis functions of electron orbitals, it would allow a significant reduction of the computational expense. The point group symmetry adapted functions can be obtained by the group projection operators via its actions on the atomic orbital functions. We have proposed an efficient and simple method to obtain all irreducible representation matrices, which are the basis of the group projection operators, of any finite double point group. Both double point group symmetry and time-reversal symmetry are automatically imposed on the representation matrices. This is achieved by the symmetrized random matrix (SRM) approach, where the SRM is constructed in the regular representation space of a finite group and the eigenfunctions of SRM provide all irreducible representation matrices of the given point group.

Keywords Time-reversal symmetry · Double point group symmetry · Regular representation · Irreducible representation matrices · Random matrix

Dedicated to Professor Pekka Pyykkö on the occasion of his 70th birthday and published as part of the Pyykkö Festschrift Issue.

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1 Introduction

In order to reduce the cost of electronic structure calculations, it is always advantageous to exploit the consequence of the molecular system having spatial symmetry. In non-relativistic or scalar-relativistic calculation, both spatial and spin symmetry can be used simultaneously by employing point group and spin group. If spin-orbit coupling terms are included in a relativistic Hamiltonian, it is no longer possible to factorize spin and spatial components of the wave functions. At this juncture, the double point group symmetry [1, 2] is used but at the cost of spin symmetry loss. As a result, the molecular Hamiltonian exhibits time-reversal symmetry. However, the combination of double point group symmetry with time-reversal symmetry is harder than that of single point group symmetry with spin symmetry. Because the time-reversal operator is not a linear operator and consequently does not offer an independent group as spin operator does in non-relativistic case. Nonetheless, if the action of time-reversal operator on the molecular Hamiltonian and the basis are known, additional information on the Hamiltonian matrix can be obtained to reduce further computational cost.

The main task in relativistic molecular symmetry adaption is then to make the double point group adapted symmetry functions also form Kramers pairs (time-reversal pairs), in such a way that the resulting Hamiltonian matrix must have the desired structure (i.e., quaternion, complex, or real [3, 4]). This goal has been achieved only for some limited groups (D_{2h}^{*} and its subgroups or Abelian double point groups) [4–8] so far. In a series of articles, Meyer [9–13] proposed a scheme that is applicable for all point groups. However, the resultant symmetry functions have a complicated time-reversal relation rather than the simplest Kramers paired structure. The previous study [3] proposed

a more general scheme for arbitrary point groups to construct Kramers paired double point group symmetry adapted functions, which is not only applicable for molecular one-electron basis but also for product basis. But there remains an unsolved problem. The irrep (irreducible representation) matrices used for T-symmetrization (time-reversal symmetrization) must fulfil a special transform condition, see Eq. 44 of Ref. [9] or Eq. 49 in this article. The constraint of the irrep matrices plays a key role in the T-symmetrization process. Although Wigner [14] had proved that the T-symmetrization constraint is possible in principle but no approach exists to construct such irrep matrices for point groups in a systematic way. In the practical implementation of the method described in Ref. [3], the irrep matrices of point groups are chosen from the tabulated data of Altmann [15]. Some of the irrep matrices that do not satisfy the T-symmetrization constraint are adjusted by intuition. However, in this article, we will exhibit the SRM method for the generation of irrep matrices, where the T-symmetrization constraint is automatically satisfied.

There are several strategies to generate symmetry adapted molecular bases, for example, the projection technique [3, 11, 16], algebraic approaches [17], matrix diagonalization [18, 19], the method of generator orbitals [20, 21] and the eigenfunction method [22, 23]. We prefer the projection technique since it is the most systematic method and has many advantages over other methods. Firstly, it provides a general algorithm for both single point group and double point group. To treat the fermion representation of double point group using projective representation [24] technique, the forms of projection operators are identical for both boson irreps and fermion irreps. Secondly, it is simple to calculate the vector coupling coefficients (Clebsch–Gordan coefficients), which is hard to obtain for some of the other strategies listed above since they are designed only for the symmetry adaption of one-electron bases. Moreover, projection method provides consistent phase factor for the bases of multidimensional irreps that are important for the symmetry reduction of post-SCF methods such as the TDDFT [25–27] (time-dependent density functional theory) calculation where the vector coupling functions are regarded as molecular bases. Many of the point group symmetry adaption approaches cannot provide consistent bases for multidimensional irreps. In other words, the resultant different set of bases belong to same irrep but the transformation matrices of rotation operators are not identical while the bases generated from projection operators transform naturally according to the same matrix.

The drawback of projection method is its heavy dependence on tabulated group-theoretical information. The irrep matrices of all group operators are a huge amount of data especially for high-order point groups. Therefore, it would be tedious to write a program for projection method with the need of extensive tabulated data. A simplification strategy is to calculate the irrep matrices from the action of group operators on the represented vectors instead of direct input of the irrep matrices. The represented vectors are linear combination of either spherical harmonics or two-component spinors. Altmann [15] has extensively collected the symmetrized vectors for irreps of point groups. With these collected information, it can be further summarized to some rules for the selection of represented vectors. The rules are different for each series of point groups such as C_n series, D_n series, and so on. These rules make the implementation of the projection method more simpler. However, if the irrep matrices can be automatically generated from a computer program, then it is no longer a drawback. The SRM approach introduced in this article provides a general algorithm for arbitrary finite point groups to produce the irreducible representation matrices. It makes the requirement of tabulated data as low as possible since only the definition of group (the group multiplication table) is needed. We follow the pioneer work of Lee and Chen [28], where matrices constructed from random numbers are used to obtain the irrep matrices. Their complicated procedures are simplified in this article. Moreover, the method is extended to treat double point group irreps, T-symmetrization as well as subgroup chain adaption.

The article is organized as follows. First, we introduce the definition of regular representation which is the fundamental representation of a finite point group in Sect. 2 The regular representation includes all irreducible representations, and the SRM is constructed within this linear space. We will then show you that the eigenfunctions of SRM must span an irreducible representation of the given point group in Sect. 3 The irrep matrices can thus be calculated via the action of group operators on the eigenfunction spaces. The procedure of generating irrep matrices is illustrated by an example of C_{3v} point group. In Sect. 4, the SRM approach is extended to relativistic double point group realm, where the fermion irreps are treated via projective representation technique. The T-symmetrization of irrep matrices is discussed as well. In Sect. 4, the subgroup chain adaption of multidimensional irreps is introduced. This is necessary for the unique determination of multidimensional irrep bases, and it is also important for the T-symmetrization of high-dimensional (not less than 4) irreps.

2 Regular representation

The projection method of molecular symmetry adaption needs all point group projection operators

$$\hat{P}^{\mu}_{ij} = \sum_a D^{(\mu)*}_{ij}(g_a) g_a, \tag{1}$$

where D are the representation matrices of group elements g_a, ij denotes row and column index of D, a runs over all elements g_a of group G and μ denotes the irreps. Thus, for a given group G, we need to find representation matrices of all irreps to construct the projection operators. Fortunately, the regular representation of group G contains all irreps and the SRM approach is the way to decompose it.

In the theory of group representations, the regular representation of a finite group G is the linear representation afforded by the group action of G on itself. The dimension of the linear representation space is then the order of group G where each group element g_a has a corresponding vector $|g_a\rangle$ in the linear space. The left regular representation $\hat{g}_a$ of group elements g_a in the linear space is defined as

$$\hat{g}_a|g_b\rangle = |g_a g_b\rangle = |g_{ab}\rangle \tag{2}$$

where g_{ab} denotes $g_a g_b$ for the sake of simplicity. Therefore, $\hat{g}_a$ can be looked as a matrix

$$\hat{g}_a|g_b\rangle = \sum_c D_{cb}(\hat{g}_a)|g_c\rangle = |g_{ab}\rangle \tag{3}$$

$$\Rightarrow D_{cb}(\hat{g}_a) = \delta_{c,ab} = \begin{cases} 1, & \text{when } g_c = g_a g_b \\ 0, & \text{otherwise} \end{cases} \tag{4}$$

It is a real square matrix, and the matrix elements are either 0 or 1. The set of matrices of all group elements form a representation of group G since

$$D(\hat{g}_a)D(\hat{g}_b) = D(\widehat{g_a g_b}) = D(\hat{g}_{ab}). \tag{5}$$

This representation is in general reducible. Starting from here, we will not distinguish the operator $\hat{g}_a$ and its matrix definition since we will only discuss them within the regular representation space.

The right regular representations of group elements g_a in the linear space are defined as

$$\hat{g}^R_a|g_b\rangle = |g_b g_a^{-1}\rangle. \tag{6}$$

$\hat{g}^R_a$ also form a representation of group G, but it is not necessary to use them in this article. Instead, another set of operators (matrices) $\tilde{g_a}$

$$\tilde{g}_a|g_b\rangle = |g_b g_a\rangle \tag{7}$$

$$\Rightarrow D_{cb}(\tilde{g}_a) = \delta_{c,ba} \tag{8}$$

play an important role in the SRM approach. With the map relation

$$\tilde{g}_a \mapsto g_a, \tag{9}$$

set $\{\tilde{g}_a\}$ do not form a representation of group G since

$$\tilde{g}_a\tilde{g}_b = \widetilde{g_b g_a} \neq \widetilde{g_a g_b}, \tag{10}$$

except Abelian groups where all its elements are commutable. However, set $\{\tilde{g}_a\}$ form a new group $\tilde{G}$, which is called the intrinsic group of G. The anti-isomorphic map (9, 10) defines the intrinsic group. We can see all intrinsic operators $\tilde{g}_a$ commute with left regular operators $\hat{g}_b$

$$\forall a, b \quad \tilde{g}_a\hat{g}_b = \hat{g}_b\tilde{g}_a. \tag{11}$$

The intrinsic group $\tilde{G}$ is also isomorphic to its original group G by means of the map

$$\tilde{g}_a^{-1} \mapsto g_a. \tag{12}$$

Therefore, almost all the conclusions about group G, e.g., the number and dimension of irreducible representations, apply to $\tilde{G}$ as well.

The regular representation of G contains all irreps of G and each irrep μ occurs d_μ times, where d_μ is the dimension of irrep μ. The set $\{d_\mu\}$ satisfy the equation

$$\sum_\mu d_\mu^2 = n_g, \tag{13}$$

where μ sums over all irreps and n_g denotes the order of group G. There exist at least two ways to obtain all irrep matrices. One is to find a uniform matrix U, which transforms (by similarity transformation) all $\hat{g}_a$ to irreducible blocks simultaneously. Another way is to find the irrep basis via the linear combination of vectors $|g_a\rangle$. The irrep matrices are then calculated from the action of group operators in the vector spaces. Actually, the two approaches are tightly connected, as the linear combination coefficients of irrep vectors are just the matrix elements of U. We will follow the idea of latter.

3 Symmetrized random matrix

The irrep vectors can be obtained from the eigenfunctions of a totally symmetric matrix. We call a square matrix A in the linear space (of dimension n_g) is totally symmetric in G, if it commutes with all operators $\hat{g}_a$ of G

$$\forall a, \quad A\hat{g}_a = \hat{g}_a A. \tag{14}$$

The eigenfunctions of A with same eigenvalue then must span an irrep of group G.

$$A|v_i^\alpha\rangle = \omega_\alpha|v_i^\alpha\rangle, \quad i = 1\ldots n_\alpha \tag{15}$$

$$D^{(\alpha)}_{ij}(g_a) = \langle v_i^\alpha|\hat{g}_a|v_j^\alpha\rangle. \tag{16}$$

Where the eigenvectors are linear combination of regular space basis

$$|v\rangle = \sum_a c_a|g_a\rangle, \tag{17}$$

and the inner product is defined as

$$\langle g_a | g_b \rangle = \delta_{a,b}. \tag{18}$$

The representation matrices $D^{(\alpha)}(g_a)$ would be unitary matrices if the eigenvectors v_i are orthonormalized. The representations α are indeed irreducible since no other constraints except Eq. 14 were applied on the matrix A. There are at least two ways to obtain the totally symmetric matrix:

Type (I): Symmetrization of a square matrix composed of random numbers. Suppose F is the random matrix, we symmetrize it by

$$A = \sum_a^G \hat{g}_a^{-1} F \hat{g}_a = \sum_a^G \hat{g}_a^T F \hat{g}_a, \tag{19}$$

where a sums over all group elements. It is easy to verify that A in Eq. 19 satisfies Eq. 14 and is therefore totally symmetric in G.

Type (II): Linear combination of the intrinsic operators (matrices). f_a is a series of complex random numbers and

$$A = \sum_a^G f_a \tilde{g}_a. \tag{20}$$

Since all $\tilde{g}_a$ commute with any $\hat{g}_b, A$ in Eq. 20 is obviously a totally symmetric matrix in G.

Matrix A obtained from either approach (I) or (II) is what we called symmetrized random matrix (SRM) in this article. In fact, type (I) and (II) are not two independent symmetrization approaches, (I) can be rewritten as the form of (II) where Eq. 19 becomes

$$A = \sum_a^G \left(\sum_b^G F_{ba,b} \right) \tilde{g}_a. \tag{21}$$

Proof the explicit matrix elements of A in Eq. 19 are

$$A_{ij} = \sum_{a,m,n} \delta_{ai,m} F_{m,n} \delta_{n,aj} \tag{22}$$

$$= \sum_a F_{ai,aj} \tag{23}$$

$$= \sum_b F_{bj^{-1}i,b} \tag{24}$$

$$= \sum_{a,b} F_{ba,b} \delta_{i,ja}. \tag{25}$$

□

If we look at the whole matrix, where $\delta_{i,ja}$ is just $\tilde{g}_a$ as indicated in Eq. 8, then we have Eq. 21.

Only unitary irreps are needed for further applications. As a consequence, SRM A must be a normal matrix, which can be converted to a diagonal matrix by a unitary transform. Among complex matrices, all unitary, Hermitian, and skew-Hermitian matrices are normal. Likewise, among real matrices, all orthogonal, symmetric, and skew-symmetric matrices are normal. It is convenient to generate a Hermitian SRM, not only because it is theoretically easier to deal with but also because it is convenient to be diagonalized by a computer program. In case (I), F is Hermitian ensures A is also Hermitian. In case (II), the coefficients must be complex conjugation of each other among the pair of inverse operators,

$$f_a = f_b^*, \quad \text{if} \quad g_a = g_b^{-1}, \tag{26}$$

and the coefficients of self-inverse operators are real. If time-reversal symmetry of real boson irreps are taken into account, where all irrep matrices are real, the SRM must be real. In this case, we need to engage a real symmetric F for type (I), or make the two numbers in Eq. 26 real and identical for type (II).

The multidimensional irrep occurs more than one time in the regular representation. But we need only one set of its representation matrices. Therefore, the equivalent irreps should be identified. This is done by the help of second SRM B construct from a different set of stochastic numbers. Suppose there exist two sets of irrep eigenvectors $\left\{ |v_i^\alpha\rangle, |v_i^\beta\rangle \right\}$ where the degeneracy degrees are same. (Irreps with different dimensions must be inequivalent.) We need to calculate the connection matrix C via

$$C_{ij} = \left\langle v_i^\alpha | B | v_j^\beta \right\rangle, \tag{27}$$

where the vectors are looked as either row or column set of numbers. If irrep α and β are inequivalent, all the elements of matrix C would be zero. It is a natural application of Wigner-Eckart theorem [1, 2]. Consequently, by checking the values of the connection matrix C, we can distinguish equivalent and inequivalent irreps.

The procedure of generating irrep matrices is illustrated by the C_{3v} point group. The treatment of fermion (projective) irreps of double point group will be discussed in next section. We only show the example for single point group and its boson (vector) irreps.

The C_{3v} point group has 6 members

$$\{E, C_3; C_{3,2}; \sigma_{v,1}; \sigma_{v,2}; \sigma_{v,3}\}, \tag{28}$$

where E the identity operator, C_3 the rotation operator about the main axis with degree $2\pi/3$ and $C_{3,2}$ with degree $4\pi/3$, $\sigma_{v,i}$ the 3 mirrors. The multiplication table of them is listed in Table 1. The irrep matrices are generated by the following steps :

Step (1): Calculation of the regular operators and intrinsic operators. All operators are stored as 6 by 6 square matrices. The matrices are evaluated from its

Table 1 Multiplication table of C_{3v} point group

Operator	E	C_3	$C_{3,2}$	$\sigma_{v,1}$	$\sigma_{v,2}$	$\sigma_{v,3}$
E	E	C_3	$C_{3,2}$	$\sigma_{v,1}$	$\sigma_{v,2}$	$\sigma_{v,3}$
C_3	C_3	$C_{3,2}$	E	$\sigma_{v,3}$	$\sigma_{v,1}$	$\sigma_{v,2}$
$C_{3,2}$	$C_{3,2}$	E	C_3	$\sigma_{v,2}$	$\sigma_{v,3}$	$\sigma_{v,1}$
$\sigma_{v,1}$	$\sigma_{v,1}$	$\sigma_{v,2}$	$\sigma_{v,3}$	E	C_3	$C_{3,2}$
$\sigma_{v,2}$	$\sigma_{v,2}$	$\sigma_{v,3}$	$\sigma_{v,1}$	$C_{3,2}$	E	C_3
$\sigma_{v,3}$	$\sigma_{v,3}$	$\sigma_{v,1}$	$\sigma_{v,2}$	C_3	$C_{3,2}$	E

definition Eq. 4 and Eq. 8 as well as the point group multiplication table.

Step (2): Construction of Hermitian SRM. The example includes only boson irreps, and we take account of the T-symmetrization. We thus must make a real symmetric SRM. It is more convenient to employ the type (II) symmetrization as illustration. Since C_3 and $C_{3,2}$ are inverse operators, the form of SRM is

$$A = p\tilde{E} + q(\tilde{C}_3 + \tilde{C}_{3,2}) + r\tilde{\sigma}_{v,1} + s\tilde{\sigma}_{v,2} + t\tilde{\sigma}_{v,3} \tag{29}$$

where p, q, r, s, and t are real random numbers. The explicit form of above SRM A is

$$A = \begin{pmatrix} p & q & q & r & s & t \\ q & p & q & s & t & r \\ q & q & p & t & r & s \\ r & s & t & p & q & q \\ s & t & r & q & p & q \\ t & r & s & q & q & p \end{pmatrix}. \tag{30}$$

Step (3): Diagonalization of SRM and check the number of degeneracy. As an illustration, we choose

$$p = 0, \quad q = 1, \quad r = 2, \quad s = 3, \quad t = 4 \tag{31}$$

and diagonalize the SRM by a computer program. We found that the eigenvalues are $\{11, -7, \sqrt{3}-1, \sqrt{3}-1, -\sqrt{3}-1, -\sqrt{3}-1\}$, so there exist 4 eigenfunction spaces. The representations of different dimensions are indeed inequivalent, and the one-dimensional irrep occurs only once in the regular representation. We then only need to check the equivalency of the two two-dimensional representations. The matrix elements of the connection matrix, calculated from a second SRM via Eq. 27, are not all zero. That means they are equivalent. Hence, we get 3 independent irreps for C_{3v} point group, where the dimensions are {1, 1, 2} respectively. They fulfill the Eq. 13 that

$$1^2 + 1^2 + 2^2 = 6. \tag{32}$$

Now we can make sure that we obtained all irreps of C_{3v} point group.

There may exist occasional degeneracy due to numerical errors. Some eigenvalues of inequivalent irreps happen to be same (within numerical accuracy) in that case. This can be detected by check Eq. 13. Although the probability is very low, even if it happens, we can remove it by choosing new set of random numbers until Eq. 13 is satisfied.

Step (4): Calculation of the irrep matrices. They are evaluated from Eq. 16. Because the vectors are obtained from the eigenfunctions of a Hermitian matrix, they are already orthogonal to each other. If we normalize the coefficients of the vectors, we could obtain unitary irrep matrices.

4 Double point group adaption

In relativistic molecular calculations employing spinor functions, any rotation of group G would correspond to two matrices that differ only in sign. That is, it looks like that such spinor functions form "two-valued" representations of group G. In order to overcome the difficulty of such two-valuedness, an artificial element $\bar{E}$, corresponding to a rotation of 2π, can be introduced to group G. This leads to a doubling of the number of elements and therefore the name of double point group (denoted as G^*). Any irrep of G can be expanded to an irrep of G^*. Such irreps can be spanned by scalar functions and are thus called boson irreps. The extra irreps of G^* are instead spanned by spinor functions and are therefore denoted as fermion irreps.

If we start from the multiplication table of G^* and follow the procedure described in Sect. 3, we would obtain all the boson irreps and fermion irreps. Actually, an elegant way is to treat the fermion irreps by using the projective representation theory [24]. The introduction of G^* is then not necessary. All irreps are generated within the definition of group G. As the boson irreps are treated by the approach described in Sect. 3, while the fermion irreps are obtained by the approach described in this section.

The projective representation theory modifies the definition of representation by introducing a unimodular factor to the product of two representation matrices

$$D(g_a)D(g_b) = [g_a, g_b]D(g_{ab}). \tag{33}$$

Matrices satisfy Eq. 33 are said to form a projective representation of group G, where the factors $[g_a, g_b]$ depend on the order of group elements. All factors of group G form a factor system, and they must satisfy the associativity condition

$$[g_a, g_b][g_{ab}, g_c] = [g_a, g_{bc}][g_b, g_c]. \tag{34}$$

For point groups, the factors are either $+1$ or -1. Altmann [24] had proposed the quaternion parametrization approach to determine the values of the factors.

The projective left regular operators $\hat{\mathbf{g}}_a$ and projective intrinsic operators $\tilde{\mathbf{g}}_a$ in regular representation space are defined as

$$\hat{\mathbf{g}}_a|g_b\rangle = [g_a, g_b]|g_{ab}\rangle, \tag{35}$$

$$\tilde{\mathbf{g}}_a|g_b\rangle = [g_b, g_a]|g_{ba}\rangle. \tag{36}$$

It is easy to verify that $\hat{\mathbf{g}}_a$ form a projective representation of G. All operators $\hat{\mathbf{g}}_a$ commute with any $\tilde{\mathbf{g}}_c$ since

$$\hat{\mathbf{g}}_a\tilde{\mathbf{g}}_c|g_b\rangle = [g_a, g_{bc}][g_b, g_c]|g_{abc}\rangle \tag{37}$$

$$= [g_a, g_b][g_{ab}, g_c]|g_{abc}\rangle = \tilde{\mathbf{g}}_c\hat{\mathbf{g}}_a|g_b\rangle. \tag{38}$$

We follow the process of the discussion in Sect. 3 The conclusion about projective totally symmetric matrix A becomes: if A commutes with all $\hat{\mathbf{g}}_a$, its eigenfunctions would span a projective (fermion) irrep of group G. The fermion irrep matrices are calculated from the eigenvectors $\{|v_i^\alpha\rangle\}$ of A via

$$D_{ij}^{(\alpha)}(g_a) = \left\langle v_i^\alpha|\hat{\mathbf{g}}_a|v_j^\alpha\right\rangle. \tag{39}$$

The projective SRM can be obtained from the symmetrization of a random matrix F via

$$A = \sum_a^G \hat{\mathbf{g}}_a^{-1}F\hat{\mathbf{g}}_a = \sum_a^G \hat{\mathbf{g}}_a^T F\hat{\mathbf{g}}_a. \tag{40}$$

The form is same as the type (I) symmetrization approach in Sect. 3, where the normal group operators are substituted by its corresponding projective operators. F is Hermitian also ensures us to obtain a Hermitian projective SRM. The linear combination of projective intrinsic operators would also provide us a projective SRM. However, the conditions for getting a Hermitian SRM are little bit different. Because the inverse of projective operators are not always the operator of inverse group elements

$$\tilde{\mathbf{g}}_{a^{-1}}\tilde{\mathbf{g}}_a = [g_a^{-1}, g_a] \quad \Rightarrow \quad \tilde{\mathbf{g}}_a^{-1} = \pm\tilde{\mathbf{g}}_{a^{-1}}. \tag{41}$$

Anyhow, the Hermitian projective SRM of type (II) can be written as

$$A = \sum_a \left(f_a\tilde{\mathbf{g}}_a + f_a^*\tilde{\mathbf{g}}_a^T\right). \tag{42}$$

Equation 42 is still the linear combination of projective intrinsic operators since $\tilde{\mathbf{g}}_a^T = \tilde{\mathbf{g}}_a^{-1} = \pm\tilde{\mathbf{g}}_{a^{-1}}$, and thus provides projective totally symmetric matrices.

The connection of type (I) and (II) SRM is

$$A = \sum_a \left(\sum_b F_{ba,b}[g_b, g_a]^{-1}\right)\tilde{\mathbf{g}}_a. \tag{43}$$

Proof is

$$A_{ij} = \sum_a F_{ai,aj}[g_a, g_i]^{-1}[g_a, g_j] \tag{44}$$

$$= \sum_a F_{ai,aj}[g_{aj}, g_{j^{-1}i}]^{-1}[g_j, g_{j^{-1}i}] \tag{45}$$

$$= \sum_b F_{bj^{-1}i,b}[g_b, g_{j^{-1}i}]^{-1}[g_j, g_{j^{-1}i}] \tag{46}$$

$$= \sum_{a,b} F_{ba,b}[g_b, g_a]^{-1}\delta_{i,ja}[g_j, g_a]. \tag{47}$$

We employed the associativity condition

$$[g_a, g_j][g_{aj}, g_{j^{-1}i}] = [g_a, g_i][g_j, g_{j^{-1}i}]. \tag{48}$$

The T-symmetrization of fermion irreps requires that the irrep matrices of pseudoreal irreps, the class (c) irreps of Frobenius-Schur [1, 29] classes in Ref. [3, 9], must satisfy the following transform condition

$$\forall g_a, \quad D^{(\mu)*}(g_a) = J^\dagger D^{(\mu)}(g_a)J, \tag{49}$$

$$J = I_m \otimes \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}. \tag{50}$$

Where I_m is an m-dimensional unit matrix and μ is a $2m$-dimensional pseudoreal irrep. The irrep matrices of μ and its complex conjugation are complex and equivalent. We can prove that, for two-dimensional pseudoreal irreps, the unitary irrep matrices obtained from the Hermitian SRM automatically satisfy the condition in Eq. 49. However, for high dimensional (≥ 4) pseudoreal irreps, we need the help of subgroup chain adaption to satisfy the condition. This will be discussed in Sect. 5.

Suppose ν is a two-dimensional pseudoreal irrep. Therefore, its complex conjugates are equivalent to themselves by a unitary transformation V

$$\forall g_a, \quad D^{(\nu)*}(g_a) = V^\dagger D^{(\nu)}(g_a)V. \tag{51}$$

The general structure of two-dimensional unitary matrix is

$$V = \begin{pmatrix} a & b \\ -b^*\theta & a^*\theta \end{pmatrix} \tag{52}$$

where $aa^* + bb^* = 1$ and θ is a unimodular complex number. From group representation theory, we know that the transform matrix V of pseudoreal irrep must be skew-symmetric [1]

$$V = -V^T. \tag{53}$$

As a consequence, we have

$$V = \begin{pmatrix} 0 & b \\ -b & 0 \end{pmatrix} = -b\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}, \tag{54}$$

where b is now a unimodular complex number. Substitute it into Eq. 51 we get

$$\forall g_a, \quad D^{(\nu)*}(g_a) = J^\dagger D^{(\nu)}(g_a)J. \tag{55}$$

The unimodular factor b was canceled. That is just what we need for the T-symmetrization of pseudoreal irrep.

Therefore, any two-dimensional pseudoreal irrep automatically fulfil the T-symmetrization constraint Eq. 49.

The process of calculating the fermion irrep matrices is demonstrated by an example of D_2 point group. The D_2 point group has four group elements $\{E, C_{2z}, C_{2x}, C_{2y}\}$. The multiplication table as well as projective factors are listed in Table 2. The fermion irrep matrices are generated by the following steps:

Step (1): The projective operators (matrices) are computed by using their definitions Eq. 35 and Eq. 36.

Step (2): As an illustration, we employ the type (II) approach to construct the Hermitian SRM. From Eq. 42 we know that, if $\tilde{\mathbf{g}}_a^{-1} = \tilde{\mathbf{g}}_{a^{-1}}$ its coefficient must be real, if $\tilde{\mathbf{g}}_a^{-1} = -\tilde{\mathbf{g}}_{a^{-1}}$ its coefficient must be pure imaginary. Therefore, the Hermitian SRM of D_2 point group is

$$A = p\tilde{\mathbf{E}} + i\left(q\tilde{\mathbf{C}}_{2z} + r\tilde{\mathbf{C}}_{2x} + s\tilde{\mathbf{C}}_{2y}\right), \tag{56}$$

where p, q, r, and s all are real random numbers. The explicit form of above SRM A is

$$A = \begin{pmatrix} p & iq & ir & is \\ -iq & p & -is & ir \\ -ir & is & p & -iq \\ -is & -ir & iq & p \end{pmatrix}. \tag{57}$$

Step (3): We set

$$p = 0, \quad q = 1, \quad r = 2, \quad s = 3 \tag{58}$$

and diagonalize the SRM. The eigenvalues are $\{-\sqrt{14}, -\sqrt{14}, \sqrt{14}, \sqrt{14}\}$, so there exist two eigenfunction spaces. The equivalence of these two representations is identified by the same approach (checking the connection matrix) described in Sect. 3, and we found they are equivalent. The D_2 point group then contains only one two-dimensional fermion irrep. Equation 13 must be satisfied also for the fermion irreps of point group G. The results fulfill the Eq. 13 that $2^2 = 4$.

Step (4): Fermion irrep matrices are computed via Eq. 39 from orthonormalized eigenvectors.

In summary, the procedures are almost same as that for boson irreps except projective factors are involved and complex numbers are used, even T-symmetrization is taken into account.

Table 2 Multiplication and projective factor table of D_2 point group

Operator	E	C_{2z}	C_{2x}	C_{2y}
E	E	C_{2z}	C_{2x}	C_{2y}
C_{2z}	C_{2z}	$-E$	C_{2y}	$-C_{2x}$
C_{2x}	C_{2x}	$-C_{2y}$	$-E$	C_{2z}
C_{2y}	C_{2y}	C_{2x}	$-C_{2z}$	$-E$

5 Subgroup chain adaption

For a multidimensional irrep α of group G, the choices of its basis vectors are not unique. Suppose the set of vectors $\{|v_i^\alpha\rangle\}$ span a representation space of irrep α, the transformed vectors

$$\{|v_1^\alpha\rangle, |v_2^\alpha\rangle, \ldots\}U \tag{59}$$

by a unitary matrix U also span the space of irrep α. Obviously, the choices of basis eigenvectors within an eigenfunction space are arbitrary, the same applies to the corresponding irrep matrices. Anyhow, the choice of the irrep matrices does not affect the symmetry reduction in molecular calculations. But for the purpose of molecular symmetry analysis, it is convenient to fix the choice of irrep vectors by adapting them to be the common irrep vectors of a subgroup chain

$$G \supset G(s_1) \supset G(s_2) \supset \cdots \supset G(s_N), \tag{60}$$

where the last group $G(s_N)$ must be an Abelian group. Moreover, the T-symmetrization of pseudoreal fermion irreps can be accomplished by the help of subgroup chain adaption. We will therefore discuss subgroup chain adaption of the SRM approach in this section.

It requires N steps to decompose the irreps of group G completely, where N denotes the length of the subgroup chain. At each step, we need to construct the SRMs that are totally symmetric in the corresponding subgroup. In the kth step, suppose μ is the common irrep of truncated subgroup chain

$$G \supset G(s_1) \supset G(s_2) \supset \cdots \supset G(s_{k'}), \tag{61}$$

where $k' = k - 1$ and $G(s_0)$ denotes G. We need to calculate the represented group operators in each multidimensional irrep μ via its basis vectors $\{|v_i^\mu\rangle\}$

$$D_{ij}(\hat{g}_{a,\mu}) = \langle v_i^\mu | \hat{g}_a | v_j^\mu \rangle. \tag{62}$$

The SRM of group $G(s_k)$ in the space of irrep μ is then

$$A = \sum_a^{G(s_k)} \hat{g}_{a,\mu}^\dagger F \hat{g}_{a,\mu}, \tag{63}$$

where F is a Hermitian random matrix of dimension n_μ. The eigenfunctions of A would further decompose the irrep μ. After N steps, all irreps of group G are decomposed to one-dimensional irreps, which are common irreps of the subgroup chain. If the final set of irrep vectors are employed as the irrep vectors of group G, they are then uniquely defined (within arbitrary phase factors).

The T-symmetrization of pseudoreal fermion irrep requires the subgroup chain end up with an Abelian point group which only includes complex fermion irreps, for example, the C_2 and C_4 point group. This is possible for all point groups that have pseudoreal fermion irreps. Such

subgroup chain is called time-reversal adapted subgroup chain in this article. We can prove that, with additional modification of the phase factors of irrep vectors, the irrep matrices of pseudoreal fermion irrep satisfy the T-symmetrization constraint Eq. 49. The proof is discussed as follows. Suppose the irrep vectors of time-reversal adapted subgroup chain within a pseudoreal fermion irrep α of group G are

$$\{|v_{i,1}\rangle, |v_{i,2}\rangle, \quad i = 1 \ldots m\}, \tag{64}$$

where $\{|v_{i,1}\rangle, |v_{i,2}\rangle\}$ are basis vectors of the complex conjugated pair irreps of the last group $G(s_N)$. The dimension of irrep α is $2m$. Suppose this set of vectors form an irrep of G with irrep matrices $D^{(\alpha)}(g_a)$. The complex conjugation of them

$$\left\{|v^*_{i,1}\rangle, |v^*_{i,2}\rangle, \quad i = 1 \ldots m\right\} \tag{65}$$

would then span a space with irrep matrices $D^{(\alpha)*}(g_a)$. Because α is a pseudoreal irrep, its complex conjugated irrep must be equivalent to itself. Consequently, there exists a unitary matrix V to connect the complex conjugated pairs

$$\forall g_a, \quad D^{(\alpha)*}(g_a) = V^\dagger D^{(\alpha)}(g_a) V. \tag{66}$$

Because the vectors are common irrep vectors of a time-reversal adapted subgroup chain, $|v^*_{i,1}\rangle$ must belong to the group chain irrep that same as $|v_{i,2}\rangle$ belong, $|v^*_{i,2}\rangle$ must belong to the group chain irrep that $|v_{i,1}\rangle$ belongs. Therefore, $\left\{|v^*_{i,2}\rangle, |v^*_{i,1}\rangle, i = 1 \ldots m\right\}$ also span a space of α, and the irrep matrices differ from $D^{(\alpha)}(g_a)$ only in phase factors. Taking into account of the restriction of Eq. 53, the form of unitary matrix V in Eq. 66 must be

$$V = \begin{pmatrix} 0 & -\theta_1 \\ \theta_1 & 0 \end{pmatrix} \oplus \begin{pmatrix} 0 & -\theta_2 \\ \theta_2 & 0 \end{pmatrix} \oplus \cdots. \tag{67}$$

where θ_i are unimodular numbers. The factors θ_i can be evaluated from the parallelization technique, which will be discussed soon. If we add additional phase factors η_i to the set of irrep vectors

$$\{\eta_i |v_{i,1}\rangle, \eta_i |v_{i,2}\rangle, i = 1 \cdots m\} \tag{68}$$

where $\eta_i^2 = \theta_i$, the irrep matrices of the new set of vectors would fulfill the T-symmetrization constraint. As we can see, irrep matrices of the new set Eq. 68 are

$$D^{(\alpha')}(g_a) = W^\dagger D^{(\alpha)}(g_a) W, \tag{69}$$

$$W = \begin{pmatrix} \eta_1 & 0 \\ 0 & \eta_1 \end{pmatrix} \oplus \begin{pmatrix} \eta_2 & 0 \\ 0 & \eta_2 \end{pmatrix} \oplus \cdots. \tag{70}$$

It is easy to verify that

$$\forall g_a, \quad D^{(\alpha')*}(g_a) = J^\dagger D^{(\alpha')}(g_a) J, \tag{71}$$

where J is defined in Eq. 50. Therefore, with the help of time-reversal adapted subgroup chain, the irrep matrices of pseudoreal fermion irrep satisfy the T-symmetrization constraint are obtained.

The parallelization technique makes two set of vectors that belong to same irreps also transform according to same irrep matrices. Because the multidimensional irrep μ occurs many times, we denote it as $\{\mu 1, \mu 2, \ldots\}$. The representation matrices

$$D^{(\mu 1)}(g_a), D^{(\mu 2)}(g_a), \ldots \tag{72}$$

are in general different, but they are equivalent by a similarity transformation since they belong to same irrep. We choose the vectors of $\mu 1$ as benchmark and parallelize the vectors of μk with respect to $\mu 1$. That means, we apply a unitary transformation U of dimension n_μ to vectors of μk to make

$$\forall g_a \quad U^\dagger D^{(\mu k)}(g_a) U = D^{(\mu 1)}(g_a). \tag{73}$$

U can be obtained with the help of a second SRM B. We need to construct the connection matrix C

$$C_{ij} = \left\langle v_i^{\mu 1} | B | v_j^{\mu k} \right\rangle. \tag{74}$$

If we apply the transformation U to the right vectors of above equation

$$\left\{|v_{j'}^{\mu k}\rangle\right\} = \left\{|v_j^{\mu k}\rangle\right\} U, \tag{75}$$

the Wigner-Eckart theorem tells us the matrix elements between transformed vectors would be

$$\left\langle v_i^{\mu 1} | B | v_{j'}^{\mu k} \right\rangle = \delta_{ij'} \left\langle v_i^{\mu 1} | B | v_i^{\mu k} \right\rangle, \tag{76}$$

because the vectors $\left\{|v_{j'}^{\mu k}\rangle\right\}$ transform according to same matrices as $\left\{|v_i^{\mu 1}\rangle\right\}$. The resulting matrix must be the production of unit matrix I with a real number d (since the general phase factor of U is arbitrary, we suppose it is the case where d is real)

$$CU = dI \quad \Rightarrow \quad CC^\dagger = d^2 I. \tag{77}$$

Therefore, U is obtained form C

$$U = C^\dagger / (CC^\dagger)^{\frac{1}{2}}. \tag{78}$$

Now coming to the remaining problem of T-symmetrization. If the set of Eq. 65 is employed as the benchmark set, the set of Eq. 64 as the set to be adjusted, we then would obtain the factors what we need in Eq. 67.

In fact, if the subgroup chain has only one subgroup $G \supset G(s)$, we do not need to construct the SRMs for subgroup in each multidimensional irrep spaces. The irrep vectors of such subgroup chain can be obtained simultaneously from the eigenvectors of one SRM, which needs double symmetrization

$$A = \sum_{a}^{G(s)} \hat{g}_a^{-1} \left(\sum_{b}^{G} \tilde{g}_b^{-1} F \tilde{g}_b \right) \hat{g}_a \tag{79}$$

where F is a Hermitian random matrix. It is obvious that A is totally symmetric in both $G(s)$ and $\tilde{G}$. The eigenfunctions of A form a complete space of intrinsic operators $\tilde{g}_a$ instead of $\hat{g}_a$ in group G. In order to obtain the irrep vectors of $G \supset G(s)$, further parallelization steps are needed. The multidimensional irrep μ of $\tilde{G}$ is also the irrep μ of G, but their irrep spaces are perpendicular. There must exist n_μ spaces of irrep μ in the eigenfunction spaces of A. We parallelize the vectors by the parallelization technique discussed above, and pick up the first vector of each space to form a new set. The new vector set is complete with respect to operators $\hat{g}_a$ in group G. The irrep matrices are therefore evaluated within the selected vector set, and they are the irreps of subgroup chain $G \supset G(s)$.

6 Summary

The SRM approach introduced in this article provides an efficient method to obtain all irrep matrices of a given point group. The subgroup chain conventions for the multidimensional irreps are compatible with our SRM approach. Based on the irrep matrices, the group theoretical projection operators can be obtained. The projection techniques are used to construct the point group symmetry adapted molecular functions as well as the vector coupling coefficients (Clebsch–Gordan coefficients) for the symmetry reduction of molecular electronic structure calculations. For the irreps of double point groups, which are required in the relativistic molecular calculations including spin-orbit interaction, they are consistently treated by the SRM approach. Moreover, the T-symmetrization of fermion irreps is realized by the SRM approach. Combining it with the projection technique described in Ref. [3], we can obtain double point group symmetry and time-reversal symmetry adapted molecular functions. The problem of relativistic molecular symmetry adaption is therefore completely solved. The SRM method has minimum requirement of the external tabulated data, only the group multiplication table and projective factors are needed. It is then easy to implement as a computer program.

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