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Symmetry-Consistent Expansion of Interaction Kernels Between Rigid Molecules

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Abstract. We discuss the expansion of interaction kernels between anisotropic rigid molecules. The expansion decouples the correlated orientational variables, which is the crucial step to derive macroscopic free energy. It is at the level of kernel expansion, or equivalently the free energy, that the symmetries of the interacting rigid molecules can be fully recognized. Thus, writing down the form of expansion consistent with the symmetries is significant. Symmetries of two types are considered. First, we examine the symmetry of an interacting cluster, including the translation and rotation of the whole cluster, and label permutation within the cluster. The expansion is expressed by symmetric traceless tensors, with the linearly independent terms identified. Then, we study the molecular symmetry characterized by a point group in $O(3)$. The proper rotations determine what symmetric traceless tensors can appear. The improper rotations decompose these tensors into two subspaces and determine how the tensors in the two subspaces are coupled. For each point group, we identify the two subspaces, so that the expansion consistent with the point group is established.

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1 Introduction

In a system consisting of many rigid molecules, the interactions between the molecules depend not only on the relative position, but also on the relative orientation. Such interactions can lead to nonuniform orientational distribution. As a result, even in an infinitesimal volume, local anisotropy can be formed and further correlated spatially, which is the typical mechanism for liquid crystals. An example that many are familiar with is

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the (uniaxial) nematic phase formed by rod-like molecules, where no positional order is observed but an optical axis can be identified. If layer structure further arises, the smectic phases could appear. The concept of liquid crystals has been expanded to a great extent since rigid molecules of other shapes, such as bent-core molecules, have proved to possess richer phase behaviors experimentally [16, 29].

In mathematical theory, to identify liquid crystalline phases, one needs to construct free energy about some order parameters describing the local anisotropy. A simple approach is to construct phenomenological macroscopic models, typically a polynomial of the order parameters and their derivatives. For rod-like molecules, the order parameter can be chosen as a second order symmetric traceless tensor, based on which the Landau-de Gennes theory is built and has been successfully applied to both stationary and dynamic problems [2, 10, 25]. When discussing other types of liquid crystalline phases, including polar, biaxial or tetrahedral order, people also attempted to construct phenomenological models with different tensor order parameters [11, 12, 14, 26, 27, 30]. In these models, the terms are usually kept as minimum to describe specific phenomena.

Macroscopic theories can also be built upon molecular theories. Such an approach dates back to the derivation of the equations of state for gases, where a homogeneous system consisting of spherical molecules is considered [19, 21]. Inhomogeneous systems, without considering the anisotropy of the molecule, have also been discussed, leading to theories for modulated phases that can describe various materials such as amphiphilic systems and block copolymers [7, 13, 24]. Molecular theories are characterized by interaction kernel functions of several molecules, in which the variables representing the positions of these molecules are correlated. To derive a macroscopic theory, it is necessary to separate these variables, which can be done by expanding the kernel functions. After the expansion is done, each term in the expansion corresponds to a term in the free energy, so that the macroscopic theory is established.

When non-spherical rigid molecules are put into consideration, extra variables are introduced for the orientation of the molecule. Most theories developed from molecular interactions focus on the orientational variables only and are built for spatially homogeneous systems. In this case, the kernel functions are independent of spatial variables, and the expansion decouples the orientational variables. Theories of this kind possibly start from Maier–Saupe [20] for rod-like molecules. Other rigid molecules, including cuboid, bent-core, triangular and cross-like [4, 5, 28, 35, 36], have also been discussed.

Recently, the expansion has been extended to spatially inhomogeneous cases, where both spatial inhomogeneity and orientational anisotropy are included. This approach combines the techniques for spatially inhomogeneous systems of spherical molecules and for spatially homogeneous systems of non-spherical molecules. It was first proposed for rod-like molecules [15], for which a tensor model was established for both nematic and smectic phases. Later, it has been successfully applied to bent-core molecules [34], resulting in a tensor model for modulated nematic phases.

Despite the success of these works, they still cannot describe the majority of exotic liquid crystalline phases exhibited by non-spherical rigid molecules [18, 29, 39]. This is indeed not an easy task as we look into the mechanism of forming liquid crystalline phases, where symmetry is a central topic. A rigid molecule has its intrinsic symmetry, which can lead to various local orientational order of different mescoscopic symmetries. Macroscopic structures are built upon the possible spatial variation of the local orientational order. Theoretically, as we have mentioned above, order parameter tensors are responsible for classifying the local orientational order. Different molecular symmetries lead to different choice of order parameters [32], so that the classification of local orientational order would be distinct. To fully recognize the symmetry of the macroscopic structures, it calls for finding minimizers of specific free energy. For complex orientational order, it sometimes needs several high order tensors that are not considered in the free energy in existing theories. In this sense, it is crucial to understand how the free energy is constructed according to molecular symmetry. When we attempt to derive the free energy from molecular interactions, the problem converts into understanding how the kernel expansion is determined by molecular symmetry.

It shall now be clear that the expansion of interaction kernels is the core of building macroscopic models from molecular theories. In particular, when complex symmetries are considered and multiple tensors are adopted as order parameters, it is nontrivial to build phenomenological theories directly. In this work, we derive the expansion of interaction kernels for *all* molecular symmetries. Symmetry yields a few arguments on interaction kernels. These arguments determine what terms will appear in the expansion, and each term in the expansion leads to a term expressed by tensors in the free energy. Thus, together with suitable truncation, the molecular symmetry determines the form of the free energy, as well as the order parameters that are just the tensors appearing in the free energy. When the interaction kernels are specified, the coefficients can be calculated from the kernels [4, 15, 28, 34, 35]. Molecules with the same symmetry, such as bent-core and star-shaped molecules [34, 37, 38], can be distinguished in this way.

The expansion of interaction kernels is carried out in two steps.

- Write down the general form of expansion without considering molecular symmetry. In this case, the interaction kernels still possess some spontaneous symmetry arguments. We shall figure out the role of these arguments playing on the expansion.
- With certain molecular symmetry, some terms in the general expansion will vanish. We shall identify the nonvanishing terms for all molecular symmetries.

To deal with anisotropy at molecular level, we need to introduce the orientational variables. For this purpose, some notations and results about $SO(3)$ are presented in Section 2. Then, in Section 3, we study the expansion of interaction kernels in the general case. Whatever the molecular potential is, the interaction kernel for a cluster is invariant when the cluster is displaced or rotated as a whole, and when the labels of molecules within the cluster are permuted. To reveal the effect of these arguments, one crucial point is that we express the expansion by symmetric traceless tensors that have been discussed from various aspects [6,17,23,32]. With symmetric traceless tensors, it is easier to identify the linearly independent terms. The orthogonality of many terms can also be recognized, which is useful in the computation of the expansion of a specific kernel.

The use of symmetric traceless tensors also makes it clear how the molecular symmetry plays its role, which we analyze in Section 4. The molecular symmetry is described by orthogonal transformations leaving the molecule invariant, which form a point group in $O(3)$. A point group consists of proper rotations and possibly improper rotations, whose roles are different. The proper rotations constitute a subgroup in $SO(3)$. This subgroup determines that only the invariant tensors of this group can appear in the expansion. The invariant tensors have been written down explicitly in [32] for each point group in $SO(3)$. Then, the improper rotations decompose the invariant tensors into two orthogonal subspaces, and impose conditions on the coupling of tensors between these two subspaces. For each point group, we will write down explicitly the subspace decomposition. If the two point groups have the same proper rotations, the invariant tensors are identical. However, since the decomposition by improper rotations is distinct, the surviving terms in the free energy would be different. In other words, it is at the level of free energy, but not at the level of order parameters, that the molecular symmetry can be fully distinguished.

In this way, we write down the expansion of the interaction kernel for each point group.

- For the expansion in the general case, the list of all the linearly independent terms is provided;
- The proper rotations select tensors that could appear in these terms;
- The improper rotations set the rule of coupling.

This procedure clearly reflects how the molecular symmetry selects terms in the expansion, which is summarized in Section 5.

To clearly present the idea, we focus on the pairwise kernel in the main text. The whole procedure is also applicable to interaction kernels involving clusters of multiple molecules, but finding out the linearly independent terms turn out to be tedious. For this reason, the discussion about clusters of multiple molecules is left to Appendix. As for explicit expressions, we provide them for bulk energy (without spatial derivatives) and elastic energy (with spatial derivatives) from pairwise interaction, and bulk energy from clusters of three and four molecules. This is expected to meet the demands for most applications. In most previous works, only pairwise (two-molecule cluster) interaction is taken into account.

The current work can serve as a useful handbook for studying the liquid crystalline phases formed by any rigid molecule.

- When studying a particular rigid molecule, one could look up the list and choose the terms needed, no matter for molecular-based theories or for Landau theories.

The truncation criteria might be influenced by stability, symmetry of the phase, degrees of freedom of macroscopic parameters [22, 32, 34]. From the complete list of terms we provide, one could choose the terms based on the need for particular systems. In a recent paper [33], the truncation is chosen to distinguish point groups at the lowest order, and elastic terms up to second-order from the pairwise interaction are listed. The results there are actually obtained according to the procedure in the current work, but no derivation is provided in that work.

- The explicit expressions of orthogonal terms would greatly simplify the computation of their coefficients, which is merely utilized in previous works.

- Another note beyond the topic of the current work is that the subspace decomposition of invariant tensors by improper rotations makes it available for fully classifying local anisotropy by its symmetry. Such classification is discussed previously [32] only for point groups in $SO(3)$. With the help of the decomposition, we are able to further classify different chiral or achiral states by the nonzero structure of tensors. We shall discuss the classification in forthcoming works.

2 Preliminaries

We consider the system consisting of many identical rigid molecules that are generally anisotropic, so that the orientation of each molecule affects the state of the whole system. To describe the orientation, we mount a right-handed orthonormal frame $(\hat{O};\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)$ on the molecule. The position of $\hat{O}$ is denoted by $\boldsymbol{x}$, and the orientation of the frame is denoted by $\mathfrak{p}$. In this way, $(\boldsymbol{x},\mathfrak{p})$ represents the position and the orientation of the molecule. The frame $\mathfrak{p}$ is an element in $SO(3)$, which can be expressed by an orthogonal matrix, also denoted by $\mathfrak{p}$, with $\det\mathfrak{p}=1$. The components of $\mathfrak{p}$ are the coordinates of the axes $\boldsymbol{m}_i$: if we denote by $(O;\boldsymbol{e}_1,\boldsymbol{e}_2,\boldsymbol{e}_3)$ the reference frame in $\mathbb{R}^3$, then the (i,j) element of $\mathfrak{p}$ is given by $\boldsymbol{e}_i\cdot\boldsymbol{m}_j$. We can also view $\boldsymbol{m}_j$ as functions of $\mathfrak{p}$, and use the notation $\boldsymbol{m}_j(\mathfrak{p})$ to represent the axis $\boldsymbol{m}_j$ of certain $\mathfrak{p}$. The uniform probability measure on $SO(3)$ is denoted by $\mathrm{d}\mathfrak{p}$.

The operations on tensors will appear throughout the paper, so let us introduce some notations for tensors. A k-th order tensor U can be expressed by the basis in $\mathbb{R}^3$ as follows,

$$U=U_{j_1\cdots j_k}\boldsymbol{e}_{j_1}\otimes\cdots\otimes\boldsymbol{e}_{j_k}. \tag{2.1}$$

Hereafter, we adopt the Einstein convention on summation over repeated indices. Oftentimes, we write a tensor U^k with *superscript* to explicitly indicate its *order*.

For two tensors U_1 and U_2, we use $U_1\otimes U_2$ to represent their tensor product, where the U_1-components come first. The dot product of two tensors with the same order, giving a scalar, is defined by

$$U\cdot V=U_{j_1\cdots j_k}V_{j_1\cdots j_k}. \tag{2.2}$$

Next, we define the rotation $\mathfrak{p}$ acting on a tensor. By expanding the tensor using the basis $\boldsymbol{e}_{j_1}\otimes\cdots\otimes\boldsymbol{e}_{j_k}$, the rotation is done by transforming $\boldsymbol{e}_i$ into $\boldsymbol{m}_i$, giving

$$\mathfrak{p}\circ U = U_{j_1\cdots j_k}\boldsymbol{m}_{j_1}\otimes\cdots\otimes\boldsymbol{m}_{j_k}. \tag{2.3}$$

Since $\boldsymbol{m}_i$ can be viewed as functions of $\mathfrak{p}$, we regard $\mathfrak{p}\circ U$ as a function of $\mathfrak{p}$ and denote it as $U(\mathfrak{p})$. We have $U(\mathfrak{p}_1\mathfrak{p}_2)=\mathfrak{p}_1\circ U(\mathfrak{p}_2)$, and

$$U_1(\mathfrak{s}\mathfrak{p}_1)\cdot U_2(\mathfrak{s}\mathfrak{p}_2)=U_1(\mathfrak{p}_1)\cdot U_2(\mathfrak{p}_2),\quad \forall \mathfrak{s}\in SO(3). \tag{2.4}$$

We then introduce the notations for symmetric tensors. For a k-th order tensor U, define its symmetrization as

$$U_{\text{sym}}=\frac{1}{k!}\sum_{1\le j_1,\cdots,j_k\le 3}\sum_{\sigma}U_{j_{\sigma(1)}\cdots j_{\sigma(k)}}\boldsymbol{e}_{j_1}\otimes\cdots\otimes\boldsymbol{e}_{j_k}, \tag{2.5}$$

where the summation inside is taken over all permutations σ of $(1,\cdots,k)$. For any symmetric tensor U, its trace is defined by contracting two of its components, resulting in a $(k-2)$-th order tensor,

$$(\text{tr}U)_{j_1\cdots j_{k-2}}=U_{j_1\cdots j_{k-2}ii}.$$

If a symmetric tensor U satisfies $\text{tr}U=0$, it is called a symmetric traceless tensor. The symmetric and traceless properties are kept under rotations, i.e. U is symmetric traceless implies $U(\mathfrak{p})$ is. To express symmetric tensors, we introduce the monomial notation below, like

$$\boldsymbol{m}_1^{k_1}\boldsymbol{m}_2^{k_2}\boldsymbol{m}_3^{k_3}=(\underbrace{\boldsymbol{m}_1\otimes\cdots}_{k_1}\otimes\underbrace{\boldsymbol{m}_2\otimes\cdots}_{k_2}\otimes\underbrace{\boldsymbol{m}_3\otimes\cdots}_{k_3})_{\text{sym}}. \tag{2.6}$$

It is easy to see that for $k_1+k_2+k_3=k$, the tensors $\boldsymbol{m}_1^{k_1}\boldsymbol{m}_2^{k_2}\boldsymbol{m}_3^{k_3}$ give an orthogonal basis of k-th order symmetric tensors. In this way, a polynomial about $\boldsymbol{m}_i$ can be regarded as a symmetric tensor, if every term in the polynomial has the same order.

We also use Kronecker delta and Levi-Civita symbol, which are given by

$$\delta_{ij}=\begin{cases}1, & i=j,\\ 0, & i\neq j,\end{cases}\qquad \epsilon_{ijk}=\begin{cases}1, & (ijk)=(123),(231),(312),\\ -1, & (ijk)=(132),(213),(321),\\ 0, & \text{otherwise.}\end{cases}$$

Two closely related tensors are the second order identity tensor,

$$\mathfrak{i}=\boldsymbol{m}_1^2+\boldsymbol{m}_2^2+\boldsymbol{m}_3^2,$$

and the third order determinant tensor,

$$\begin{aligned}\epsilon&=\epsilon_{ijk}\boldsymbol{m}_i\otimes\boldsymbol{m}_j\otimes\boldsymbol{m}_k\\&=\boldsymbol{m}_1\otimes\boldsymbol{m}_2\otimes\boldsymbol{m}_3+\boldsymbol{m}_2\otimes\boldsymbol{m}_3\otimes\boldsymbol{m}_1+\boldsymbol{m}_3\otimes\boldsymbol{m}_1\otimes\boldsymbol{m}_2\\&\quad-\boldsymbol{m}_1\otimes\boldsymbol{m}_3\otimes\boldsymbol{m}_2-\boldsymbol{m}_2\otimes\boldsymbol{m}_1\otimes\boldsymbol{m}_3-\boldsymbol{m}_3\otimes\boldsymbol{m}_2\otimes\boldsymbol{m}_1.\end{aligned}$$

One can verify that the above two equalities hold for any right-handed orthonormal frame $(\boldsymbol{m}_j)$. If U is a symmetric tensor, we will use the notation

$$\mathfrak{i}^q U = (\mathfrak{i}^q \otimes U)_{\text{sym}}.$$

To construct symmetric traceless tensors, we have the following proposition (see [32]).

Proposition 2.1. *For each k-th order symmetric tensor U, there exists a unique $(k-2)$-th symmetric tensor V such that $U - \mathfrak{i}V$ is a symmetric traceless tensor, which is denoted by $(U)_0$. The space of k-th order symmetric traceless tensors has the dimension $2k+1$.*

We denote an orthogonal basis of k-th order symmetric traceless tensors by

$$\mathbb{W}^k = \{W_1^k, \cdots, W_{2k+1}^k\}. \tag{2.7}$$

From any orthogonal basis of symmetric traceless tensors, we can obtain a complete orthogonal basis of $L^2(SO(3))$, the space of square integrable functions. The following proposition is the result of group representation theory (see, for example, [31]).

Proposition 2.2. *The functions $W_i^k(\mathfrak{i}) \cdot W_j^k(\mathfrak{p})$ of $\mathfrak{p}$ for $k = 0, 1, \cdots$ and $1 \le i, j \le 2k+1$ give a complete orthogonal basis of $L^2(SO(3))$.*

The inner product is defined for tensor-valued functions about multiple $\mathfrak{p}$-variables: for two tensor-valued functions $A(\mathfrak{p}_1, \cdots, \mathfrak{p}_l)$ and $B(\mathfrak{p}_1, \cdots, \mathfrak{p}_l)$, if A and B have the same order, we define

$$(A, B) = \int A(\mathfrak{p}_1, \cdots, \mathfrak{p}_l) \cdot B(\mathfrak{p}_1, \cdots, \mathfrak{p}_l) \mathrm{d}\mathfrak{p}_1 \cdots \mathrm{d}\mathfrak{p}_l. \tag{2.8}$$

3 General form of expansion

In this section, we discuss the expansion of interaction kernels in the general case, i.e. without considering molecular symmetry. First, we introduce the gradient expansion to decouple the spatial variables, which has been used previously to deal with various systems without orientational variables. Then, starting from the formula after the gradient expansion is done, we discuss how to deal with the orientational variables.

3.1 Molecular model and gradient expansion

Based on microscopic potential and statistical mechanics, one could write down a molecular model, which may involve various approaches such as mean-field theory or cluster expansion [19, 21]. No matter what approaches are used, the free energy typically takes a form including the contribution of local entropy term and nonlocal interactions of molecule clusters of two, three, and so on. Let $f(\boldsymbol{x}, \mathfrak{p}) \ge 0$ be the number density of the molecule at the position $\boldsymbol{x}$ and of the orientation $\mathfrak{p}$, which we assume is smooth to facilitate the expansion afterwards. The molecular model is written as

$$\beta_0\mathscr{F}[f]=\int \mathrm{d}\boldsymbol{x}\mathrm{d}\mathfrak{p} f(\boldsymbol{x},\mathfrak{p})\ln f(\boldsymbol{x},\mathfrak{p})+\mathscr{F}_2+\mathscr{F}_3+\cdots,$$

where the nonlocal interactions terms are given by

$$\begin{aligned}\mathscr{F}_2&=\frac{1}{2!}\int \mathrm{d}\boldsymbol{x}_1\mathrm{d}\mathfrak{p}_1\mathrm{d}\boldsymbol{x}_2\mathrm{d}\mathfrak{p}_2\mathscr{G}_2(\boldsymbol{r}_2,\mathfrak{p}_1,\mathfrak{p}_2)f(\boldsymbol{x}_1,\mathfrak{p}_1)f(\boldsymbol{x}_2,\mathfrak{p}_2),\\ \mathscr{F}_3&=\frac{1}{3!}\int \mathrm{d}\boldsymbol{x}_1\mathrm{d}\mathfrak{p}_1\mathrm{d}\boldsymbol{x}_2\mathrm{d}\mathfrak{p}_2\mathrm{d}\boldsymbol{x}_3\mathrm{d}\mathfrak{p}_3\mathscr{G}_3(\boldsymbol{r}_2,\boldsymbol{r}_3,\mathfrak{p}_1,\mathfrak{p}_2,\mathfrak{p}_3)f(\boldsymbol{x}_1,\mathfrak{p}_1)f(\boldsymbol{x}_2,\mathfrak{p}_2)f(\boldsymbol{x}_3,\mathfrak{p}_3).\end{aligned} \tag{3.1}$$

Here, $(\boldsymbol{x}_j,\mathfrak{p}_j)$ represents the position and orientation of the molecule j, $\boldsymbol{r}_j=\boldsymbol{x}_j-\boldsymbol{x}_1$ is the relative position to the molecule 1, and β_0 is the inverse of the product of the Boltzmann constant and the absolute temperature. Since we would not like to discuss boundary terms, we simply assume that each $\mathrm{d}\boldsymbol{x}_j$ is integrated in a periodic box $\Omega\in\mathbb{R}^3$. The orientation variable $\mathfrak{p}_j$ is integrated on $SO(3)$. To shorten the notations, we do not write them out in the integrals.

The entropy is a local term that can be handled in different ways. One possible approach is to use the so-called Bingham closure for rod-like molecules [1,3,15], which is actually the maximum entropy state that could be extended to general rigid molecules. This approach can always be carried out if we are able to deal with the nonlocal interaction terms. Therefore, we do not discuss this term in this paper.

Our focus is the nonlocal interaction terms $\mathscr{F}_l$. The interaction kernels $\mathscr{G}_l$ are functions of the molecular potential that might involve numerous types of forces, which we will not try to specify and only assume to be square integrable. The nonlocal interaction terms $\mathscr{F}_l$ are typically truncated somewhere. As an example, if the concentration is low, it would suffice to keep the $\mathscr{F}_2$ term only. In this case, one could use $\mathscr{G}_2=1-\exp\big(-\beta_0\mathscr{U}(\boldsymbol{r}_2,\mathfrak{p}_1,\mathfrak{p}_2)\big)$ where $\mathscr{U}$ is the potential for a pair of molecules.

We start from doing Taylor expansions on $f(\boldsymbol{x}_j,\mathfrak{p}_j)=f(\boldsymbol{x}_1+\boldsymbol{r}_j,\mathfrak{p}_j)$ about $\boldsymbol{r}_j$,

$$f(\boldsymbol{x}_j,\mathfrak{p}_j)=\sum\frac{1}{k_j!}\boldsymbol{r}_j^{k_j}\cdot\nabla^{k_j}f(\boldsymbol{x}_1,\mathfrak{p}_j). \tag{3.2}$$

Here, we recall that the monomial $\boldsymbol{r}_j^{k_j}$ represents a k_j-th order symmetric tensor

$$\underbrace{\boldsymbol{r}_j\otimes\cdots\otimes\boldsymbol{r}_j}_{k_j}.$$

Taking the above into the interaction terms, we obtain

$$\begin{aligned}\mathscr{F}_l[f]=\sum_{k_2,\cdots,k_l}\frac{1}{l!k_2!\cdots k_l!}\int \mathrm{d}\boldsymbol{x}_1\mathrm{d}\mathfrak{p}_1\cdots\mathrm{d}\mathfrak{p}_l f(\boldsymbol{x}_1,\mathfrak{p}_1)\\ \mathscr{M}_l^{k_2,\cdots,k_l}(\mathfrak{p}_1\cdots,\mathfrak{p}_l)\cdot\nabla^{k_2}f(\boldsymbol{x}_1,\mathfrak{p}_2)\otimes\cdots\otimes\nabla^{k_l}f(\boldsymbol{x}_1,\mathfrak{p}_l),\end{aligned} \tag{3.3}$$

where we define the tensors $\mathscr{M}_l^{k_2,\cdots,k_l}$ as follows,

$$\mathscr{M}_l^{k_2,\cdots,k_l}(\mathfrak{p}_1,\cdots,\mathfrak{p}_l)=\int \mathscr{G}_l(\boldsymbol{r}_2,\cdots,\boldsymbol{r}_l,\mathfrak{p}_1,\cdots,\mathfrak{p}_l)\boldsymbol{r}_2^{k_2}\otimes\cdots\otimes\boldsymbol{r}_l^{k_l}\,\mathrm{d}\boldsymbol{r}_2\cdots\mathrm{d}\boldsymbol{r}_l. \tag{3.4}$$

In the above, we have effectively done the gradient expansion. It has been adopted in many systems where no orientational variables are involved (such as [8]), where $\mathscr{M}_l^{k_2,\cdots,k_l}$ are constant tensors, so that $\mathscr{F}$ becomes a functional about f and their derivatives. In some systems, such a manipulation is done in the Fourier space, where the expansion is done about Fourier modes. It leads to polynomials of Fourier modes [7, 13], which is formally equivalent to the gradient expansion after Fourier transformations. It certainly requires some conditions for the gradient expansion to be appropriate. In this work, however, we assume its appropriateness and start our discussion from (3.3) and (3.4).

The focus of this paper is the expansion of $\mathscr{M}_l^{k_2,\cdots,k_l}$ about the orientational variables $\mathfrak{p}_i$. After the expansion, the variables $\mathfrak{p}_i$ are separated, so that the integrals $\int \mathrm{d}\mathfrak{p}_i$ can be decoupled. The interaction terms $\mathscr{F}_l$ then become functionals about several quantities averaged by $f(\boldsymbol{x},\mathfrak{p})$, denoted by $\langle h\rangle$ that we define as

$$\langle h\rangle=\int h(\mathfrak{p})f(\boldsymbol{x},\mathfrak{p})\,\mathrm{d}\mathfrak{p}. \tag{3.5}$$

The average is taken over $SO(3)$, so that $\langle h\rangle$ is a function of $\boldsymbol{x}$.

The expansion shall satisfy several symmetry arguments, which we will discuss throughout the rest of paper. To clearly present the idea, we discuss $\mathscr{M}_2^k$ in a detailed manner. The discussion for cluster of multiple molecules, along with explicit expressions from $\mathscr{M}_3^{0,0}$ and $\mathscr{M}_4^{0,0,0}$, will be given in Appendix. As indicated by the Landau-de Gennes theory, this is expected to cover most applications.

3.2 Separation of orientational variables

We begin with writing down the symmetry arguments that the kernel function shall satisfy. Regardless of the molecular potential, the interaction between a pair of molecules shall only depend on their relative position and orientation, and be invariant when two molecules interchange. When the two molecules are rotated together by $\mathfrak{t}$, the positions and orientations of two molecules are converted into $(\mathfrak{t}\boldsymbol{x}_1,\mathfrak{t}\mathfrak{p}_1)$ and $(\mathfrak{t}\boldsymbol{x}_2,\mathfrak{t}\mathfrak{p}_2)$. Thus, their relative position becomes $\mathfrak{t}(\boldsymbol{x}_2-\boldsymbol{x}_1)=\mathfrak{t}\boldsymbol{r}_2$. When the label of two molecules are switched, $(\boldsymbol{x}_1,\mathfrak{p}_1)$ and $(\boldsymbol{x}_2,\mathfrak{p}_2)$ interchange, so that the relative position becomes $\boldsymbol{x}_1-\boldsymbol{x}_2=-\boldsymbol{r}_2$. Thus, we arrive at natural symmetries in the kernel function $\mathscr{G}_2$, given by

$$\mathscr{G}_2(\mathfrak{t}\boldsymbol{r}_2,\mathfrak{t}\mathfrak{p}_1,\mathfrak{t}\mathfrak{p}_2)=\mathscr{G}_2(\boldsymbol{r}_2,\mathfrak{p}_1,\mathfrak{p}_2),\quad \forall\mathfrak{t}\in SO(3), \tag{3.6}$$

$$\mathscr{G}_2(-\boldsymbol{r}_2,\mathfrak{p}_2,\mathfrak{p}_1)=\mathscr{G}_2(\boldsymbol{r}_2,\mathfrak{p}_1,\mathfrak{p}_2). \tag{3.7}$$

We first seek the expansion consistent with (3.6). By the definition (3.4), we have

$$\mathscr{M}_2^k(\mathfrak{t}\mathfrak{p}_1,\mathfrak{t}\mathfrak{p}_2)=\int \boldsymbol{r}_2^k\mathscr{G}_2(\boldsymbol{r}_2,\mathfrak{t}\mathfrak{p}_1,\mathfrak{t}\mathfrak{p}_2)\,\mathrm{d}\boldsymbol{r}_2.$$

Changing the dumb variable of the integral from r_2 to $\mathfrak{t}r_2$, then using (3.6), we derive that

$$\begin{aligned}\mathscr{M}_2^k(\mathfrak{t}\mathfrak{p}_1,\mathfrak{t}\mathfrak{p}_2)=&\int(\mathfrak{t}r_2)^k\mathscr{G}_2(\mathfrak{t}r_2,\mathfrak{t}\mathfrak{p}_1,\mathfrak{t}\mathfrak{p}_2)\mathrm{d}(\mathfrak{t}r_2)\\ =&\int(\mathfrak{t}r_2)^k\mathscr{G}_2(r_2,\mathfrak{p}_1,\mathfrak{p}_2)\mathrm{d}r_2\\ =&\,\mathfrak{t}\circ\int r_2^k\mathscr{G}_2(r_2,\mathfrak{p}_1,\mathfrak{p}_2)\mathrm{d}r_2\\ =&\,\mathfrak{t}\circ\mathscr{M}_2^k(\mathfrak{p}_1,\mathfrak{p}_2),\end{aligned}$$

where we incorporate the definition (2.3).

Note that $\mathscr{M}_2^k$ is a k-th order symmetric tensor. Since $\mathscr{M}_2^k$ rotates with $\mathfrak{t}$, we could choose a basis also rotating with $\mathfrak{t}$, so that the coefficients under this basis are invariant of $\mathfrak{t}$. It is thus natural to choose the basis generated by the frame $\boldsymbol{m}_i(\mathfrak{p}_1)$, yielding

$$\mathscr{M}_2^k=\sum_{k_1+k_2+k_3=k}\big(\mathscr{M}_2^k\cdot\boldsymbol{m}_1^{k_1}(\mathfrak{p}_1)\boldsymbol{m}_2^{k_2}(\mathfrak{p}_1)\boldsymbol{m}_3^{k_3}(\mathfrak{p}_1)\big)\frac{k!}{k_1!k_2!k_3!}\boldsymbol{m}_1^{k_1}(\mathfrak{p}_1)\boldsymbol{m}_2^{k_2}(\mathfrak{p}_1)\boldsymbol{m}_3^{k_3}(\mathfrak{p}_1). \tag{3.8}$$

Here, the monomial notation is still adopted in $\boldsymbol{m}_1^{k_1}(\mathfrak{p}_1)\boldsymbol{m}_2^{k_2}(\mathfrak{p}_1)\boldsymbol{m}_3^{k_3}(\mathfrak{p}_1)$. Indeed, the coefficients $\mathscr{M}_2^k\cdot\boldsymbol{m}_1^{k_1}(\mathfrak{p}_1)\boldsymbol{m}_2^{k_2}(\mathfrak{p}_1)\boldsymbol{m}_3^{k_3}(\mathfrak{p}_1)$ are scalar functions of the relative orientation $\mathfrak{p}_1^{-1}\mathfrak{p}_2$, because we have the following by noticing (2.4),

$$\begin{aligned}&\mathscr{M}_2^k(\mathfrak{t}\mathfrak{p}_1,\mathfrak{t}\mathfrak{p}_2)\cdot\boldsymbol{m}_1^{k_1}(\mathfrak{t}\mathfrak{p}_1)\boldsymbol{m}_2^{k_2}(\mathfrak{t}\mathfrak{p}_1)\boldsymbol{m}_3^{k_3}(\mathfrak{t}\mathfrak{p}_1)\\ =&\Big(\mathfrak{t}\circ\mathscr{M}_2^k(\mathfrak{p}_1,\mathfrak{p}_2)\Big)\cdot\mathfrak{t}\circ\Big(\boldsymbol{m}_1^{k_1}(\mathfrak{p}_1)\boldsymbol{m}_2^{k_2}(\mathfrak{p}_1)\boldsymbol{m}_3^{k_3}(\mathfrak{p}_1)\Big)\\ =&\mathscr{M}_2^k(\mathfrak{p}_1,\mathfrak{p}_2)\cdot\boldsymbol{m}_1^{k_1}(\mathfrak{p}_1)\boldsymbol{m}_2^{k_2}(\mathfrak{p}_1)\boldsymbol{m}_3^{k_3}(\mathfrak{p}_1).\end{aligned}$$

Choosing $\mathfrak{t}=\mathfrak{p}_1^{-1}$, we get

$$\mathscr{M}_2^k(\mathfrak{t}\mathfrak{p}_1,\mathfrak{t}\mathfrak{p}_2)\cdot\boldsymbol{m}_1^{k_1}(\mathfrak{t}\mathfrak{p}_1)\boldsymbol{m}_2^{k_2}(\mathfrak{t}\mathfrak{p}_1)\boldsymbol{m}_3^{k_3}(\mathfrak{t}\mathfrak{p}_1)=\mathscr{M}_2^k(\mathfrak{i},\mathfrak{p}_1^{-1}\mathfrak{p}_2)\cdot\boldsymbol{e}_1^{k_1}\boldsymbol{e}_2^{k_2}\boldsymbol{e}_3^{k_3}.$$

Such an expression is ready for variable separation. We then expand the scalar $\mathscr{M}_2^k(\mathfrak{i},\mathfrak{p}_1^{-1}\mathfrak{p}_2)\cdot\boldsymbol{e}_1^{k_1}\boldsymbol{e}_2^{k_2}\boldsymbol{e}_3^{k_3}$ by the orthogonal basis given in Proposition 2.2. It can be written as the sum of some terms given by $V_1^m(\mathfrak{i})\cdot V^m(\mathfrak{p}_1^{-1}\mathfrak{p}_2)$, where V_1^m and V^m are two symmetric traceless tensors of m-th order. Plugging it into (3.8), we know that $(\mathscr{M}_2^k)_{i_1\cdots i_k}$ can be expanded into the sum of terms of the following form,

$$\begin{aligned}&Y_1^k(\mathfrak{p}_1)_{i_1\cdots i_k}\big(V_1^m(\mathfrak{i})\cdot V^m(\mathfrak{p}_1^{-1}\mathfrak{p}_2)\big)\\ \text{(use (2.4))}\quad=&Y_1^k(\mathfrak{p}_1)_{i_1\cdots i_k}\big(V_1^m(\mathfrak{p}_1)\cdot V^m(\mathfrak{p}_2)\big)\\ =&\big(Y_1^k(\mathfrak{p}_1)\otimes V_1^m(\mathfrak{p}_1)\big)_{i_1\cdots i_kj_1\cdots j_m}V^m(\mathfrak{p}_2)_{j_1\cdots j_m}\\ \triangleq&\,Y(\mathfrak{p}_1)_{i_1\cdots i_kj_1\cdots j_m}V^m(\mathfrak{p}_2)_{j_1\cdots j_m},\end{aligned} \tag{3.9}$$

where $Y_1^k(\mathfrak{p}_1)$ can take any $\boldsymbol{m}_1(\mathfrak{p}_1)^{k_1}\boldsymbol{m}_2(\mathfrak{p}_1)^{k_2}\boldsymbol{m}_3(\mathfrak{p}_1)^{k_3}$ for $k_1+k_2+k_3=k$, and we denote $Y=Y_1^k\otimes V_1^m$. The above expansion is already variable separated: we could take it back into the Taylor expansion (3.3) and obtain one term in it,

$$\begin{aligned}
&\int f(\boldsymbol{x},\mathfrak{p}_1)Y(\mathfrak{p}_1)_{i_1\cdots i_k j_1\cdots j_m}V^m(\mathfrak{p}_2)_{j_1\cdots j_m}\partial_{i_1\cdots i_k}f(\boldsymbol{x},\mathfrak{p}_2)\mathrm{d}\boldsymbol{x}\mathrm{d}\mathfrak{p}_1\mathrm{d}\mathfrak{p}_2\\
=&\int\left(\int Y(\mathfrak{p}_1)_{i_1\cdots i_k j_1\cdots j_m}f(\boldsymbol{x},\mathfrak{p}_1)\mathrm{d}\mathfrak{p}_1\right)\partial_{i_1\cdots i_k}\left(\int V^m(\mathfrak{p}_2)_{j_1\cdots j_m}f(\boldsymbol{x},\mathfrak{p}_2)\mathrm{d}\mathfrak{p}_2\right)\mathrm{d}\boldsymbol{x}\\
=&\int\langle Y\rangle_{i_1\cdots i_k j_1\cdots j_m}\partial_{i_1\cdots i_k}\langle V^m\rangle_{j_1\cdots j_m}\mathrm{d}\boldsymbol{x}. \qquad (3.10)
\end{aligned}$$

We can see that the last expression is already a term about two averaged tensors $\langle Y\rangle$ and $\langle V^m\rangle$. As a result, $\mathscr{F}_2$ has been expanded into several terms in the form (3.10), which meets our motivation.

Since the space of k-th order symmetric tensors has the dimension $\binom{k+2}{2}$, we actually expand $\binom{k+2}{2}$ scalar functions on $SO(3)$. Therefore, when Y_1^k takes the basis tensors $\boldsymbol{m}_1^{k_1}\boldsymbol{m}_2^{k_2}\boldsymbol{m}_3^{k_3}$ and V_1^m, V^m take the basis tensors in $\mathbb{W}^m$, the terms in (3.9) are linearly independent. When m is fixed, we note that Y_1^k has $\binom{k+2}{2}$ choices, V_1^m and V^m both have $2m+1$ choices. Thus, the total number of these terms is $\binom{k+2}{2}(2m+1)^2$. In addition, we know that $\mathscr{M}_2^k$ is square integrable since we have assumed $\mathscr{G}_2$ is, which implies that the $\binom{k+1}{2}$ scalars are all within $L^2(SO(3))$. From Proposition 2.2 we know that when m takes throughout all nonnegative integers, these terms form a complete orthogonal basis.

However, the above form is inconvenient when discussing (3.7) and molecular symmetries afterwards. In what follows, we decompose Y into symmetric traceless tensors and identify the linearly independent terms after the decomposition.

3.3 Expansion by symmetric traceless tensors

We shall first focus on what types of terms might appear in the decomposition of a tensor into symmetric traceless tensors, and write down the corresponding terms when taking them into (3.9). Then, we shall identify the linearly independent terms.

For an s-th order tensor X^s, we could express it as the sum of several tensors whose components are all from symmetric traceless tensors. The decomposition is described briefly in Appendix. Here, we only present the result. If we write out the coordinates of X^s as $X^s_{\mu_1\cdots\mu_s}$, we have three types of terms,

$$\delta_{\mu_{\alpha_1}\mu_{\alpha_2}}\cdots\delta_{\mu_{\alpha_{2\sigma-1}}\mu_{\alpha_{2\sigma}}}U^r_{\mu_{\gamma_1}\cdots\mu_{\gamma_r}}, \qquad (3.11a)$$

$$\epsilon_{\mu_{\zeta_1}\mu_{\zeta_2}\nu}\delta_{\mu_{\alpha_1}\mu_{\alpha_2}}\cdots\delta_{\mu_{\alpha_{2\sigma-1}}\mu_{\alpha_{2\sigma}}}U^r_{\nu\mu_{\gamma_2}\cdots\mu_{\gamma_r}}, \qquad (3.11b)$$

$$\epsilon_{\mu_{\zeta_1}\mu_{\zeta_2}\mu_{\zeta_3}}\delta_{\mu_{\alpha_1}\mu_{\alpha_2}}\cdots\delta_{\mu_{\alpha_{2\sigma-1}}\mu_{\alpha_{2\sigma}}}U^r_{\mu_{\gamma_1}\cdots\mu_{\gamma_r}}. \qquad (3.11c)$$

In the above, U^r represents an r-th order symmetric traceless tensor. The indices not repeated give exactly all the indices of X^s. For example, in (3.11a) we have

$\{\alpha_1\cdots,\alpha_{2\sigma},\gamma_1,\cdots,\gamma_r\}=\{1,\cdots,s\}$. These terms are generated by a symmetric traceless tensor, some identity tensors, and possibly one determinant tensor. The order of the tensor U^r, r, and the number of identity tensors, σ, can vary, provided that the term gives a tensor of the same order as X^s. To write down explicitly, the three terms in (3.11) shall satisfy

$$\begin{aligned} 2\sigma+r&=s, \quad \text{in (3.11a)},\\ 2\sigma+r+1&=s, \quad \text{in (3.11b)},\\ 2\sigma+r+3&=s, \quad \text{in (3.11c)}. \end{aligned} \tag{3.12}$$

Now we apply the decomposition to the tensor $Y=Y_1^k\otimes V_1^m$ in (3.9). We shall keep in mind that Y_1^k is a k-th order symmetric tensor, and V_1^m, V^m are m-th order symmetric traceless tensors. Let us examine the indices of δ and ϵ in the decomposition. Note that in a symmetric tensor, every index is equivalent. Thus, we only need to examine how many of the indices are located in Y_1^k or V_1^m.

- If both indices in a δ are located in V_1^m, the resulting term is zero when taking into (3.9), because it leads to the contraction of two indices in V^m.

- For the three indices in ϵ, if any two of them are located in Y_1^k (or V_1^m), then the term will vanish because Y_1^k and V_1^m are symmetric. The nonvanishing term must have one index in Y_1^k, one in V_1^m, and the third can only be the ν of $U_{\nu\cdots}$ in (3.11b). In other words, (3.11c) contributes nothing in (3.9).

Thus, we can specify the following.

- Some indices of U^r are located in V_1^m. These indices are contracted between U^r and V^m. Suppose the number of such indices is p.

- For some δ, both indices in it are located in Y_1^k. Suppose the number of such δ is q.

- For other δ, one index is located in Y_1^k, while the other is located in V_1^m. The number of such δ is $m-p$ in (3.11a), because it equals the number of indices in V^m not contracted with U^r. Similarly, the number of such δ is $m-p-1$ in (3.11b).

Summarizing these cases, we obtain some terms expressed by a pair of symmetric traceless tensors. They can be written as the *symmetrization* of tensors of the two types below, which we denote by A_1 and A_2 respectively,

$$(A_1)_{i_1\cdots i_k}=\delta_{i_{\alpha_1}i_{\alpha_2}}\cdots\delta_{i_{\alpha_{2q-1}}i_{\alpha_{2q}}}U^r(\mathfrak{p}_1)_{i_{\beta_1}\cdots i_{\beta_{r-p}}j_1\cdots j_p}V^m(\mathfrak{p}_2)_{i_{\gamma_1}\cdots i_{\gamma_{m-p}}j_1\cdots j_p}, \tag{3.13a}$$

$$(A_2)_{i_1\cdots i_k}=\epsilon_{\zeta_1\zeta_2 i_\nu}\delta_{i_{\alpha_1}i_{\alpha_2}}\cdots\delta_{i_{\alpha_{2q-1}}i_{\alpha_{2q}}}U^r(\mathfrak{p}_1)_{\zeta_1 i_{\beta_1}\cdots i_{\beta_{r-p-1}}j_1\cdots j_p}V^m(\mathfrak{p}_2)_{\zeta_2 i_{\gamma_1}\cdots i_{\gamma_{m-p-1}}j_1\cdots j_p}. \tag{3.13b}$$

The indices $i_{\cdots}$ on the right hand side also give exactly all $i_1,\cdots,i_k$. Let us define two short notations,

$$U^r \overset{p}{\cdot} V^m = (Z_1)_{\rm sym}, \quad (Z_1)_{i_1\cdots i_{r+m-2p}} = U^r_{j_1\cdots j_p i_1\cdots i_{r-p}} V^m_{j_1\cdots j_p i_{r-p+1}\cdots i_{r+m-2p}}, \tag{3.14a}$$

$$U^r \overset{p}{\times} V^m = (Z_2)_{\rm sym}, \quad (Z_2)_{i_1\cdots i_{r+m-2p-1}} = \epsilon_{\zeta_1\zeta_2 i_1} U^r_{\zeta_1 j_1\cdots j_p i_2\cdots i_{r-p}} V^m_{\zeta_2 j_1\cdots j_p i_{r-p+1}\cdots i_{r+m-2p-1}}, \tag{3.14b}$$

where we write the number of indices shared by U^r and V^m, the integer p, over the operator between the two tensors. Rewriting $(A_1)_{\rm sym}$ and $(A_2)_{\rm sym}$ for A_1 and A_2 in (3.13), any term given by (3.9) can be expressed linearly by the following terms,

$$\mathrm{i}^q U^r(\mathfrak{p}_1) \overset{p}{\cdot} V^m(\mathfrak{p}_2), \quad k = 2q+r+m-2p, \tag{3.15a}$$

$$\mathrm{i}^q U^r(\mathfrak{p}_1) \overset{p}{\times} V^m(\mathfrak{p}_2), \quad k = 2q+r+m-2p-1. \tag{3.15b}$$

The relation of tensor order is a direct result of (3.12).

Note that V^m is the same tensor in (3.9) and (3.15). We shall prove the following by counting the number of terms given by (3.15).

Theorem 3.1. *Let k and V^m be fixed. Let r,p,q vary and $U^r \in \mathbb{W}^r$. The terms given in* (3.15) *are linearly independent, and are linearly equivalent to the terms given in* (3.9).

Proof. In the above derivation, we actually show that (3.9) can be linearly expressed by the terms given in (3.15). Recall that when V^m is fixed, the total number of linearly independent terms given by (3.9) is $\frac{1}{2}(k+2)(k+1)\cdot(2m+1)$. Thus, we only need to prove that this is exactly the number of terms given by (3.15) (when $U^r \in \mathbb{W}^r$).

Since k and m are fixed, the relation of tensor order in (3.15) is actually about p, q and r. The r-th order symmetric traceless tensor U^r has $2r+1$ choices. We shall count the choices of (p,q) with a fixed r, which can be done by counting the choices of either p or q. In (3.15), the indices shall be nonnegative integers. Moreover, it requires $p \le r,m$ in (3.15a) and $p+1 \le r,m$ in (3.15b). Thus, we deduce the range for the indices,

$$\begin{aligned}
&(3.15a): \quad r+m-k \text{ even}, \max\left\{0, \frac{r+m-k}{2}\right\} \le p \le \min\{m,r\};\\
&(3.15b): \quad r+m-k \text{ odd}, \max\left\{0, \frac{r+m-k-1}{2}\right\} \le p \le \min\{m,r\}-1.
\end{aligned}$$

If $k \le m$, by requiring the upper bounds no less than the lower bounds in (3.15), we deduce that $m-k \le r \le m+k$. The number of p available is given by

$$\begin{aligned}
&(3.15a): \quad \frac{k-|r-m|}{2}+1,\\
&(3.15b): \quad \frac{k-|r-m|-1}{2}+1.
\end{aligned}$$

Hence, the total number of terms is

$$\sum_{k-|r-m|\geq 0 \text{ even}} \frac{k-|r-m|+2}{2}(2r+1)+\sum_{k-|r-m|\geq 0 \text{ odd}} \frac{k-|r-m|+1}{2}(2r+1).$$

Let $u=r-m$ so that $r=m+u$. The above number is calculated as

$$\begin{aligned}
&\sum_{k-|u|\geq 0 \text{ even}} \frac{k-|u|+2}{2}(2m+1+2u)+\sum_{k-|u|\geq 0 \text{ odd}} \frac{k-|u|+1}{2}(2m+1+2u)\\
=&\sum_{k-|u|\geq 0 \text{ even}} \frac{k-|u|+2}{2}(2m+1)+\sum_{k-|u|\geq 0 \text{ odd}} \frac{k-|u|+1}{2}(2m+1)\\
=&(2m+1)\Big(\sum_{k-|u|\geq 0 \text{ even}} \frac{k-|u|+2}{2}+\sum_{k-|u|\geq 0 \text{ odd}} \frac{k-|u|+1}{2}\Big)\\
=&(2m+1)\cdot\frac{1}{2}(k+1)(k+2).
\end{aligned}$$

If $k>m$, let us do induction about k, based on $k=m,m-1$ that have been shown above. Suppose that for $k-2$, the total number is $\frac{1}{2}k(k-1)(2m+1)$. If $q>0$, a term for k corresponds to a term for $k-2$ by substituting q with $q-1$. Now we count the number of terms where $q=0$. There are two cases:

- $r=k-m+2p$ for $0\leq p\leq m$;
- $r=k-m+2p+1$ for $0\leq p\leq m-1$.

Summarizing the two cases, we have $k-m\leq r\leq k+m$ and p is determined correspondingly. The total number of terms when $q=0$ is thus

$$\sum_{r=k-m}^{k+m}(2r+1)=(2k+1)(2m+1)=\frac{1}{2}(k+2)(k+1)(2m+1)-\frac{1}{2}k(k-1)(2m+1).$$

The only case remaining is $m=0$, $k=1$, for which we can count directly. □

Remark 3.1. It follows from the paragraph below (3.10) that when $(U^r,V^m)\in\mathbb{W}^r\times\mathbb{W}^m$ with both r and m varying, the terms in (3.15) are linearly independent. We shall point out that it is not always the case that the terms expressed by symmetric traceless tensors are linearly independent, as we will see in the expansion of $\mathscr{M}_4^{0,0,0}$ in Appendix. In that case, the approach in the proof above is also useful.

We next deal with the property (3.7). From the definition of $\mathscr{M}_2^k$, it leads to

$$\mathscr{M}_2^k(\mathfrak{p}_2,\mathfrak{p}_1)=(-1)^k\mathscr{M}_2^k(\mathfrak{p}_1,\mathfrak{p}_2). \tag{3.16}$$

From (3.15), it is straightforward to write down a set of basis functions for the expansion. For $(U^r,V^m)\in\mathbb{W}^r\times\mathbb{W}^m$, we consider the following two sets,

$$\begin{aligned}&\mathbb{X}^k_{n,+1}\\=&\left\{\mathrm{i}^qU^r(\mathfrak{p}_1)\overset{p}{\cdot}V^m(\mathfrak{p}_2)+\mathrm{i}^qV^m(\mathfrak{p}_1)\overset{p}{\cdot}U^r(\mathfrak{p}_2):\ k=2q+r+m-2p,\ r,m\le n\right\}\\&\cup\left\{\mathrm{i}^qU^r(\mathfrak{p}_1)\overset{p}{\times}V^m(\mathfrak{p}_2)-\mathrm{i}^qV^m(\mathfrak{p}_1)\overset{p}{\times}U^r(\mathfrak{p}_2):\ k=2q+r+m-2p-1,\ r,m\le n,\ U^r\ne V^m\right\},\end{aligned}\tag{3.17a}$$

$$\begin{aligned}&\mathbb{X}^k_{n,-1}\\=&\left\{\mathrm{i}^qU^r(\mathfrak{p}_1)\overset{p}{\cdot}V^m(\mathfrak{p}_2)-\mathrm{i}^qV^m(\mathfrak{p}_1)\overset{p}{\cdot}U^r(\mathfrak{p}_2):\ k=2q+r+m-2p,\ r,m\le n,\ U^r\ne V^m\right\}\\&\cup\left\{\mathrm{i}^qU^r(\mathfrak{p}_1)\overset{p}{\times}V^m(\mathfrak{p}_2)+\mathrm{i}^qV^m(\mathfrak{p}_1)\overset{p}{\times}U^r(\mathfrak{p}_2):\ k=2q+r+m-2p-1,\ r,m\le n\right\}.\end{aligned}\tag{3.17b}$$

Here, we require $U^r\ne V^m$ in some sets to avoid zero. The terms in $\mathbb{X}^k_{n,1}\cup\mathbb{X}^k_{n,-1}$ are also linearly independent and linearly equivalent to (3.15).

Any term $\Phi(\mathfrak{p}_1,\mathfrak{p}_2)\in\mathbb{X}^k_{n,\pm1}$ satisfies $\Phi(\mathfrak{p}_2,\mathfrak{p}_1)=\pm\Phi(\mathfrak{p}_1,\mathfrak{p}_2)$. Thus, it is easy to verify that the two spaces are orthogonal using the definition (2.8): suppose $\Phi_1(\mathfrak{p}_1,\mathfrak{p}_2)\in\mathbb{X}^k_{n,+1}$ and $\Phi_2(\mathfrak{p}_1,\mathfrak{p}_2)\in\mathbb{X}^k_{n,-1}$, then

$$\begin{aligned}&\int\Phi_1(\mathfrak{p}_1,\mathfrak{p}_2)\cdot\Phi_2(\mathfrak{p}_1,\mathfrak{p}_2)\mathrm{d}\mathfrak{p}_1\mathrm{d}\mathfrak{p}_2\\ \text{(change dumb variables)}=&\int\Phi_1(\mathfrak{p}_2,\mathfrak{p}_1)\cdot\Phi_2(\mathfrak{p}_2,\mathfrak{p}_1)\mathrm{d}\mathfrak{p}_1\mathrm{d}\mathfrak{p}_2\\=&\int\Phi_1(\mathfrak{p}_1,\mathfrak{p}_2)\cdot\big(-\Phi_2(\mathfrak{p}_1,\mathfrak{p}_2)\big)\mathrm{d}\mathfrak{p}_1\mathrm{d}\mathfrak{p}_2.\end{aligned}$$

It follows from (3.16) that $(\mathscr{M}^k_2,\Phi)=0$ for any $\Phi(\mathfrak{p}_1,\mathfrak{p}_2)\in\mathbb{X}^k_{n,(-1)^{k+1}}$. Therefore, for odd k, the expansion of $\mathscr{M}^k_2$ can only have terms in $\mathbb{X}^k_{n,-1}$, while for even k it can only have terms in $\mathbb{X}^k_{n,+1}$.

Corollary 3.1. *When $(U^r,V^m)\in\mathbb{W}^r\times\mathbb{W}^m$ for $r,m\le n$, the terms in $\mathbb{X}^k_{n,(-1)^k}$ satisfy* (3.6) *and* (3.7)*, and are linearly independent. When n ranges throughout the integers, they give complete basis functions for the expansion of $\mathscr{M}^k_2$.*

3.3.1 Summary of explicit expressions, relation to the free energy

Here, we summarize the explicit formulae for the terms in the expansion of $\mathscr{M}^k_2$ where $0\le k\le 4$ in Table 1, from $\mathbb{X}^k_{n,(-1)^k}$. When taking these terms back into (3.3), the integrals $\mathrm{d}\mathfrak{p}_i$ are decoupled like what is done in (3.10), leading to the terms in the free energy expressed by tensors that are also listed in Table 1. We do not distinguish terms that coincide under

Table 1: Linearly independent terms in the expansion and the corresponding terms in the free energy. All the tensors are symmetric traceless. The notation $\langle U\rangle$ represents the average of $U(\mathfrak{p})$ about the density $f(\boldsymbol{x},\mathfrak{p})$.

	Orientational expansion	Free energy
$\mathscr{M}_2^0$	$U^n(\mathfrak{p}_1)\cdot V^n(\mathfrak{p}_2)+V^n(\mathfrak{p}_1)\cdot U^n(\mathfrak{p}_2)$	$\langle U^n\rangle_{i_1\cdots i_n}\langle V^n\rangle_{i_1\cdots i_n}=U^n\cdot V^n$
$\mathscr{M}_2^1$	$U^{n-1}(\mathfrak{p}_1)\overset{n-1}{\cdot}V^n(\mathfrak{p}_2)-V^n(\mathfrak{p}_1)\overset{n-1}{\cdot}U^{n-1}(\mathfrak{p}_2)$	$\langle U^{n-1}\rangle_{i_1\cdots i_{n-1}}\partial_j\langle V^n\rangle_{i_1\cdots i_{n-1}j}$
	$U^n(\mathfrak{p}_1)\overset{n-1}{\times}V^n(\mathfrak{p}_2)+V^n(\mathfrak{p}_1)\overset{n-1}{\times}U^n(\mathfrak{p}_2)$	$\epsilon_{ijk}\langle U^n\rangle_{i_1\cdots i_{n-1}i}\partial_k\langle V^n\rangle_{i_1\cdots i_{n-1}j}$
$\mathscr{M}_2^2$	$\mathrm{i}(U^n(\mathfrak{p}_1)\cdot V^n(\mathfrak{p}_2)+V^n(\mathfrak{p}_1)\cdot U^n(\mathfrak{p}_2))$	$\partial_j\langle U^n\rangle_{i_1\cdots i_n}\partial_j\langle V^n\rangle_{i_1\cdots i_n}$
	$U^n(\mathfrak{p}_1)\overset{n-1}{\cdot}V^n(\mathfrak{p}_2)+V^n(\mathfrak{p}_1)\overset{n-1}{\cdot}U^n(\mathfrak{p}_2)$	$\partial_{j_1}\langle U^n\rangle_{i_1\cdots i_{n-1}j_1}\partial_{j_2}\langle V^n\rangle_{i_1\cdots i_{n-1}j_2}$
	$U^{n-2}(\mathfrak{p}_1)\overset{n-2}{\cdot}V^n(\mathfrak{p}_2)+V^n(\mathfrak{p}_1)\overset{n-2}{\cdot}U^{n-2}(\mathfrak{p}_2)$	$\partial_j\langle U^{n-2}\rangle_{i_1\cdots i_{n-2}}\partial_k\langle V^n\rangle_{i_1\cdots i_{n-2}jk}$
	$U^n(\mathfrak{p}_1)\overset{n-2}{\times}V^{n-1}(\mathfrak{p}_2)-V^{n-1}(\mathfrak{p}_1)\overset{n-2}{\times}U^n(\mathfrak{p}_2)$	$\epsilon_{ijk}\partial_l\langle U^n\rangle_{i_1\cdots i_{n-2}il}\partial_k\langle V^{n-1}\rangle_{i_1\cdots i_{n-2}j}$
$\mathscr{M}_2^3$	$\mathrm{i}U^{n-1}(\mathfrak{p}_1)\overset{n-1}{\cdot}V^n(\mathfrak{p}_2)-\mathrm{i}V^n(\mathfrak{p}_1)\overset{n-1}{\cdot}U^{n-1}(\mathfrak{p}_2)$	$\partial_{j_1}\langle U^{n-1}\rangle_{i_1\cdots i_{n-1}}\partial_{j_1j_2}\langle V^n\rangle_{i_1\cdots i_{n-1}j_2}$
	$\mathrm{i}U^n(\mathfrak{p}_1)\overset{n-1}{\times}V^n(\mathfrak{p}_2)+\mathrm{i}V^n(\mathfrak{p}_1)\overset{n-1}{\times}U^n(\mathfrak{p}_2)$	$\epsilon_{ijk}\partial_l\langle U^n\rangle_{i_1\cdots i_{n-1}i}\partial_{kl}\langle V^n\rangle_{i_1\cdots i_{n-1}j}$
	$U^{n-1}(\mathfrak{p}_1)\overset{n-2}{\cdot}V^n(\mathfrak{p}_2)-V^n(\mathfrak{p}_1)\overset{n-2}{\cdot}U^{n-1}(\mathfrak{p}_2)$	$\partial_{j_1}\langle U^{n-1}\rangle_{i_1\cdots i_{n-2}j_1}\partial_{j_2j_3}\langle V^n\rangle_{i_1\cdots i_{n-2}j_2j_3}$
	$U^n(\mathfrak{p}_1)\overset{n-2}{\times}V^n(\mathfrak{p}_2)+V^n(\mathfrak{p}_1)\overset{n-2}{\times}U^n(\mathfrak{p}_2)$	$\epsilon_{ijk}\partial_{j_1}\langle U^n\rangle_{i_1\cdots i_{n-2}j_1i}\partial_{kj_2}\langle V^n\rangle_{i_1\cdots i_{n-2}j_2j}$
	$U^{n-3}(\mathfrak{p}_1)\overset{n-3}{\cdot}V^n(\mathfrak{p}_2)-V^n(\mathfrak{p}_1)\overset{n-3}{\cdot}U^{n-3}(\mathfrak{p}_2)$	$\partial_{j_1}\langle U^{n-3}\rangle_{i_1\cdots i_{n-3}}\partial_{j_2j_3}\langle V^n\rangle_{i_1\cdots i_{n-2}j_1j_2j_3}$
	$U^{n-2}(\mathfrak{p}_1)\overset{n-3}{\times}V^n(\mathfrak{p}_2)+V^n(\mathfrak{p}_1)\overset{n-3}{\times}U^{n-2}(\mathfrak{p}_2)$	$\epsilon_{ijk}\partial_k\langle U^{n-2}\rangle_{i_1\cdots i_{n-3}i}\partial_{j_1j_2}\langle V^n\rangle_{i_1\cdots i_{n-3}j_1j_2j}$
$\mathscr{M}_2^4$	$\mathrm{i}^2(U^n(\mathfrak{p}_1)\cdot V^n(\mathfrak{p}_2)+V^n(\mathfrak{p}_1)\cdot U^n(\mathfrak{p}_2))$	$\partial_{j_1j_2}\langle U^n\rangle_{i_1\cdots i_n}\partial_{j_1j_2}\langle V^n\rangle_{i_1\cdots i_n}$
	$\mathrm{i}U^n(\mathfrak{p}_1)\overset{n-1}{\cdot}V^n(\mathfrak{p}_2)+\mathrm{i}V^n(\mathfrak{p}_1)\overset{n-1}{\cdot}U^n(\mathfrak{p}_2)$	$\partial_{j_1j_3}\langle U^n\rangle_{i_1\cdots i_{n-1}j_1}\partial_{j_2j_3}\langle V^n\rangle_{i_1\cdots i_{n-1}j_2}$
	$U^n(\mathfrak{p}_1)\overset{n-2}{\cdot}V^n(\mathfrak{p}_2)+V^n(\mathfrak{p}_1)\overset{n-2}{\cdot}U^n(\mathfrak{p}_2)$	$\partial_{j_1j_2}\langle U^n\rangle_{i_1\cdots i_{n-2}j_1j_2}\partial_{j_3j_4}\langle V^n\rangle_{i_1\cdots i_{n-2}j_3j_4}$
	$\mathrm{i}U^{n-2}(\mathfrak{p}_1)\overset{n-2}{\cdot}V^n(\mathfrak{p}_2)+\mathrm{i}V^n(\mathfrak{p}_1)\overset{n-2}{\cdot}U^{n-2}(\mathfrak{p}_2)$	$\partial_{j_1j_2}\langle U^{n-2}\rangle_{i_1\cdots i_{n-2}}\partial_{j_1j_3}\langle V^n\rangle_{i_1\cdots i_{n-2}j_2j_3}$
	$U^{n-2}(\mathfrak{p}_1)\overset{n-3}{\cdot}V^n(\mathfrak{p}_2)+V^n(\mathfrak{p}_1)\overset{n-3}{\cdot}U^{n-2}(\mathfrak{p}_2)$	$\partial_{j_1j_2}\langle U^{n-2}\rangle_{i_1\cdots i_{n-3}j_1}\partial_{j_3j_4}\langle V^n\rangle_{i_1\cdots i_{n-3}j_2j_3j_4}$
	$\mathrm{i}U^{n-1}(\mathfrak{p}_1)\overset{n-2}{\times}V^n(\mathfrak{p}_2)-\mathrm{i}V^n(\mathfrak{p}_1)\overset{n-2}{\times}U^{n-1}(\mathfrak{p}_2)$	$\epsilon_{ijk}\partial_{j_1j_2}\langle U^n\rangle_{i_1\cdots i_{n-2}j_2i}\partial_{kj_1}\langle V^{n-1}\rangle_{i_1\cdots i_{n-2}j}$
	$U^n(\mathfrak{p}_1)\overset{n-3}{\times}V^{n-1}(\mathfrak{p}_2)-V^{n-1}(\mathfrak{p}_1)\overset{n-3}{\times}U^n(\mathfrak{p}_2)$	$\epsilon_{ijk}\partial_{j_1j_2}\langle U^n\rangle_{i_1\cdots i_{n-3}j_1j_2i}\partial_{kj_3}\langle V^{n-1}\rangle_{i_1\cdots i_{n-3}j_3j}$
	$U^{n-3}(\mathfrak{p}_1)\overset{n-4}{\times}V^n(\mathfrak{p}_2)-V^n(\mathfrak{p}_1)\overset{n-4}{\times}U^{n-3}(\mathfrak{p}_2)$	$\epsilon_{ijk}\partial_{kj_1}\langle U^{n-3}\rangle_{i_1\cdots i_{n-4}i}\partial_{j_2j_3}\langle V^n\rangle_{i_1\cdots i_{n-4}j_1j_2j_3j}$
	$U^{n-4}(\mathfrak{p}_1)\overset{n-4}{\cdot}V^n(\mathfrak{p}_2)+V^n(\mathfrak{p}_1)\overset{n-4}{\cdot}U^{n-4}(\mathfrak{p}_2)$	$\partial_{j_1j_2}\langle U^{n-4}\rangle_{i_1\cdots i_{n-4}}\partial_{j_3j_4}\langle V^n\rangle_{i_1\cdots i_{n-4}j_1j_2j_3j_4}$

For the notations: $\overset{p}{\cdot}$ and $\overset{p}{\times}$, see (3.14).

integration by parts. For example, we consider

$$
\begin{aligned}
&\int\big(U^{n-1}(\mathfrak{p}_1)\overset{n-1}{\cdot}V^n(\mathfrak{p}_2)-V^n(\mathfrak{p}_1)\overset{n-1}{\cdot}U^{n-1}(\mathfrak{p}_2)\big)f(\boldsymbol{x},\mathfrak{p}_1)f(\boldsymbol{x},\mathfrak{p}_2)\mathrm{d}\mathfrak{p}_1\mathrm{d}\mathfrak{p}_2\\
=&\langle U^{n-1}\rangle_{i_1\cdots i_{n-1}}\partial_j\langle V^n\rangle_{i_1\cdots i_{n-1}j}-\langle V^n\rangle_{i_1\cdots i_{n-1}j}\partial_j\langle U^{n-1}\rangle_{i_1\cdots i_{n-1}}\\
=&2\langle U^{n-1}\rangle_{i_1\cdots i_{n-1}}\partial_j\langle V^n\rangle_{i_1\cdots i_{n-1}j}-\partial_j\Big(\langle V^n\rangle_{i_1\cdots i_{n-1}j}\langle U^{n-1}\rangle_{i_1\cdots i_{n-1}}\Big).
\end{aligned}
$$

When integrated about $\mathrm{d}\boldsymbol{x}$, the second term in the last line leads to a surface integral. In this sense, we regard $\langle U^{n-1}\rangle_{i_1\cdots i_{n-1}}\partial_j\langle V^n\rangle_{i_1\cdots i_{n-1}j}$ and $\langle V^n\rangle_{i_1\cdots i_{n-1}j}\partial_j\langle U^{n-1}\rangle_{i_1\cdots i_{n-1}}$ as the same term.

The correspondence of terms in the free energy and the terms in the expansion is crucial for computing the coefficients in tensor model from the microscopic interaction [4, 15, 28, 34, 35]. The molecular potential determines $\mathscr{G}$, then determines $\mathscr{M}$, on which the expansion is done. In this way, the coefficients of the expansion, which is also the coefficients of the free energy, can be computed as functions of parameters in the molecular potential. When actually implementing the above procedure, it is significant to find out the orthogonality of the terms in the expansion, which we discuss below.

3.4 Orthogonal basis

Corollary 3.1 has claimed that basis functions for the expansion of $\mathscr{M}_2^k$ can be given by $\mathbb{X}^k_{n,\pm1}$. Thus, we only need to find some linear combinations of them that form an orthogonal basis.

Note that for a fixed pair of tensors (U^r,V^m), there can be multiple terms in (3.15) involving them. To achieve orthogonality for these terms, we derive some symmetric traceless tensors related to these terms. We know from Proposition 2.1 that there exists a unique symmetric traceless tensor generated by $U^r\overset{p}{\cdot}V^m$. Below, we would like to derive the explicit formulae.

We could express

$$(U^r\overset{p}{\cdot}V^m)_0=U^r\overset{p}{\cdot}V^m+\sum_{l=1}^{\min\{r,m\}-p}a_l^{r,m,p}\mathfrak{i}^lU\overset{p+l}{\cdot}V. \tag{3.18}$$

Calculating the trace using (2.5), we deduce that

$$\begin{aligned}\mathrm{tr}\Big(\mathfrak{i}^lU^r\overset{p+l}{\cdot}V^m\Big)=&2l\big(2(r+m-2p)+1-2l\big)\mathfrak{i}^{l-1}U^r\overset{p+l}{\cdot}V^m\\&+2(r-p-l)(m-p-l)\mathfrak{i}^lU^r\overset{p+l+1}{\cdot}V^m.\end{aligned}$$

So we have

$$2l\big(2(r+m-2p)+1-2l\big)a_l^{r,m,p}+2(r-p-l+1)(m-p-l+1)a_{l-1}^{r,m,p}=0.$$

Therefore, we solve recursively that

$$a_l^{r,m,p}=(-1)^l\frac{(r-p)!(m-p)!\big(2(r+m-2p)-1-2l\big)!!}{l!(r-p-l)!(m-p-l)!\big(2(r+m-2p)-1\big)!!}.$$

Similarly, we deduce that

$$(U^r\overset{p}{\times}V^m)_0=U^r\overset{p}{\times}V^m+\sum_{l=1}^{\min\{r,m\}-p-1}b_l^{r,m,p}\mathfrak{i}^lU^r\overset{p+l}{\times}V^m, \tag{3.19}$$

where the coefficients are

$$b_l^{r,m,p}=(-1)^l\frac{(r-p-1)!(m-p-1)!\big(2(r+m-2p)-3-2l\big)!!}{l!(r-p-l-1)!(m-p-l-1)!\big(2(r+m-2p)-3\big)!!}.$$

Theorem 3.2. *The following terms give an orthogonal basis of the space* $\mathrm{span}\mathbb{X}^k_{n,(-1)^k}$,

$$\mathfrak{i}^q\Big(U^r(\mathfrak{p}_1)\overset{p}{\cdot}V^m(\mathfrak{p}_2)+(-1)^kV^m(\mathfrak{p}_1)\overset{p}{\cdot}U^r(\mathfrak{p}_2)\Big)_0,\quad k=2q+r+m-2p, \tag{3.20a}$$

$$\mathfrak{i}^q\Big(U^r(\mathfrak{p}_1)\overset{p}{\times}V^m(\mathfrak{p}_2)-(-1)^kV^m(\mathfrak{p}_1)\overset{p}{\times}U^r(\mathfrak{p}_2)\Big)_0,\quad k=2q+r+m-2p-1, \tag{3.20b}$$

where U^r *and* V^m *take symmetric traceless tensors in* $\mathbb{W}^r$ *and* $\mathbb{W}^m$*, respectively, for* $r,m\le n$.

Proof. The expressions (3.18) and (3.19) indicate that the terms in (3.20) are linearly equivalent to $\mathbb{X}^k_{n,(-1)^k}$, and are linearly independent. Therefore, we only need to show orthogonality.

First, we need to notice that if $r\neq m$ or $j\neq l$, then we have

$$\int(W_j^r(\mathfrak{p})\otimes W_l^m(\mathfrak{p}))_{i_1\cdots i_r i'_1\cdots i'_m}\mathrm{d}\mathfrak{p}=\int(W_j^r(\mathfrak{p}))_{i_1\cdots i_r}(W_l^m(\mathfrak{p}))_{i'_1\cdots i'_m}\mathrm{d}\mathfrak{p}=0. \tag{3.21}$$

Here, we could write

$$\begin{aligned}(W_j^r(\mathfrak{p}))_{i_1\cdots i_r}&=W_j^r(\mathfrak{p})\cdot\boldsymbol{e}_{i_1}\cdots\boldsymbol{e}_{i_r}=W_j^r(\mathfrak{p})\cdot(\boldsymbol{e}_{i_1}\cdots\boldsymbol{e}_{i_r})_0\\&=\sum_{j'}W_j^r(\mathfrak{p})\cdot\lambda_{j'}W_{j'}^r(\mathfrak{i}),\end{aligned}$$

where in the second equality we use the fact that W_j^r is symmetric traceless, and in the last equality we express $(\boldsymbol{e}_{i_1}\cdots\boldsymbol{e}_{i_r})_0$ by the basis in $\mathbb{W}^r$. Eq. (3.21) then comes directly from the orthogonality in Proposition 2.2.

To deal with the terms in (3.20), we go back to (3.15). Let us denote in short a term in (3.15) by $\Phi(U^r(\mathfrak{p}_1),V^m(\mathfrak{p}_2))$. Consider two terms in (3.15), $\Phi_1(U_1^{r_1}(\mathfrak{p}_1),V_1^{m_1}(\mathfrak{p}_2))$ and $\Phi_2(U_2^{r_2}(\mathfrak{p}_1),V_2^{m_2}(\mathfrak{p}_2))$, where $(U_i^{r_i},V_i^{m_i})\in\mathbb{W}^{r_i}\times\mathbb{W}^{m_i}$. If $U_1^{r_1}\neq U_2^{r_2}$ or $V_1^{m_1}\neq V_2^{r_2}$, we show the orthogonality using (3.21). To recognize this, we notice that a dot product of two tensors can be rewritten as

$$R\cdot S=R_{j_1\cdots j_k}S_{j'_1\cdots j'_k}\delta_{j_1j'_1}\cdots\delta_{j_kj'_k}=(R\otimes S)\cdot Z, \tag{3.22}$$

where the tensor Z is composed by those δ. In the same way, the inner product (Φ_1,Φ_2) can be written in the following form,

$$\begin{aligned}(\Phi_1,\Phi_2)&=\int U_1^{r_1}(\mathfrak{p}_1)\otimes U_2^{r_2}(\mathfrak{p}_1)\otimes V_1^{m_1}(\mathfrak{p}_2)\otimes V_2^{m_2}(\mathfrak{p}_2)\cdot Z\mathrm{d}\mathfrak{p}_1\mathrm{d}\mathfrak{p}_2\\&=\Big(\int U_1^{r_1}(\mathfrak{p}_1)\otimes U_2^{r_2}(\mathfrak{p}_1)\mathrm{d}\mathfrak{p}_1\Big)\otimes\Big(\int V_1^{m_1}(\mathfrak{p}_2)\otimes V_2^{m_2}(\mathfrak{p}_2)\mathrm{d}\mathfrak{p}_2\Big)\cdot Z,\end{aligned}$$

where Z is some constant tensor. In the case of $U_1^{r_1} \neq U_2^{r_2}$ or $V_1^{m_1} \neq V_2^{r_2}$, at least one of the two integrals is zero, so $(\Phi_1,\Phi_2)=0$. Since the terms in (3.20) are linear combinations of the terms in (3.15), we deduce the orthogonality if the tensor pairs are not identical in two terms.

Next, we consider the case $U_1^{r_1}=U_2^{r_2}=U^r$ and $V_1^{m_1}=V_2^{m_2}=V^m$. Under this assumption, the different terms in the (3.20) must have different q. We shall use the following fact: for a symmetric traceless tensor X no less than second order, it holds

$$(\mathrm{i}^q X) \overset{2q+2}{\cdot} \mathrm{i}^{q+1} = a\,\mathrm{tr}X = 0,$$

where a is some constant. Therefore, when calculating the inner product (Φ_1,Φ_2), we can verify that the integrand will be zero. □

When one attempts to compute the coefficients, one is actually doing the projection to the function subspace. Thus, the explicit expressions of orthogonal basis are able to greatly simplify the calculation. The coefficients are calculated for rod-like [15] analytically and bent-core molecules [34] numerically. In these works, the results presented in this section are not utilized, so that lengthy calculation has to be done.

4 Molecular symmetry

Molecular symmetry is characterized by orthogonal transformations that leave the molecule invariant. Under these transformations, the kernel function $\mathscr{G}_k$ shall also be invariant. Therefore, the molecular symmetry enforces symmetries on the interaction kernels, thus affects the expansion of these kernels. In the previous section, we express the expansion by symmetric traceless tensors. This will bring conveniences when discussing molecular symmetry, since the conditions from molecular symmetry are reflected on symmetric traceless tensors.

All the orthogonal transformations leaving the molecule invariant form a point group $\mathcal{G}$ in $O(3)$, of which all the proper rotations (determinant-one transformations) form a $SO(3)$-subgroup $\mathcal{G}_1$. If $\mathcal{G}$ does not have improper rotations, then $\mathcal{G}_1=\mathcal{G}$. Otherwise, $\mathcal{G}$ can be divided into the union of two cosets,

$$\mathcal{G}=\mathcal{G}_1\cup(-\mathfrak{k})\mathcal{G}_1=\mathcal{G}_1\cup\mathcal{G}_1(-\mathfrak{k}), \tag{4.1}$$

where $-\mathfrak{k}$ is any improper rotation in $\mathcal{G}$. Here, we intentionally write the improper rotation as $-\mathfrak{k}$ so that $\mathfrak{k}\in SO(3)$ that later will frequently act on tensors.

The effect of proper and improper rotations is different on what terms survive in the expansion. In this section, we first derive the general rule, then discuss all the point groups according to this rule. Still, we focus on $\mathscr{M}_2^k$, but the rule can be applied directly to clusters of multiple molecules.

4.1 Role of proper and improper rotations

Let us first examine proper rotations. For a proper rotation $\mathfrak{s}\in SO(3)$ in the symmetry group $\mathcal{G}$, the kernel function shall be invariant if we rotate any molecule by $\mathfrak{s}$ in the body-fixed frame, i.e. $\mathfrak{p}\to\mathfrak{p}\mathfrak{s}$. Thus, we have

$$\mathscr{G}_2(\boldsymbol{r}_2,\mathfrak{p}_1,\mathfrak{p}_2\mathfrak{s})=\mathscr{G}_2(\boldsymbol{r}_2,\mathfrak{p}_1\mathfrak{s},\mathfrak{p}_2)=\mathscr{G}_2(\boldsymbol{r}_2,\mathfrak{p}_1,\mathfrak{p}_2). \tag{4.2}$$

It tells us

$$\mathscr{M}_2^k(\mathfrak{p}_1\mathfrak{s},\mathfrak{p}_2)=\mathscr{M}_2^k(\mathfrak{p}_1,\mathfrak{p}_2\mathfrak{s})=\mathscr{M}_2^k(\mathfrak{p}_1,\mathfrak{p}_2). \tag{4.3}$$

Recall that for the $SO(3)$-subgroup $\mathcal{G}_1$, the l-th order symmetric traceless tensors can be decomposed into two orthogonal subspaces $\mathbb{A}^{\mathcal{G}_1,l}$ and $(\mathbb{A}^{\mathcal{G}_1,l})^\perp$, such that [32]

$$\begin{aligned}
&A(\mathfrak{p}\mathfrak{s})=A(\mathfrak{p}),\quad \forall A\in\mathbb{A}^{\mathcal{G}_1,l},\ \mathfrak{s}\in\mathcal{G}_1;\\
&\frac{1}{\#\mathcal{G}_1}\sum_{\mathfrak{s}\in\mathcal{G}_1}A(\mathfrak{p}\mathfrak{s})=0,\quad \forall A\in(\mathbb{A}^{\mathcal{G}_1,l})^\perp.
\end{aligned}$$

Let us denote by $\Phi\big(U_1(\mathfrak{p}_1),U_2(\mathfrak{p}_2)\big)$ any term in the expansion of $\mathscr{M}_2^k$, i.e. one term in Table 1. It is easy to notice that $\Phi\big(U_1(\mathfrak{p}_1),U_2(\mathfrak{p}_2)\big)$ is bilinear about (U_1,U_2).

Theorem 4.1. *For each term $\Phi\big(U_1(\mathfrak{p}_1),U_2(\mathfrak{p}_2)\big)$ in the expansion of $\mathscr{M}_2^k$, the tensors U_i can only take invariant tensors of $\mathcal{G}_1$.*

Proof. From the bilinearity, we deduce that

$$\begin{aligned}
&\Big(\mathscr{M}_2^k(\mathfrak{p}_1,\mathfrak{p}_2),\Phi\big(U_1(\mathfrak{p}_1),U_2(\mathfrak{p}_2)\big)\Big)\\
=&\int\mathscr{M}_2^k(\mathfrak{p}_1,\mathfrak{p}_2)\cdot\Phi\big(U_1(\mathfrak{p}_1),U_2(\mathfrak{p}_2)\big)\,\mathrm{d}\mathfrak{p}_1\mathrm{d}\mathfrak{p}_2\\
=&\frac{1}{\#\mathcal{G}_1}\sum_{\mathfrak{s}\in\mathcal{G}_1}\int\mathscr{M}_2^k(\mathfrak{p}_1\mathfrak{s},\mathfrak{p}_2)\cdot\Phi\big(U_1(\mathfrak{p}_1),U_2(\mathfrak{p}_2)\big)\,\mathrm{d}\mathfrak{p}_1\mathrm{d}\mathfrak{p}_2\\
=&\frac{1}{\#\mathcal{G}_1}\sum_{\mathfrak{s}\in\mathcal{G}_1}\int\mathscr{M}_2^k(\mathfrak{p}_1,\mathfrak{p}_2)\cdot\Phi\big(U_1(\mathfrak{p}_1\mathfrak{s}^{-1}),U_2(\mathfrak{p}_2)\big)\,\mathrm{d}(\mathfrak{p}_1\mathfrak{s})\mathrm{d}\mathfrak{p}_2\\
=&\int\mathscr{M}_2^k(\mathfrak{p}_1,\mathfrak{p}_2)\cdot\Phi\big(\frac{1}{\#\mathcal{G}_1}\sum_{\mathfrak{s}\in\mathcal{G}_1}U_1(\mathfrak{p}_1\mathfrak{s}^{-1}),U_2(\mathfrak{p}_2)\big)\,\mathrm{d}\mathfrak{p}_1\mathrm{d}\mathfrak{p}_2.
\end{aligned}$$

Thus, when $U_1\in\mathbb{A}^{\mathcal{G}_1,l}$, the terms $\mathscr{M}_2^k$ and $\Phi\big(U_1(\mathfrak{p}_1),U_2(\mathfrak{p}_2)\big)$ are orthogonal. We could choose the basis $\mathbb{W}^l$ as the combination of the basis of $\mathbb{A}^{\mathcal{G}_1,l}$ and that of its orthogonal complement. In this way, for a general $\mathscr{M}_2^k$, its complete expansion can be given by the terms where U_1 and U_2 take either invariant tensors or vanishing tensors of $\mathcal{G}_1$. Therefore, together with the orthogonality of the terms (see Theorem 3.2), in an $\mathscr{M}_2^k$ satisfying the symmetry given by $\mathcal{G}_1$, those terms with vanishing tensors (i.e. in $(\mathbb{A}^{\mathcal{G}_1,l})^\perp$) must vanish. □

Next, we discuss improper rotations. Let us consider the following operations. For a pair of molecules, we inverse them as a whole. The body-fixed frames are transformed from $(\boldsymbol{x}_i,\mathfrak{p}_i)$ into $(-\boldsymbol{x}_i,-\mathfrak{p}_i)$. The frames are now left-handed, which can be recovered to right-handed ones by an improper rotation $-\mathfrak{k}$. The final result is

$$(\boldsymbol{x}_i,\mathfrak{p}_i)\longrightarrow(-\boldsymbol{x}_i,\mathfrak{p}_i\mathfrak{k}).$$

The interaction kernel is invariant under the above operations, so that

$$\mathscr{G}_2(-\boldsymbol{r}_2,\mathfrak{p}_1\mathfrak{k},\mathfrak{p}_2\mathfrak{k})=\mathscr{G}_2(\boldsymbol{r}_2,\mathfrak{p}_1,\mathfrak{p}_2). \tag{4.4}$$

It tells us

$$\mathscr{M}_2^k(\mathfrak{p}_1\mathfrak{k},\mathfrak{p}_2\mathfrak{k})=(-1)^k\mathscr{M}_2^k(\mathfrak{p}_1,\mathfrak{p}_2). \tag{4.5}$$

Following the same derivation above Theorem 4.1, we need to examine what the tensors $V(\mathfrak{p}\mathfrak{k})$ are for the invariant tensors $V(\mathfrak{p})\in\mathbb{A}^{\mathcal{G}_1,l}$.

Proposition 4.1. *According to the improper rotation $-\mathfrak{k}\in\mathcal{G}$, the space of invariant tensors $\mathbb{A}^{\mathcal{G}_1,l}$ can be decomposed into the sum of two orthogonal subspaces,*

$$\mathbb{A}_{+1}^{\mathcal{G},l}=\{V(\mathfrak{p})\in\mathbb{A}^{\mathcal{G}_1,l}:V(\mathfrak{p}\mathfrak{k})=V(\mathfrak{p})\},\quad \mathbb{A}_{-1}^{\mathcal{G},l}=\{V(\mathfrak{p})\in\mathbb{A}^{\mathcal{G}_1,l}:V(\mathfrak{p}\mathfrak{k})=-V(\mathfrak{p})\}.$$

Proof. We shall notice that for any proper rotation $\mathfrak{s}$ in the point group $\mathcal{G}$, the proper rotation $\mathfrak{k}\mathfrak{s}\mathfrak{k}$ is also an element in $\mathcal{G}$. This can be recognized by writing it as $(-\mathfrak{k})\mathfrak{s}(-\mathfrak{k})$, a composition of three elements in the group, two of which are improper rotations.

For an invariant tensor $V(\mathfrak{p})$, we can express it as

$$V(\mathfrak{p})=\frac{1}{2}(V(\mathfrak{p})+V(\mathfrak{p}\mathfrak{k}))+\frac{1}{2}(V(\mathfrak{p})-V(\mathfrak{p}\mathfrak{k})),$$

where $V(\mathfrak{p})+V(\mathfrak{p}\mathfrak{k})$ is invariant under $\mathfrak{k}$, and $V(\mathfrak{p})-V(\mathfrak{p}\mathfrak{k})$ is transformed into its opposite $V(\mathfrak{p}\mathfrak{k})-V(\mathfrak{p}\mathfrak{k}^2)=V(\mathfrak{p}\mathfrak{k})-V(\mathfrak{p})$. □

Definition 4.1. *For the tensors in $\mathbb{A}_{\pm1}^{\mathcal{G},l}$, we call them tensors of type ±1.*

The improper rotations impose conditions on how the tensors of the types ±1 shall be coupled.

Theorem 4.2. *In the expansion of $\mathscr{M}_2^k$, when k is even, the coupling shall be between two tensors of type $+1$, or two of type -1; when k is odd, the coupling shall be between one tensor of type $+1$ and one of type -1.*

Proof. Without loss of generality, we assume k is even. For a term $\Phi\big(U_1(\mathfrak{p}_1),U_2(\mathfrak{p}_2)\big)$ in the expansion, suppose U_1 is type $+1$ and U_2 is type -1. We shall deduce that

$$\Big(\mathscr{M}_2^k(\mathfrak{p}_1,\mathfrak{p}_2),\Phi\big(U_1(\mathfrak{p}_1),U_2(\mathfrak{p}_2)\big)\Big)=0, \tag{4.6}$$

so that it vanishes.

Similar to the derivation for Theorem 4.1, we have

$$\begin{aligned}&\Big(\mathscr{M}_2^k(\mathfrak{p}_1,\mathfrak{p}_2),\Phi\big(U_1(\mathfrak{p}_1),U_2(\mathfrak{p}_2)\big)\Big)\\=&\int\mathscr{M}_2^k(\mathfrak{p}_1,\mathfrak{p}_2)\cdot\Phi\big(U_1(\mathfrak{p}_1),U_2(\mathfrak{p}_2)\big)\,\mathrm{d}\mathfrak{p}_1\mathrm{d}\mathfrak{p}_2\\=&\int(-1)^k\mathscr{M}_2^k(\mathfrak{p}_1\mathfrak{k},\mathfrak{p}_2\mathfrak{k})\cdot\Phi\big(U_1(\mathfrak{p}_1),U_2(\mathfrak{p}_2)\big)\,\mathrm{d}\mathfrak{p}_1\mathrm{d}\mathfrak{p}_2\\=&(-1)^k\int\mathscr{M}_2^k(\mathfrak{p}_1,\mathfrak{p}_2)\cdot\Phi\big(U_1(\mathfrak{p}_1\mathfrak{k}^{-1}),U_2(\mathfrak{p}_2\mathfrak{k}^{-1})\big)\,\mathrm{d}\mathfrak{p}_1\mathrm{d}\mathfrak{p}_2.\end{aligned}$$

By Definition 4.1, we have $U_1(\mathfrak{p}_1\mathfrak{k}^{-1})=U_1(\mathfrak{p}_1)$ and $U_2(\mathfrak{p}_1\mathfrak{k}^{-1})=-U_2(\mathfrak{p}_1)$. Together with the bilinearity of Φ, we arrive at (4.6). □

We pay attention to the case where the group $\mathcal{G}$ has the inversion, i.e. it allows the improper rotation $-\mathfrak{i}$ where we recall $\mathfrak{i}$ represents the identity. In this case, the decomposition of type ±1 tensors is obvious.

Corollary 4.1. *If $\mathcal{G}$ has the inversion, then $\mathbb{A}^{\mathcal{G},l}_{+1}=\mathbb{A}^{\mathcal{G}_1,l}$ and $\mathbb{A}^{\mathcal{G},l}_{-1}=\{0\}$ where $\mathcal{G}_1$ is the $SO(3)$-subgroup of $\mathcal{G}$.*

If the group $\mathcal{G}$ does not include the inversion, we need to identify the two spaces.

4.2 Tensors of two types for each point group

We are now ready to discuss each point group, respectively. Based on Theorem 4.2, our task is to write down the decomposition in Proposition 4.1, i.e. to find out the tensors of type ±1. For the point groups having the common $SO(3)$-subgroup, note that the invariant tensors $\mathbb{A}^{\mathcal{G}_1,l}$ are the same. However, since the improper rotations are different, the resulting decomposition into type ±1 tensors would be different. It is from this decomposition that we will see how these point groups are distinguished by the improper rotations at the level of tensors.

To explicitly write down the decomposition, we need to calculate how the tensors are transformed under the rotation $\mathfrak{k}$ where $-\mathfrak{k}\in\mathcal{G}$ is an improper rotation. Thus, we need to write down an element $-\mathfrak{k}$ in each point group. To give a $-\mathfrak{k}$ in matrix for a point group, it is necessary to specify how to pose the body-fixed frame $\mathfrak{p}=(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)$, which we explain below. For the sake of finding the decomposition of the space of invariant tensors, we only write down generating elements of the $SO(3)$-subgroup (which reflect how the body-fixed frame is posed), and specify an improper rotation $-\mathfrak{k}$ in the point group. For more information of the point groups, such the structure of generating elements and illustrations, we refer to other works [9,33].

Recall that a rotation within the body-fixed frame is expressed by $\mathfrak{p} \to \mathfrak{p}\mathfrak{s}$. We begin with introducing some rotations,

$$\mathfrak{j}_\theta = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix}, \quad \mathfrak{b}_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \mathfrak{r}_3 = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix},$$
$$\mathfrak{v}_5 = \frac{1}{2}\begin{pmatrix} \phi & -1 & \phi-1 \\ 1 & \phi-1 & -\phi \\ \phi-1 & \phi & 1 \end{pmatrix}, \quad \phi = \frac{1+\sqrt{5}}{2}. \tag{4.7}$$

In the above, $\mathfrak{j}_\theta$ is the rotation round $\boldsymbol{m}_1$ by the angle θ. To comprehend this rotation, we could write out

$$\begin{aligned} \mathfrak{p}\mathfrak{s} &= (\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3) \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \\ &= (\boldsymbol{m}_1, \cos\theta \boldsymbol{m}_2 + \sin\theta \boldsymbol{m}_3, -\sin\theta \boldsymbol{m}_2 + \cos\theta \boldsymbol{m}_3). \end{aligned}$$

Moreover, for two angles θ_1 and θ_2, we have

$$\mathfrak{j}_{\theta_1}\mathfrak{j}_{\theta_2} = \mathfrak{j}_{\theta_1+\theta_2}.$$

Thus, for an integer m we have

$$\mathfrak{j}_\theta^m = \mathfrak{j}_{m\theta}.$$

The second one, $\mathfrak{b}_2$, is the rotation round $\boldsymbol{m}_2$ by the angle π; $\mathfrak{r}_3$ is the rotation round $(\boldsymbol{m}_1+\boldsymbol{m}_2+\boldsymbol{m}_3)/\sqrt{3}$ by $2\pi/3$, transforming $(\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3)$ into $(\boldsymbol{m}_2, \boldsymbol{m}_3, \boldsymbol{m}_1)$; and $\mathfrak{v}_5$ is a five-fold rotation.

Now, let us write down the rotation subgroup and one improper rotation in each point group. We shall present in the following way: describe a point group in $SO(3)$ (with only proper rotations); then, for all the groups containing it as the rotation subgroup, we specify an improper rotation $-\mathfrak{k}$. Because the inversion is a special improper rotation leading to trivial decomposition of the invariant tensor space, we pay special attention whether inversion is allowed and always choose $\mathfrak{k} = \mathfrak{i}$ if it is valid.

- The group $\mathcal{C}_\infty$ consists of rotations round an axis by arbitrary angle. We choose $\boldsymbol{m}_1$ as the axis, so that $\mathcal{C}_\infty = \{\mathfrak{j}_\theta, \forall\theta\}$.
  - $\mathcal{C}_{\infty v}$ has a mirror plane $\hat{O}\boldsymbol{m}_1\boldsymbol{m}_2$, so an improper rotation is $-\mathfrak{k} = \mathrm{diag}(1,1,-1) = -\mathfrak{j}_\pi\mathfrak{b}_2$.
  - $\mathcal{C}_{\infty h}$ has a mirror plane $\hat{O}\boldsymbol{m}_2\boldsymbol{m}_3$, so an improper rotation is $\mathrm{diag}(-1,1,1) = -\mathfrak{j}_\pi$. We multiply it with a proper rotation $\mathfrak{j}_\pi$ to recognize that the inversion $-\mathfrak{i}$ belongs to $\mathcal{C}_{\infty h}$.

- The group $\mathcal{D}_\infty$ contains $\mathcal{C}_\infty$ as a subset, and also allows $\mathfrak{b}_2$.
  - $\mathcal{D}_{\infty h}$ has a mirror plane $\hat{O}\boldsymbol{m}_2\boldsymbol{m}_3$, so it contains the inversion.
- $\mathcal{C}_n$ is generated by the rotation round $\boldsymbol{m}_1$ by the angle $2\pi/n$, i.e. is generated by $\mathfrak{j}_{2\pi/n}$.
  - $\mathcal{C}_{nv}$ has an improper rotation $\mathrm{diag}(1,1,-1)=-\mathfrak{j}_\pi\mathfrak{b}_2$.
  - $\mathcal{C}_{nh}$ has an improper rotation $\mathrm{diag}(-1,1,1)=-\mathfrak{j}_\pi$. When n is even, we multiply it by $\mathfrak{j}_{2\pi/n}^{n/2}=\mathfrak{j}_\pi$ to get the inversion. When n is odd, we multiply it by $\mathfrak{j}_{2\pi/n}^{(n+1)/2}=\mathfrak{j}_{(n+1)\pi/n}$ and let $\mathfrak{k}=\mathfrak{j}_{\pi/n}$.
  - $\mathcal{S}_{2n}$ allows a roto-reflection round $\boldsymbol{m}_1$, i.e. to rotate round $\boldsymbol{m}_1$ by the angle π/n, followed by a reflection about the plane $\hat{O}\boldsymbol{m}_2\boldsymbol{m}_3$. Such an improper rotation can be expressed by $\mathfrak{j}_{\pi/n}(-\mathfrak{j}_\pi)=-\mathfrak{j}_{(n+1)\pi/n}$. When n is odd, we multiply it by $\mathfrak{j}_{2\pi/n}^{(n-1)/2}=\mathfrak{j}_{(n-1)\pi/n}$ to get the inversion. When n is even, we multiply it by $\mathfrak{j}_{2\pi/n}^{n/2}=\mathfrak{j}_\pi$ and let $\mathfrak{k}=\mathfrak{j}_{\pi/n}$.
- $\mathcal{D}_n$ is generated by $\mathfrak{j}_{2\pi/n}$ and $\mathfrak{b}_2$.
  - $\mathcal{D}_{nh}$ has an improper rotation $\mathrm{diag}(-1,1,1)=-\mathfrak{j}_\pi$. When n is even, the group contains the inversion. When n is odd, we let $\mathfrak{k}=\mathfrak{j}_{\pi/n}$.
  - $\mathcal{D}_{nd}$ has an improper rotation $-\mathfrak{j}_\pi\mathfrak{j}_{\pi/n}=-\mathfrak{j}_{(n+1)\pi/n}$. When n is odd, the group contains the inversion. When n is even, we let $\mathfrak{k}=\mathfrak{j}_{\pi/n}$.
- $\mathcal{T}$ contains all the proper rotations allowed by a regular tetrahedron, which can be generated by $\mathfrak{j}_\pi$, $\mathfrak{b}_2$ and $\mathfrak{r}_3$.
  - $\mathcal{T}_d$ allows the improper rotation
    $$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}=\mathfrak{j}_{\pi/2}\mathrm{diag}(1,1,-1)=-\mathfrak{j}_{3\pi/2}\mathfrak{b}_2.$$
    We multiply it by the proper rotation $\mathfrak{j}_\pi\mathfrak{b}_2$ in $\mathcal{T}$, so that we may let $\mathfrak{k}=\mathfrak{j}_{\pi/2}$.
  - $\mathcal{T}_h$ has a mirror plane $\hat{O}\boldsymbol{m}_2\boldsymbol{m}_3$, so it contains the inversion.
- $\mathcal{O}$ contains all the proper rotations allowed by a cube, which can be generated by $\mathfrak{j}_{\pi/2}$, $\mathfrak{b}_2$ and $\mathfrak{r}_3$.
  - $\mathcal{O}_h$ contains all the $O(3)$ transformations of a cube, allowing the inversion.
- $\mathcal{I}$ contains all the proper rotations allowed by a regular icosahedron, generated by $\mathfrak{j}_\pi$, $\mathfrak{b}_2$, $\mathfrak{r}_3$, $\mathfrak{v}_5$.

– $\mathcal{I}_h$ contains all the $O(3)$ transformations of a regular icosahedron, allowing the inversion.

We now turn to the invariant symmetric traceless tensors. To express symmetric traceless tensors, we introduce the polynomials

$$\tilde{T}_n(y,z)=z^{n/2}T_n(y/\sqrt{z}),\ \tilde{U}_n(y,z)=z^{n/2}U_n(y/\sqrt{z}),\ \tilde{P}_n^{(\mu,\mu)}(y,z)=z^{n/2}P_n^{(\mu,\mu)}(y/\sqrt{z}), \quad (4.8)$$

where $T_n(\cos\theta)=\cos n\theta$ and $U_{n-1}(\cos\theta)\sin\theta=\sin n\theta$ are the Chebyshev polynomials of the first and the second kind, and $P_n^{(\mu,\mu)}(x)$ is the Jacobi polynomial with two identical indices (μ,μ). Since the Chebyshev and Jacobi polynomials only have the terms with the same parity as the order n (see Appendix for explicit expressions), the above definition indeed gives polynomials of y and z. According to the monomial notation (2.6), when we substitute y,z by some polynomials of $\boldsymbol{m}_i$, we define a symmetric tensor.

We are now ready to discuss the decomposition of the space of invariant tensors. The invariant tensors for point groups in $SO(3)$ have been identified completely in [32]. For each point group in $SO(3)$, we write down the invariant tensors, then find out the two types of tensors using the improper rotations. For all the point groups having improper rotations, the tensors of type ±1 are listed in Table 2, which we explain below.

4.2.1 Axisymmetries

We first look into two rotation groups $\mathcal{C}_\infty$, $\mathcal{D}_\infty$. The invariant tensors are given by

$$\mathbb{A}^{\mathcal{C}_\infty,l}=\mathrm{span}\left\{\tilde{P}_l^{(0,0)}(\boldsymbol{m}_1,\mathrm{i})\right\}, \quad (4.9)$$

$$\mathbb{A}^{\mathcal{D}_\infty,l}=\mathrm{span}\left\{\tilde{P}_l^{(0,0)}(\boldsymbol{m}_1,\mathrm{i})\right\},\ l \text{ even};\quad \mathbb{A}^{\mathcal{D}_\infty,l}=\{0\},\ l \text{ odd}. \quad (4.10)$$

For the groups $\mathcal{C}_{\infty h}$, $\mathcal{D}_{\infty h}$, since they possess the inversion, the type $+1$ tensors are just the invariant tensors, and the only type -1 tensor is the zero tensor.

For $\mathcal{C}_{\infty v}$, we have chosen $\mathfrak{k}=\mathrm{diag}(-1,-1,1)$. Thus, in type $+1$ tensors, $\boldsymbol{m}_1$ shall appear even times, while in type -1 tensors, $\boldsymbol{m}_1$ shall appear odd times. As a result, the type $+1$ tensors are those whose order l are even, and the type -1 tensors are those with odd order.

4.2.2 Finite order axial symmetries

Next, we look into point groups with the rotation subgroup $\mathcal{C}_n$ or $\mathcal{D}_n$.

The group $\mathcal{C}_n$ is the rotation subgroup of $\mathcal{C}_{nv}$, $\mathcal{C}_{nh}$ and $\mathcal{S}_{2n}$. The invariant tensors for $\mathcal{C}_n$ are

$$\mathbb{A}^{\mathcal{C}_n,l}=\mathrm{span}\left\{\tilde{P}_{l-jn}^{(jn,jn)}(\boldsymbol{m}_1,\mathrm{i})\tilde{T}_{jn}(\boldsymbol{m}_2,\mathrm{i}-\boldsymbol{m}_1^2),\tilde{P}_{l-jn}^{(jn,jn)}(\boldsymbol{m}_1,\mathrm{i})\tilde{U}_{jn-1}(\boldsymbol{m}_2,\mathrm{i}-\boldsymbol{m}_1^2)\boldsymbol{m}_3\right\}. \quad (4.11)$$

Table 2: Tensors of type ±1 for point groups containing improper rotations.

Group	Tensors of types ±1, two spaces $\mathbb{A}^{\mathcal{G},l}_{+1}$ and $\mathbb{A}^{\mathcal{G},l}_{-1}$
$\mathcal{C}_{\infty h},\mathcal{D}_{\infty h}$ $\mathcal{C}_{nh}$ (n even) $\mathcal{S}_{2n}$ (n odd) $\mathcal{D}_{nh}$ (n even) $\mathcal{D}_{nd}$ (n odd) $\mathcal{T}_h,\mathcal{O}_h,\mathcal{I}_h$	Improper rotation $-\mathfrak{k}=-\mathfrak{i}$ $\mathcal{G}=\mathcal{G}_1\cup(-\mathcal{G}_1)$, $\mathcal{G}_1$ rotation subgroup $\mathbb{A}^{\mathcal{G},l}_{+1}=\mathbb{A}^{\mathcal{G}_1,l}$, $\mathbb{A}^{\mathcal{G},l}_{-1}=\{0\}$ see (4.9), (4.10), (4.11), (4.13), (4.15), (4.16), (4.17)
$\mathcal{C}_{\infty v}$	l even, $+1:\mathrm{span}\left\{\tilde{P}^{(0,0)}_l(\boldsymbol{m}_1,\mathfrak{i})\right\}$; $-1:\{0\}$ l odd, $+1:\{0\}$; $-1:\mathrm{span}\left\{\tilde{P}^{(0,0)}_l(\boldsymbol{m}_1,\mathfrak{i})\right\}$
$\mathcal{C}_{nv}$	l even, $+1:\mathrm{span}\left\{\tilde{P}^{(jn,jn)}_{l-jn}(\boldsymbol{m}_1,\mathfrak{i})\tilde{T}_{jn}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2)\right\}$ $-1:\mathrm{span}\left\{\tilde{P}^{(jn,jn)}_{l-jn}(\boldsymbol{m}_1,\mathfrak{i})\tilde{U}_{jn-1}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2)\boldsymbol{m}_3\right\}$ l odd, $+1:\mathrm{span}\left\{\tilde{P}^{(jn,jn)}_{l-jn}(\boldsymbol{m}_1,\mathfrak{i})\tilde{U}_{jn-1}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2)\boldsymbol{m}_3\right\}$ $-1:\mathrm{span}\left\{\tilde{P}^{(jn,jn)}_{l-jn}(\boldsymbol{m}_1,\mathfrak{i})\tilde{T}_{jn}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2)\right\}$
$\mathcal{S}_{2n}$ (n even) $\mathcal{C}_{nh}$ (n odd)	$+1:\mathrm{span}\left\{\tilde{P}^{(jn,jn)}_{l-jn}(\boldsymbol{m}_1,\mathfrak{i})\tilde{T}_{jn}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2),\tilde{P}^{(jn,jn)}_{l-jn}(\boldsymbol{m}_1,\mathfrak{i})\tilde{U}_{jn-1}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2)\boldsymbol{m}_3,\ j\text{ even}\right\}$ $-1:\mathrm{span}\left\{\tilde{P}^{(jn,jn)}_{l-jn}(\boldsymbol{m}_1,\mathfrak{i})\tilde{T}_{jn}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2),\tilde{P}^{(jn,jn)}_{l-jn}(\boldsymbol{m}_1,\mathfrak{i})\tilde{U}_{jn-1}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2)\boldsymbol{m}_3,\ j\text{ odd}\right\}$
$\mathcal{D}_{nd}$ (n even)	l even, $+1:\mathrm{span}\left\{\tilde{P}^{(jn,jn)}_{l-jn}(\boldsymbol{m}_1,\mathfrak{i})\tilde{T}_{jn}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2),\ j\text{ even}\right\}$ $-1:\mathrm{span}\left\{\tilde{P}^{(jn,jn)}_{l-jn}(\boldsymbol{m}_1,\mathfrak{i})\tilde{T}_{jn}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2),\ j\text{ odd}\right\}$ l odd, $+1:\mathrm{span}\left\{\tilde{P}^{(jn,jn)}_{l-jn}(\boldsymbol{m}_1,\mathfrak{i})\tilde{U}_{jn-1}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2)\boldsymbol{m}_3,\ j\text{ even}\right\}$ $-1:\mathrm{span}\left\{\tilde{P}^{(jn,jn)}_{l-jn}(\boldsymbol{m}_1,\mathfrak{i})\tilde{U}_{jn-1}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2)\boldsymbol{m}_3,\ j\text{ odd}\right\}$
$\mathcal{D}_{nh}$ (n odd)	l even, $+1:\mathrm{span}\left\{\tilde{P}^{(jn,jn)}_{l-jn}(\boldsymbol{m}_1,\mathfrak{i})\tilde{T}_{jn}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2),\ j\text{ even}\right\}$ $-1:\mathrm{span}\left\{\tilde{P}^{(jn,jn)}_{l-jn}(\boldsymbol{m}_1,\mathfrak{i})\tilde{U}_{jn-1}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2)\boldsymbol{m}_3,\ j\text{ odd}\right\}$ l odd, $+1:\mathrm{span}\left\{\tilde{P}^{(jn,jn)}_{l-jn}(\boldsymbol{m}_1,\mathfrak{i})\tilde{U}_{jn-1}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2)\boldsymbol{m}_3,\ j\text{ even}\right\}$ $-1:\mathrm{span}\left\{\tilde{P}^{(jn,jn)}_{l-jn}(\boldsymbol{m}_1,\mathfrak{i})\tilde{T}_{jn}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2),\ j\text{ odd}\right\}$
$\mathcal{T}_d$ (see (4.14))	$+1:\mathrm{span}\Big\{\left\{\big(S_2^i(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)S_3^j(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)\big)_0,\ j\text{ even},\ l=4i+3j\right\}$ $\cup\left\{\big(E(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)S_2^i(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)S_3^j(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)\big)_0,\ j\text{ odd},\ l=6+4i+3j\right\}\Big\}$ $-1:\mathrm{span}\Big\{\left\{\big(S_2^i(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)S_3^j(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)\big)_0,\ j\text{ odd},\ l=4i+3j\right\}$ $\cup\left\{\big(E(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)S_2^i(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)S_3^j(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)\big)_0,\ j\text{ even},\ l=6+4i+3j\right\}\Big\}$

- For $\mathcal{C}_{nv}$, we have chosen $\mathfrak{k}=\text{diag}(-1,-1,1)$. Therefore, in type $+1$ tensors $\boldsymbol{m}_1$ and $\boldsymbol{m}_2$ shall appear even times in total, while if $\boldsymbol{m}_1$ and $\boldsymbol{m}_2$ appear odd times in total, the tensors are type -1. According to this requirement, the two types of tensors are given in Table 2.

- For $\mathcal{S}_{2n}$ where n is odd, and $\mathcal{C}_{nh}$ where n is even, these groups have the inversion.

- For $\mathcal{S}_{2n}$ where n is even, and $\mathcal{C}_{nh}$ where n is odd, we have chosen $\mathfrak{k}=\mathfrak{j}_{\pi/n}$. Now, we use the fact that

$$(\boldsymbol{m}_2+\sqrt{-1}\boldsymbol{m}_3)^n=\tilde{T}_n(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2)+\sqrt{-1}\tilde{U}_{n-1}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2)\boldsymbol{m}_3. \tag{4.12}$$

We substitute $\boldsymbol{m}_i$ with $\boldsymbol{m}_i(\mathfrak{p}\mathfrak{j}_\theta)$ in the above. The left-hand side gives

$$\big(\boldsymbol{m}_2(\mathfrak{p}\mathfrak{j}_\theta)+\sqrt{-1}\boldsymbol{m}_3(\mathfrak{p}\mathfrak{j}_\theta)\big)^n=e^{\sqrt{-1}n\theta}(\boldsymbol{m}_2+\sqrt{-1}\boldsymbol{m}_3)^n.$$

Let $\theta=\pi/n$. We obtain

$$\begin{aligned}&\tilde{T}_{jn}\big(\boldsymbol{m}_2(\mathfrak{p}\mathfrak{j}_{\pi/n}),\mathfrak{i}-\boldsymbol{m}_1^2(\mathfrak{p}\mathfrak{j}_{\pi/n})\big)=(-1)^j\tilde{T}_{jn}\big(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2\big),\\&\tilde{U}_{jn-1}\big(\boldsymbol{m}_2(\mathfrak{p}\mathfrak{j}_{\pi/n}),\mathfrak{i}-\boldsymbol{m}_1^2(\mathfrak{p}\mathfrak{j}_{\pi/n})\big)\boldsymbol{m}_3(\mathfrak{p}\mathfrak{j}_{\pi/n})=(-1)^j\tilde{U}_{jn-1}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2)\boldsymbol{m}_3.\end{aligned}$$

Therefore, type $+1$ tensors are those in (4.11) where j is even, and type -1 tensors are those where j is odd.

We turn to the point groups having the rotation subgroup $\mathcal{D}_n$. The invariant tensors of $\mathcal{D}_n$ are given by

$$\begin{aligned}\mathbb{A}^{\mathcal{D}_n,l}=\text{span}\Big\{&\Big\{\tilde{P}_{l-jn}^{(jn,jn)}(\boldsymbol{m}_1,\mathfrak{i})\tilde{T}_{jn}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2),\ l-jn\text{ even}\Big\}\\&\cup\Big\{\tilde{P}_{l-jn}^{(jn,jn)}(\boldsymbol{m}_1,\mathfrak{i})\tilde{U}_{jn-1}(\boldsymbol{m}_2,\mathfrak{i}-\boldsymbol{m}_1^2)\boldsymbol{m}_3,\ l-jn\text{ odd}\Big\}\Big\}.\end{aligned} \tag{4.13}$$

- The two groups, $\mathcal{D}_{nd}$ where n is odd, and $\mathcal{D}_{nh}$ where n is even, contain the inversion.

- For $\mathcal{D}_{nd}$ where n is even, and $\mathcal{D}_{nh}$ where n is odd, the discussion is similar to $\mathcal{S}_{2n}$ and $\mathcal{C}_{nh}$. By choosing $\mathfrak{k}=\mathfrak{j}_{\pi/n}$, we conclude that type $+1$ tensors are those with even j, and type -1 tensors are those with odd j.

4.2.3 Polyhedral symmetries

There are three polyhedral rotation groups, $\mathcal{T}$, $\mathcal{O}$, $\mathcal{I}$. Define

$$S_2(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)=\boldsymbol{m}_1^2\boldsymbol{m}_2^2+\boldsymbol{m}_2^2\boldsymbol{m}_3^2+\boldsymbol{m}_3^2\boldsymbol{m}_1^2, \tag{4.14a}$$
$$S_3(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)=\boldsymbol{m}_1\boldsymbol{m}_2\boldsymbol{m}_3, \tag{4.14b}$$
$$E(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)=(\boldsymbol{m}_1^2-\boldsymbol{m}_2^2)(\boldsymbol{m}_2^2-\boldsymbol{m}_3^2)(\boldsymbol{m}_3^2-\boldsymbol{m}_1^2). \tag{4.14c}$$

Using these notations, the invariant tensors are given by

$$\begin{aligned}
\mathbb{A}^{\mathcal{T},l}=&\mathrm{span}\Big\{\Big\{\big(S_2^i(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)S_3^j(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)\big)_0,\ l=4i+3j\Big\}\\
&\cup\Big\{\big(E(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)S_2^i(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)S_3^j(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)\big)_0,\ l=6+4i+3j\Big\}\Big\}, \qquad (4.15)\\
\mathbb{A}^{\mathcal{O},l}=&\mathrm{span}\Big\{\Big\{\big(S_2^i(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)S_3^j(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)\big)_0,\ j\ \text{even}, l=4i+3j\Big\}\\
&\cup\Big\{\big(E(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)S_2^i(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)S_3^j(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)\big)_0,\ j\ \text{odd}, l=6+4i+3j\Big\}\Big\}, \qquad (4.16)\\
\mathbb{A}^{\mathcal{I},l}=&\{V(\mathfrak{p})\in\mathbb{A}^{\mathcal{T},l}:\ V(\mathfrak{p}\mathfrak{v}_5)=V(\mathfrak{p})\}. \qquad (4.17)
\end{aligned}$$

Here, we recall that $(U)_0$ is the symmetric traceless tensor generated by U (see Proposition 2.1). If explicit expressions are needed, one could expand the tensors into monomials and use the explicit expressions of $(\boldsymbol{m}_1^{i_1}\boldsymbol{m}_2^{i_2}\boldsymbol{m}_3^{i_3})_0$ that are provided in [32].

The three point groups $\mathcal{T}_h$, $\mathcal{O}_h$, $\mathcal{I}_h$ contain the inversion, so nothing needs to be discussed.

For the group $\mathcal{T}_d$, we have chosen $\mathfrak{k}=\mathfrak{j}_{\pi/2}$. Because $\mathfrak{j}_{\pi/2}^2=\mathfrak{j}_\pi$, it is noticed from generating element that $\mathcal{T}\cup\mathcal{T}\mathfrak{j}_{\pi/2}=\mathcal{O}$. Therefore, the type $+1$ tensors for $\mathcal{T}_d$ are just the invariant tensors of $\mathcal{O}$.

5 Summary and examples

In this paper, we discuss the expansion of interaction kernels that are functions of molecular potential. The expansion is expressed by symmetric traceless tensors and is consistent with symmetry arguments, including the translations, rotations and label permutations of the whole cluster, and the molecular symmetry described by a point group. The orthogonality of terms is recognized, which is useful if the coefficients need to be calculated from microscopic potential.

The form of expansion is summarized in two tables presented in the main text, together with an extra one in Appendix. If one would like to write down the expansion for certain point group, the procedure below can be followed:

1) Choose tensors from the invariant tensors of the rotation subgroup.

2) Use Table 2 to identify the types ±1 of these tensors.

3) Insert these tensors into the terms in Table 1 (and Table 3 in Appendix). Notice that Theorem 4.2 gives the conditions on the how many times the type -1 tensors shall appear.

We illustrate the procedure by a couple of examples. Consider two point groups $\mathcal{C}_{2v}$ and $\mathcal{S}_4$, both having the rotation subgroup $\mathcal{C}_2$. The invariant tensors up to second order are picked up: 1 (zeroth order tensor), $\boldsymbol{m}_1$, $\boldsymbol{m}_1^2-\frac{1}{3}\mathfrak{i}$, $\boldsymbol{m}_2^2-\boldsymbol{m}_3^2$, $\boldsymbol{m}_2\boldsymbol{m}_3$. Then, from Table 2, we find out the type ±1 for each tensor:

	1	$\boldsymbol{m}_1$	$\boldsymbol{m}_1^2-\frac{1}{3}\mathfrak{i}$	$\boldsymbol{m}_2^2-\boldsymbol{m}_3^2$	$\boldsymbol{m}_2\boldsymbol{m}_3$
$\mathcal{C}_{2v}$	$+1$	-1	$+1$	$+1$	-1
$\mathcal{S}_4$	$+1$	$+1$	$+1$	-1	-1

For the terms in Table 1, substitute the tensors in these terms by the above five tensors, with noticing Theorem 4.2. For example, let us look at the term $U^n(\mathfrak{p}_1)\overset{n-1}{\times}V^n(\mathfrak{p}_2)+V^n(\mathfrak{p}_1)\overset{n-1}{\times}U^n(\mathfrak{p}_2)$ in $\mathscr{M}_2^1$. The tensor order shall be equal for U^n and V^n with $n\geq1$. Since we choose tensors up to second order, we have $n=1$ or 2. If $n=1$, the only first order invariant tensor above is $\boldsymbol{m}_1$. But we cannot let $U^n(\mathfrak{p})=V^n(\mathfrak{p})=\boldsymbol{m}_1$, since one of U^n and V^n needs to be type $+1$ while the other is type -1. When $n=2$, for the group $\mathcal{C}_{2v}$, there are two choices $(U^n,V^n)=(\boldsymbol{m}_1^2-\frac{1}{3}\mathfrak{i},\boldsymbol{m}_2\boldsymbol{m}_3)$ or $(\boldsymbol{m}_2^2-\boldsymbol{m}_3^2,\boldsymbol{m}_2\boldsymbol{m}_3)$. For the group $\mathcal{S}_4$, there are two different choices $(U^n,V^n)=(\boldsymbol{m}_1^2-\frac{1}{3}\mathfrak{i},\boldsymbol{m}_2^2-\boldsymbol{m}_3^2)$ or $(\boldsymbol{m}_1^2-\frac{1}{3}\mathfrak{i},\boldsymbol{m}_2\boldsymbol{m}_3)$. The difference originates from the improper rotations in $\mathcal{C}_{2v}$ and $\mathcal{S}_4$, which assign different type ±1 for the tensors.

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Appendices

A Chebyshev and Jacobi polynomials

The Chebyshev polynomials of the first and second kind can be given by

$$T_n(x)=\sum_{2j\leq n}\binom{n}{2j}(x^2-1)^k x^{n-2j},\quad U_n(x)=\sum_{2j\leq n}\binom{n+1}{2j+1}(x^2-1)^k x^{n-2j}. \tag{A.1}$$

The Jacobi polynomials $P_n^{(\mu,\mu)}$, where the two indices are equal, can be given by

$$P_n^{(\mu,\mu)}(x)=\frac{\Gamma(2\mu+1)\Gamma(n+\mu+1)}{\Gamma(\mu+1)\Gamma(n+2\mu+1)}\sum_{2j\leq n}(-1)^j\frac{\Gamma(n-j+\mu+1/2)}{\Gamma(\mu+1/2)j!(n-2j)!}2^{n-2j}x^{n-2j}, \tag{A.2}$$

where Γ is the gamma function. It is clear that these polynomials have either odd order terms only, or even order terms only.

B Decomposition of a tensor into symmetric traceless tensors

Let us consider the decomposition of a general r-th order tensor X. We start from extracting the symmetric part $X_{\rm sym}$. The difference $X-X_{\rm sym}$ can be expressed by several terms of the form

$$X_{\dots i \dots j \dots} - X_{\dots j \dots i \dots}.$$

For any second order tensor Q, its antisymmetric part is

$$Q_{ij}-Q_{ji}=\begin{pmatrix} 0 & Q_{12}-Q_{21} & Q_{13}-Q_{31} \\ Q_{21}-Q_{12} & 0 & Q_{23}-Q_{32} \\ Q_{31}-Q_{13} & Q_{32}-Q_{23} & 0 \end{pmatrix}=\epsilon_{ijk}v_k, \quad v=\begin{pmatrix} Q_{23}-Q_{32} \\ Q_{31}-Q_{13} \\ Q_{12}-Q_{21} \end{pmatrix}.$$

Thus, if X is r-th order, we have the following expression,

$$X_{\dots i \dots j \dots} - X_{\dots j \dots i \dots} = \epsilon_{ijk} Z_{k \dots},$$

where Z is an $(r-1)$-th order tensor. Therefore, we arrive at

$$(X-X_{\rm sym})_{j_1\cdots j_r} = \sum_{\substack{\{\tau_1,\tau_2\}\cup\{\sigma_1,\cdots\sigma_{r-2}\} \\ =\{1,\cdots,r\}}} \epsilon_{j_{\tau_1}j_{\tau_2}\nu} Z_{\nu j_{\sigma_1}\cdots j_{\sigma_{r-2}}}. \tag{B.1}$$

In the above, we use the notation Z for any tensor. Then, we can repeat this action for each Z, decomposing it into its symmetric part and some tensors with lower order. We shall keep doing it until each tensor becomes symmetric. Note that two ϵ_{ijk} can be expressed by some δ:

$$\epsilon_{i_1j_1k_1}\epsilon_{i_2j_2k_2} = \begin{vmatrix} \delta_{i_1i_2} & \delta_{i_1j_2} & \delta_{i_1k_2} \\ \delta_{j_1i_2} & \delta_{j_1j_2} & \delta_{j_1k_2} \\ \delta_{k_1i_2} & \delta_{k_1j_2} & \delta_{k_1k_2} \end{vmatrix}.$$

So, if in any term there is no less than two ϵ_{ijk}, we write them into some δ. For example,

$$\begin{aligned} \epsilon_{j_1j_2\nu}\epsilon_{\nu j_3\nu'}Z_{\nu' j_4\cdots j_r} &= (\delta_{j_1j_3}\delta_{j_2\nu'}-\delta_{j_2j_3}\delta_{j_1\nu'})Z_{\nu' j_4\cdots j_r} \\ &= \delta_{j_1j_3}Z_{j_2j_4\cdots j_r} - \delta_{j_2j_3}Z_{j_1j_4\cdots j_r} \\ \epsilon_{j_1j_2\nu}\epsilon_{j_3j_4\nu'}Z_{\nu\nu' j_5\cdots j_r} &= (\delta_{j_1j_3}\delta_{j_2j_4}-\delta_{j_1j_4}\delta_{j_2j_3})Z_{\nu\nu j_5\cdots j_r} \\ &\quad + \delta_{j_1j_4}Z_{j_3j_2j_5\cdots j_r} + \delta_{j_2j_3}Z_{j_4j_1j_5\cdots j_r} \\ &\quad - \delta_{j_1j_3}Z_{j_4j_2j_5\cdots j_r} - \delta_{j_2j_4}Z_{j_3j_1j_5\cdots j_r}. \end{aligned}$$

Thus, we could write each term as the above so that there is at most one ϵ_{ijk}. Eventually, we get the following form,

$$\begin{aligned} X_{j_1\cdots j_r} = \sum_{\substack{0\le s\le r, s \text{ even} \\ \{\tau_1,\cdots,\tau_s\}\cup\{\sigma_1,\cdots\sigma_{r-s}\} \\ =\{1,\cdots,r\}}} & \delta_{j_{\tau_1}j_{\tau_2}}\cdots\delta_{j_{\tau_{s-1}}j_{\tau_s}} Z_{j_{\sigma_1}\cdots j_{\sigma_{r-s}}} \\ & + \epsilon_{j_{\tau_1}j_{\tau_2}\nu}\delta_{j_{\tau_3}j_{\tau_4}}\cdots\delta_{j_{\tau_{s-1}}j_{\tau_s}} Z_{\nu j_{\sigma_1}\cdots j_{\sigma_{r-s}}}. \end{aligned} \tag{B.2}$$

Here, all the tensors Z are symmetric tensors. Based on (B.2), we could write each Z as $U+\mathrm{i}Z_1$ where U is symmetric traceless, using Proposition 2.1. We might obtain another type of term. For example, when decomposing $\epsilon_{j_1j_2\nu}Z_{\nu j_3\cdots j_r}$, it will yield a term

$$\epsilon_{j_1j_2\nu}\delta_{\nu j_3}(Z_1)_{j_4\cdots j_r}=\epsilon_{j_1j_2j_3}(Z_1)_{j_4\cdots j_r}.$$

Therefore, we arrive at the three types of terms in (3.11).

C Clusters of three or more molecules

To expand the interaction kernels for clusters of three or more molecules, we could follow the same procedure of dealing with $\mathscr{M}_2^k$, and many results are similar, as we outline below. We recall that $(\boldsymbol{x}_i,\mathfrak{p}_i)$ represents the position and orientation of the molecule indexed by i and $\boldsymbol{r}_i=\boldsymbol{x}_i-\boldsymbol{x}_1$. The molecular symmetry is described by a point group $\mathcal{G}$, whose $SO(3)$-subgroup is denoted by $\mathcal{G}_1$.

- The invariance when the whole cluster is displaced or rotated requires

$$\mathscr{G}_l(\mathfrak{t}\boldsymbol{r}_2,\cdots,\mathfrak{t}\boldsymbol{r}_l,\mathfrak{t}\mathfrak{p}_1,\cdots,\mathfrak{t}\mathfrak{p}_l)=\mathscr{G}_l(\boldsymbol{r}_2,\cdots,\boldsymbol{r}_l,\mathfrak{p}_1,\cdots,\mathfrak{p}_l),\quad \mathfrak{t}\in SO(3),$$

  yielding $\mathscr{M}_l^{k_2,\cdots,k_l}(\mathfrak{t}\mathfrak{p}_1,\cdots,\mathfrak{t}\mathfrak{p}_l)=\mathscr{M}_l^{k_2,\cdots,k_l}(\mathfrak{p}_1,\cdots,\mathfrak{p}_l)$. Therefore, $\mathscr{M}_l^{k_2,\cdots,k_l}$ are functions of $\mathfrak{p}_1^{-1}\mathfrak{p}_j$ for $j=2,\cdots,l$. We could then expand $\mathscr{M}_l^{k_2,\cdots,k_l}$ about these variables like in (3.9), and decompose the tensor $Y(\mathfrak{p}_1)$ into a symmetric traceless tensor. As a result, we obtain some terms given by multi-linear maps from l symmetric traceless tensors to another tensor (cf. (3.22)),

$$\begin{aligned}\Phi\big(U_1(\mathfrak{p}_1),\cdots,U_l(\mathfrak{p}_l)\big)=\big(U_1(\mathfrak{p}_1)\otimes\cdots\otimes U_l(\mathfrak{p}_l)\big)_{i_1\cdots i_s}Z_{i_{\tau_1}\cdots i_{\tau_w}j_1\cdots j_t},\\ s-w+t=k_2+\cdots k_l,\end{aligned}\tag{C.1}$$

  where Z is a tensor containing some δ and ϵ. The terms in (3.15), giving bilinear maps about symmetric traceless tensors $U^r(\mathfrak{p}_1)$ and $V^m(\mathfrak{p}_2)$, are actually a special case of (C.1).

- The proper rotations in the point group $\mathcal{G}$ give

$$\mathscr{G}_l(\boldsymbol{r}_2,\cdots,\boldsymbol{r}_n,\mathfrak{p}_1,\cdots,\mathfrak{p}_j\mathfrak{s},\cdots)=\mathscr{G}_l(\boldsymbol{r}_2\cdots,\boldsymbol{r}_l,\mathfrak{p}_1,\cdots,\mathfrak{p}_j,\cdots).\tag{C.2}$$

  It tells us

$$\mathscr{M}_l^{k_2,\cdots,k_l}(\cdots,\mathfrak{p}_j\mathfrak{s},\cdots)=\mathscr{M}_l^{k_2,\cdots,k_l}(\cdots,\mathfrak{p}_j,\cdots).\tag{C.3}$$

  It requires that the U_j in (C.1) can only be invariant tensors of the $SO(3)$-subgroup $\mathcal{G}_1$ (cf. Theorem 4.1).

- The improper rotations require

$$\mathscr{G}_l(-r_2,\cdots,-r_l,\mathfrak{p}_1\mathfrak{k},\cdots,\mathfrak{p}_j\mathfrak{k})=\mathscr{G}_l(r_2\cdots,r_l,\mathfrak{p}_1,\cdots,\mathfrak{p}_l). \tag{C.4}$$

It tells us

$$\mathscr{M}_l^{k_2,\cdots,k_l}(\mathfrak{p}_1\mathfrak{k},\cdots,\mathfrak{p}_l\mathfrak{k})=(-1)^{k_2+\cdots+k_l}\mathscr{M}_l^{k_2,\cdots,k_l}(\mathfrak{p}_1,\cdots,\mathfrak{p}_l). \tag{C.5}$$

We need to look at $k=k_2+\cdots+k_l$. It determines the number of U_j in (C.1) of type ± 1: when k is even, the number of type -1 tensors is even; when k is odd, the number of type -1 tensors is odd (cf. Theorem 4.2).

The difficulty in expanding $\mathscr{M}_l^{k_2,\cdots,k_l}$ is to identify linearly independent terms. For the same $(U_1,\cdots,U_l)$ there are multiple terms that might have complicated linear relations, especially when combined with the arguments of switching labels (cf. (3.7)). We shall discuss two cases, $\mathscr{M}_3^{0,0}$ and $\mathscr{M}_4^{0,0,0}$, which are expected to be important in applications.

C.1 Expansion of $\mathscr{M}_3^{0,0}$

To prepare for our discussion, we introduce the notation $\mathscr{a}_3$ for a scalar by contracting indices of three symmetric traceless tensors $(U_1^{n_1},U_2^{n_2},U_3^{n_3})$,

$$\begin{aligned}&\mathscr{a}_3(U_1^{n_1},U_2^{n_2},U_3^{n_3};l_{12},l_{13},l_{23})\\ =&(U_1^{n_1})_{i_1^{(12)}\cdots i_{l_{12}}^{(12)}i_1^{(13)}\cdots i_{l_{13}}^{(13)}}(U_2^{n_2})_{i_1^{(12)}\cdots i_{l_{12}}^{(12)}i_1^{(23)}\cdots i_{l_{23}}^{(23)}}(U_3^{n_3})_{i_1^{(13)}\cdots i_{l_{13}}^{(13)}i_1^{(23)}\cdots i_{l_{23}}^{(23)}},\end{aligned} \tag{C.6a}$$

$$\begin{aligned}&\mathscr{a}_3(U_1^{n_1},U_2^{n_2},U_3^{n_3};l_{12},l_{13},l_{23},(123))\\ =&\epsilon_{j_1j_2j_3}(U_1^{n_1})_{j_1i_1^{(12)}\cdots i_{l_{12}}^{(12)}i_1^{(13)}\cdots i_{l_{13}}^{(13)}}(U_2^{n_2})_{j_2i_1^{(12)}\cdots i_{l_{12}}^{(12)}i_1^{(23)}\cdots i_{l_{23}}^{(23)}}(U_3^{n_3})_{j_3i_1^{(13)}\cdots i_{l_{13}}^{(13)}i_1^{(23)}\cdots i_{l_{23}}^{(23)}}.\end{aligned} \tag{C.6b}$$

The nonnegative integers l_{ij} represent the number of indices contracted between $U_i^{n_i}$ and $U_j^{n_j}$, and $(\tau_1\tau_2\tau_3)=(123)$ means that there is an $\epsilon_{j_1j_2j_3}$ such that j_1 appears in $U_{\tau_1}^{n_{\tau_1}}=U_1^{n_1}$, j_2 appears in $U_2^{n_2}$, and j_3 appears in $U_3^{n_3}$. The parameters l_{ij} here are actually redundant. Actually, we have

$$l_{12}+l_{13}=n_1,\ l_{12}+l_{23}=n_2,\ l_{13}+l_{23}=n_3, \tag{C.7}$$

in (C.6a), where we require that $K=n_1+n_2+n_3$ is even and $K\geq 2n_i$ for $i=1,2,3$. Similarly, we have

$$l_{12}+l_{13}=n_1-1,\ l_{12}+l_{23}=n_2-1,\ l_{13}+l_{23}=n_3-1, \tag{C.8}$$

in (C.6b), where we require that $n_i\geq 1$, $K=n_1+n_2+n_3$ is odd, and $K\geq 2n_i+1$. However, we still keep l_{ij} in the expression, because we will use similar notations for four tensors. It is noticed that when permutating the three tensors in $\mathscr{a}_3$, we could get some identical or opposite terms, such as

$$\mathscr{a}_3(U_2^{n_2},U_1^{n_1},U_3^{n_3};l_{12},l_{23},l_{13})=\mathscr{a}_3(U_1^{n_1},U_2^{n_2},U_3^{n_3};l_{12},l_{13},l_{23}), \tag{C.9a}$$

$$\mathscr{a}_3(U_2^{n_2},U_1^{n_1},U_3^{n_3};l_{12},l_{23},l_{13},(123))=-\mathscr{a}_3(U_1^{n_1},U_2^{n_2},U_3^{n_3};l_{12},l_{13},l_{23},(123)). \tag{C.9b}$$

Thus, once the three tensors are chosen, we can fix how they are arranged in a_3. In particular, if two tensors are identical in (C.6b), the term equals zero.

Now we are ready to expand $\mathscr{M}_3^{0,0}$. As we have mentioned, it is a scalar function of $\mathfrak{p}_1^{-1}\mathfrak{p}_2$ and $\mathfrak{p}_1^{-1}\mathfrak{p}_3$. When expanding about these two variables, the resulting terms can be written as

$$\big(Y_2^{n_2}(\mathfrak{p}_1)\cdot U_2^{n_2}(\mathfrak{p}_2)\big)\big(Y_3^{n_3}(\mathfrak{p}_1)\cdot U_3^{n_3}(\mathfrak{p}_3)\big)=\big(Y_2^{n_2}(\mathfrak{p}_1)\otimes Y_3^{n_3}(\mathfrak{p}_1)\big)\cdot\big(U_2^{n_2}(\mathfrak{p}_2)\otimes U_3^{n_3}(\mathfrak{p}_3)\big), \quad \text{(C.10)}$$

where $Y_i^{n_i}$ and $U_i^{n_i}$ are symmetric traceless tensors. After we decompose $Y_2^{n_2}\otimes Y_3^{n_3}$ into symmetric traceless tensors, the above terms can be expressed linearly by terms in (C.1) where $l=3$, $s=w$ and $t=0$. Using the notation a_3, they are given by

$$a_3\big(U_1^{n_1}(\mathfrak{p}_1),U_2^{n_2}(\mathfrak{p}_2),U_3^{n_3}(\mathfrak{p}_3);l_{12},l_{13},l_{23}\big), \quad \text{(C.11a)}$$

$$a_3\big(U_1^{n_1}(\mathfrak{p}_1),U_2^{n_2}(\mathfrak{p}_2),U_3^{n_3}(\mathfrak{p}_3);l_{12},l_{13},l_{23},(123)\big). \quad \text{(C.11b)}$$

Similar to Theorem 3.1, let us fix $U_2^{n_2}$ and $U_3^{n_3}$, and examine the linearly independent terms, by comparing (C.10) and (C.11). The former can be expressed linearly by the latter. On the other hand, because $l_{ij}\geq 0$ in (C.7) and (C.8), the tensor order n_1 in (C.11) ranges from $|n_2-n_3|$ to n_2+n_3. Once n_1 is determined, the l_{ij} are also determined, and $U_1^{n_1}$ has $2n_1+1$ choices. Hence, the total number of choices of $U_1^{n_1}$ is

$$\sum_{r=|n_2-n_3|}^{n_2+n_3}(2r+1)=(2n_2+1)(2n_3+1),$$

which is equal to the dimension of $Y_2^{n_2}\otimes Y_3^{n_3}$. Therefore, when we let $U_i^{n_i}$ be the tensors in $\mathbb{W}^{n_i}$, the terms given by (C.11) are linearly independent.

Then, we take the switching of labels into consideration. It requires $\mathscr{M}_3^{0,0}(\mathfrak{p}_{\sigma(1)},\mathfrak{p}_{\sigma(2)},\mathfrak{p}_{\sigma(3)})=\mathscr{M}_3^{0,0}(\mathfrak{p}_1,\mathfrak{p}_2,\mathfrak{p}_3)$ for any permutation σ of 1,2,3. Thus, the expansion can only have the terms below,

$$\sum_{\sigma}a_3\big(U_1^{n_1}(\mathfrak{p}_{\sigma(1)}),U_2^{n_2}(\mathfrak{p}_{\sigma(2)}),U_3^{n_3}(\mathfrak{p}_{\sigma(3)});l_{12},l_{13},l_{23}\big), \quad \text{(C.12a)}$$

$$\sum_{\sigma}a_3\big(U_1^{n_1}(\mathfrak{p}_{\sigma(1)}),U_2^{n_2}(\mathfrak{p}_{\sigma(2)}),U_3^{n_3}(\mathfrak{p}_{\sigma(3)});l_{12},l_{13},l_{23},(123)\big), \quad \text{(C.12b)}$$

where the σ in the summation takes all the permutations. As we mentioned in (C.9), the terms are invariant or become opposite when interchanging the three tensors $U_i^{n_i}$. In particular, in (C.12b), if any two of $U_i^{n_i}$ are identical, then the term vanishes.

C.2 Expansion of $\mathscr{M}_4^{0,0,0}$

We expand $\mathscr{M}_4^{0,0,0}$ about three variables $\mathfrak{p}_1^{-1}\mathfrak{p}_j$ for $j=2,3,4$, to obtain the terms

$$\begin{aligned}&\big(Y_2^{n_2}(\mathfrak{p}_1)\cdot U_2^{n_2}(\mathfrak{p}_2)\big)\big(Y_3^{n_3}(\mathfrak{p}_1)\cdot U_3^{n_3}(\mathfrak{p}_3)\big)\big(Y_4^{n_4}(\mathfrak{p}_1)\cdot U_4^{n_4}(\mathfrak{p}_4)\big)\\ =&\big(Y_2^{n_2}(\mathfrak{p}_1)\otimes Y_3^{n_3}(\mathfrak{p}_1)\otimes Y_4^{n_4}(\mathfrak{p}_1)\big)\cdot\big(U_2^{n_2}(\mathfrak{p}_2)\otimes U_3^{n_3}(\mathfrak{p}_3)\otimes U_4^{n_4}(\mathfrak{p}_4)\big). \quad \text{(C.13)}\end{aligned}$$

The decomposition of $Y_2^{n_2}\otimes Y_3^{n_3}\otimes Y_4^{n_4}$ into symmetric traceless tensors is followed. Similar to (C.6), we use the notation a_4 for a scalar generated by contraction of four tensors,

$$a_4\Big(U_i^{n_i}\big|_{i=1}^4;l_{12},l_{13},l_{14},l_{23},l_{24},l_{34}\Big), \tag{C.14a}$$

$$a_4\Big(U_i^{n_i}\big|_{i=1}^4;l_{12},l_{13},l_{14},l_{23},l_{24},l_{34},(\tau_1\tau_2\tau_3)\Big), \tag{C.14b}$$

where the integers l_{ij} represent how many indices are contracted between $U_i^{n_i}$ and $U_j^{n_j}$; $(\tau_1\tau_2\tau_3)$ means that there is an ϵ to contract the indices in the way $\epsilon_{j_1j_2j_3}(U_{\tau_1}^{n_{\tau_1}})_{j_1\cdots}(U_{\tau_2}^{n_{\tau_2}})_{j_2\cdots}(U_{\tau_3}^{n_{\tau_3}})_{j_3\cdots}$. These nonnegative integers shall satisfy

$$\sum_{j=i+1}^{4} l_{ij}+\sum_{j=1}^{i-1} l_{ji}=n_i-b_i, \quad b_i=\left\{\begin{array}{ll} 1, & i=\tau_1,\tau_2, \text{ or } \tau_3, \\ 0, & \text{otherwise.}\end{array}\right. \tag{C.15}$$

As we explained in (C.9), when permutating the tensors $U_i^{n_i}$, some terms are identical or opposite.

Together with the symmetry of switching the labels, we eventually obtain the terms

$$\sum_\sigma a_4\Big(U_i^{n_i}(\mathfrak{p}_{\sigma(i)})\big|_{i=1}^4;l_{ij}\big|_{1\le i<j\le 4}\Big), \tag{C.16a}$$

$$\sum_\sigma a_4\Big(U_i^{n_i}(\mathfrak{p}_{\sigma(i)})\big|_{i=1}^4;l_{ij}\big|_{1\le i<j\le 4},(\tau_1\tau_2\tau_3)\Big), \tag{C.16b}$$

where l_{ij} satisfy (C.15). However, unlike the cases we discussed above, the terms in (C.16) still have linear relations. Below, we write down the linearly independent terms. Denote $K=n_1+n_2+n_3+n_4$ and $D=n_1+n_2-n_3-n_4$. Note that in (C.16a) K and D are even with $K\ge 2n_i$, while in (C.16b) K and D are odd and $K\ge 2n_i+1$.

1. The four tensors $U_i^{n_i}$ are mutually unequal.

   - For (C.16a), D is even. If $D\le 0$, we require $l_{12}\le 1$; if $D\ge 0$ we require $l_{34}\le 1$. Notice that when $D=0$, by (C.15) we have $n_1+n_2-n_3-n_4=2l_{12}-2l_{34}=0$.
   - For (C.16b), D is odd. If $D\le -1$, we let $(\tau_1\tau_2\tau_3)=(134),(234)$ and $l_{12}=0$; if $D\ge 1$, we let $(\tau_1\tau_2\tau_3)=(123),(124)$ and $l_{34}=0$.

2. Two tensors are equal, but they are not equal to the other two. We place these two tensors in the first two, i.e. $U_1^{n_1}=U_2^{n_2}$.

   - For (C.16a), if $D\le 0$, we require $l_{12}\le 1$ and $l_{13}\le l_{23}$; if $D\ge 0$ we require $l_{34}\le 1$ and $l_{13}\le l_{23}$.
   - For (C.16b), if $D\le -1$, we let $(\tau_1\tau_2\tau_3)=(134)$ and $l_{12}=0$; if $D\ge 1$, we let $(\tau_1\tau_2\tau_3)=(123),(124)$ and $l_{34}=0$, $l_{13}<l_{23}$.

For the case $U_1^{n_1}=U_2^{n_2}$ and $U_3^{n_3}=U_4^{n_4}$, only (C.16a) appears since D is even. The above conditions still apply.

3. Three tensors are equal. We let $U_1^{n_1}=U_2^{n_2}=U_3^{n_3}$.
   - For (C.16a), we require $l_{12}=l_{13}\le l_{23}$.
   - For (C.16b), let $(\tau_1\tau_2\tau_3)=(124)$ and we look at $D=n_1-n_4$. If $D\le -1$, we require $l_{12}=l_{13}<l_{23}$; if $D\ge 1$, we require $l_{34}=l_{24}<l_{14}$.

   If four tensors are equal, only (C.16a) appears and the above conditions still apply.

The derivation is given afterwards. Here, we explain the conditions stated above by a couple of examples. We consider the case 3 with $n_1=n_2=n_3=3$, and discuss two cases: $n_4=3$ and $n_4=1$.

- $n_4=3$. From (C.15), we derive that $2l_{34}-2l_{12}=n_3+n_4-n_1-n_2=0$. So we have $l_{12}=l_{34}$, $l_{13}=l_{24}$, $l_{14}=l_{23}$. We also deduce from (C.15) that
$$2(l_{12}+l_{13}+l_{23}+l_{14}+l_{24}+l_{34})=n_1+n_2+n_3+n_4.$$
It implies that $l_{12}+l_{13}+l_{23}=3$. Therefore, with the condition $l_{12}=l_{13}\le l_{23}$, we find two choices $(l_{12},l_{13},l_{23})=(0,0,3),(1,1,1)$.
- $n_4=1$. Similarly, we can derive that $l_{12}-l_{34}=l_{13}-l_{24}=l_{14}-l_{23}=1$. Since $l_{ij}\ge 0$, we need $l_{12},l_{13},l_{23}\ge 1$. We can also find that $l_{12}+l_{13}+l_{23}=4$, which only gives us one choice $(l_{12},l_{13},l_{23})=(1,1,2)$.

D Linearly independent terms in the expansion of $\mathscr{M}_4^{0,0,0}$

In this section, we look into (C.16) and find out the linearly independent terms. We begin with two equalities.

Lemma D.1. *Suppose Q_i are second order symmetric traceless tensors; $\boldsymbol{p}_i$ are vectors. Then we have*

$$\begin{aligned}&2\mathrm{tr}(Q_1Q_2Q_3Q_4+Q_1Q_2Q_4Q_3+Q_1Q_3Q_2Q_4)\\&\qquad=\mathrm{tr}(Q_1Q_2)\mathrm{tr}(Q_3Q_4)+\mathrm{tr}(Q_1Q_3)\mathrm{tr}(Q_2Q_4)+\mathrm{tr}(Q_1Q_4)\mathrm{tr}(Q_2Q_3),\end{aligned}\tag{D.1}$$

$$\begin{aligned}&(\boldsymbol{p}_1\times\boldsymbol{p}_2)\otimes\boldsymbol{p}_3+(\boldsymbol{p}_2\times\boldsymbol{p}_3)\otimes\boldsymbol{p}_1+(\boldsymbol{p}_3\times\boldsymbol{p}_1)\otimes\boldsymbol{p}_2\\&\qquad+\boldsymbol{p}_3\otimes(\boldsymbol{p}_1\times\boldsymbol{p}_2)+\boldsymbol{p}_1\otimes(\boldsymbol{p}_2\times\boldsymbol{p}_3)+\boldsymbol{p}_2\otimes(\boldsymbol{p}_3\times\boldsymbol{p}_1)=\det(\boldsymbol{p}_1,\boldsymbol{p}_2,\boldsymbol{p}_3)\mathfrak{i}.\end{aligned}\tag{D.2}$$

Here, Q_1Q_2 is understood as matrix product, tr *is the trace of a matrix, and $\times$ is the cross product of vectors in $\mathbb{R}^3$.*

Table 3: Linearly independent terms in the expansion of $\mathscr{M}_3^{0,0}$, $\mathscr{M}_4^{0,0,0}$ and the corresponding terms in the free energy. All the tensors are symmetric traceless. The notation $\langle U\rangle$ represents the average of $U(\mathfrak{p})$ about the density $f(\boldsymbol{x},\mathfrak{p})$.

	Orientational expansion	Free energy
$\mathscr{M}_3^{0,0}$	$\sum_\sigma \mathfrak{a}_3\Big(U_i^{n_i}(\mathfrak{p}_{\sigma(i)})\big\|_{i=1}^3; l_{ij}\big\|_{1\le i<j\le 3}\Big)$	$\mathfrak{a}_3\Big(\langle U_i^{n_i}\rangle\big\|_{i=1}^3; l_{ij}\big\|_{1\le i<j\le 3}\Big)$
	$K=n_1+n_2+n_3$ even, $K\ge 2n_i$	
	$\sum_\sigma \mathfrak{a}_3\Big(U_i^{n_i}(\mathfrak{p}_{\sigma(i)})\big\|_{i=1}^3; l_{ij}\big\|_{1\le i<j\le 3}, (123)\Big)$	$\mathfrak{a}_3\Big(\langle U_i^{n_i}\rangle\big\|_{i=1}^3; l_{ij}\big\|_{1\le i<j\le 3}, (123)\Big)$
	$K=n_1+n_2+n_3$ odd, $K-1\ge 2n_i$; $U_i^{n_i}$ mutually unequal	
$\mathscr{M}_4^{0,0,0}$	$\sum_\sigma \mathfrak{a}_4\Big(U_i^{n_i}(\mathfrak{p}_{\sigma(i)})\big\|_{i=1}^4; l_{ij}\big\|_{1\le i<j\le 4}\Big)$	$\mathfrak{a}_4\Big(\langle U_i^{n_i}\rangle\big\|_{i=1}^4; l_{ij}\big\|_{1\le i<j\le 4}\Big)$
	$K=n_1+n_2+n_3+n_4$ even, $K\ge 2n_i$, $D=n_1+n_2-n_3-n_4=2l_{12}-2l_{34}$ $U_i^{n_i}$ mutually unequal: If $D\le 0$, then $l_{12}\le 1$; if $D\ge 0$, then $l_{34}\le 1$ $U_1^{n_1}=U_2^{n_2}$: If $D\le 0$, then $l_{12}\le 1$, $l_{13}\le l_{23}$; if $D>0$, then $l_{34}\le 1$, $l_{13}\le l_{23}$ $U_1^{n_1}=U_2^{n_2}=U_3^{n_3}$: $l_{12}=l_{13}\le l_{23}$	
	$\sum_\sigma \mathfrak{a}_4\Big(U_i^{n_i}(\mathfrak{p}_{\sigma(i)})\big\|_{i=1}^4; l_{ij}\big\|_{1\le i<j\le 4}, (\tau_1\tau_2\tau_3)\Big)$	$\mathfrak{a}_4\Big(\langle U_i^{n_i}\rangle\big\|_{i=1}^4; l_{ij}\big\|_{1\le i<j\le 4}, (\tau_1\tau_2\tau_3)\Big)$
	$K=n_1+n_2+n_3+n_4$ odd, $K-1\ge 2n_i$, $D=n_1+n_2-n_3-n_4$ $U_i^{n_i}$ mutually unequal: If $D\ge 1$, then $(\tau_1\tau_2\tau_3)=(123),(124)$ with $l_{34}=0$; if $D\le -1$, then $(\tau_1\tau_2\tau_3)=(134),(234)$ with $l_{12}=0$ $U_1^{n_1}=U_2^{n_2}$: If $D\ge 1$, then $(\tau_1\tau_2\tau_3)=(123),(124)$ with $l_{34}=0$, $l_{13}<l_{23}$; if $D\le -1$, then $(\tau_1\tau_2\tau_3)=(134)$ with $l_{12}=0$ $U_1^{n_1}=U_2^{n_2}=U_3^{n_3}$: $(\tau_1\tau_2\tau_3)=(124)$. If $D\le -1$, $l_{12}=l_{13}<l_{23}$; if $D\ge 1$, $l_{34}=l_{24}<l_{14}$	

For the notations: $\mathfrak{a}_3$ and $\mathfrak{a}_4$, see (C.6), (C.14), and (C.15).

Proof. For any two symmetric traceless tensors Q and B, we have

$$2\text{tr}(Q^3B)=\text{tr}(Q^2)\text{tr}(QB). \tag{D.3}$$

It can be verified by diagonalizing Q. Then, let $Q=B=Q_1+Q_2$ to derive

$$2\text{tr}(2Q_1^2Q_2^2+Q_1Q_2Q_1Q_2)=2(\text{tr}(Q_1Q_2))^2+\text{tr}(Q_1^2)\text{tr}(Q_2^2). \tag{D.4}$$

Substituting Q_1 with Q_1+Q_3, we deduce that

$$2\text{tr}(2Q_1Q_3Q_2^2+Q_1Q_2Q_3Q_2)=2\text{tr}(Q_1Q_2)\text{tr}(Q_2Q_3)+\text{tr}(Q_1Q_3)\text{tr}(Q_2^2). \tag{D.5}$$

Finally, substitute Q_2 with Q_2+Q_4 to obtain what is stated in the lemma.

The second equality can be verified directly. □

To simplify the notation, from now on, we omit the tensor order of $U_i^{n_i}$, i.e. write $U_i^{n_i}$ in short as U_i. Although we do not write out, we always use n_i as the order of U_i. The above lemma leads to

$$\begin{aligned}
&2a_4(U_1,U_2,U_3,U_4;l_{12}+1,l_{13}+1,l_{14},l_{23},l_{24}+1,l_{34}+1)\\
&\quad+2a_4(U_1,U_2,U_3,U_4;l_{12}+1,l_{13},l_{14}+1,l_{23}+1,l_{24},l_{34}+1)\\
&\quad+2a_4(U_1,U_2,U_3,U_4;l_{12},l_{13}+1,l_{14}+1,l_{23}+1,l_{24}+1,l_{34})\\
=&a_4(U_1,U_2,U_3,U_4;l_{12}+2,l_{13},l_{14},l_{23},l_{24},l_{34}+2)\\
&+a_4(U_1,U_2,U_3,U_4;l_{12},l_{13}+2,l_{14},l_{23},l_{24}+2,l_{34})\\
&+a_4(U_1,U_2,U_3,U_4;l_{12},l_{13},l_{14}+2,l_{23}+2,l_{24},l_{34}).
\end{aligned} \tag{D.6}$$

In the above, $n_1+n_2+n_3+n_4$ is even. Thus, in $a_4(U_i;l_{ij})$, for all the terms with $l_{12},l_{34}\geq 2$, they can be expressed linearly by those with $\min\{l_{12},l_{34}\}\leq 1$. From (C.15), we have $n_1+n_2-2l_{12}=n_3+n_4-2l_{34}$. So we can choose the terms where

$$l_{12}\leq 1 \ \text{ if } n_1+n_2\leq n_3+n_4; \quad l_{34}\leq 1, \ \text{ if } n_1+n_2\geq n_3+n_4. \tag{D.7}$$

Here, we notice that $l_{12}=l_{34}$ if $n_1+n_2=n_3+n_4$.

For terms involving ϵ, the lemma implies

$$\begin{aligned}
&a_4(U_1,U_2,U_3,U_4;l_{12},l_{13},l_{14}+1,l_{23},l_{24},l_{34},(123))\\
&\qquad-a_4(U_1,U_2,U_3,U_4;l_{12},l_{13}+1,l_{14},l_{23},l_{24},l_{34},(124))\\
&\qquad+a_4(U_1,U_2,U_3,U_4;l_{12}+1,l_{13},l_{14},l_{23},l_{24},l_{34},(134))=0,\\
&a_4(U_1,U_2,U_3,U_4;l_{12},l_{13},l_{14},l_{23},l_{24}+1,l_{34},(123))\\
&\qquad-a_4(U_1,U_2,U_3,U_4;l_{12},l_{13},l_{14},l_{23}+1,l_{24},l_{34},(124))\\
&\qquad-a_4(U_1,U_2,U_3,U_4;l_{12}+1,l_{13},l_{14},l_{23},l_{24},l_{34},(234))=0,\\
&a_4(U_1,U_2,U_3,U_4;l_{12},l_{13},l_{14},l_{23},l_{24},l_{34}+1,(123))\\
&\qquad+a_4(U_1,U_2,U_3,U_4;l_{12},l_{13},l_{14},l_{23}+1,l_{24},l_{34},(134))\\
&\qquad-a_4(U_1,U_2,U_3,U_4;l_{12},l_{13}+1,l_{14},l_{23},l_{24},l_{34},(234))=0,\\
&a_4(U_1,U_2,U_3,U_4;l_{12},l_{13},l_{14},l_{23},l_{24},l_{34}+1,(124))\\
&\qquad-a_4(U_1,U_2,U_3,U_4;l_{12},l_{13},l_{14},l_{23},l_{24}+1,l_{34},(134))\\
&\qquad+a_4(U_1,U_2,U_3,U_4;l_{12},l_{13},l_{14}+1,l_{23},l_{24},l_{34},(234))=0.
\end{aligned} \tag{D.8}$$

Notice that $n_1+n_2+n_3+n_4$ is odd in these equalities. Similarly, in $a_4(U_i;l_{ij},(\tau_1\tau_2\tau_3))$, we can choose the terms where

$$\begin{aligned}
&(\tau_1\tau_2\tau_3)=(123),(124),\ l_{34}=0,\ \text{if } n_1+n_2\geq n_3+n_4+1,\\
&(\tau_1\tau_2\tau_3)=(134),(234),\ l_{12}=0,\ \text{if } n_1+n_2+1\leq n_3+n_4,
\end{aligned} \tag{D.9}$$

because other terms can be linearly expressed by them.

Let us consider the linearly independent terms in $a_4(U_i(\mathfrak{p}_i);l_{ij})$ and $a_4(U_i(\mathfrak{p}_i);l_{ij},(\tau_1\tau_2\tau_3))$. Here, we use the same approach as in Theorem 3.1.

Theorem D.1. *Let U_2,U_3,U_4 be fixed and $U_1 \in \mathbb{W}^{n_1}$ where n_1 takes all the possible values. The terms $a_4(U_i(\mathfrak{p}_i);l_{ij})$ with the condition* (D.7)*, and $a_4(U_i(\mathfrak{p}_i);l_{ij},(\tau_1\tau_2\tau_3))$ with the condition* (D.9)*, are linearly independent.*

Proof. Recall that these terms can express (C.13) linearly. In (C.13), the tensor $Y_2\otimes Y_3\otimes Y_4$ has $(2n_2+1)(2n_3+1)(2n_4+1)$ choices. In what follows, we show that the number of terms expressed by U_i is exactly $(2n_2+1)(2n_3+1)(2n_4+1)$.

We use induction on n_2 and n_3. When any of n_2, n_3 or n_4 is zero, it reduces to the case a_3 (see the discussion below (C.11)). So, we discuss the case where $n_2,n_3,n_4 \geq 1$. If $l_{23}\geq 1$, the number of terms equals the case where U_2, U_3 and U_4 are of the order n_2-1, n_3-1, and n_4, respectively, which is $(2n_2-1)(2n_3-1)(2n_4+1)$ by the assumption of induction. Now let $l_{23}=0$. To count the number, we use (C.15) and notice the constraints $l_{ij}\geq 0$. There are six cases:

1. $a_4(U_i(\mathfrak{p}_i);l_{ij})$ where $l_{12}=0$ or $l_{34}=0$. In this case, $n_1+n_2+n_3+n_4$ is even, and

$$l_{12}+l_{24}=n_2, \quad l_{13}+l_{34}=n_3.$$

   (a) When $l_{12}=0$, we solve $l_{24}=n_2$, and

$$l_{34}=\frac{n_3+n_4-n_1-n_2}{2}, \quad l_{13}=\frac{n_1+n_2+n_3-n_4}{2}, \quad l_{14}=\frac{n_1+n_4-n_2-n_3}{2}.$$

   It yields

$$n_1\leq n_3+n_4-n_2, \quad n_1\geq n_2+n_3-n_4, \quad n_1\geq n_4-n_3-n_2.$$

   (b) When $l_{34}=0$, we solve $l_{13}=n_3$, and

$$l_{12}=\frac{n_1+n_2-n_3-n_4}{2}, \quad l_{24}=\frac{n_2+n_3+n_4-n_1}{2}, \quad l_{14}=\frac{n_1+n_4-n_2-n_3}{2}.$$

   It yields

$$n_1\geq n_3+n_4-n_2, \quad n_1\leq n_2+n_3+n_4, \quad n_1\geq n_2+n_3-n_4.$$

   We combine (a) and (b). If $n_3+n_4-n_2<0$, then the range of n_1 is $n_2+n_3-n_4\leq n_1\leq n_2+n_3+n_4$. If $n_3+n_4-n_2\geq 0$, then $|n_2+n_3-n_4|\leq n_1\leq n_2+n_3+n_4$. So, we have $|n_2+n_3-n_4|\leq n_1\leq n_2+n_3+n_4$ where n_1 has the same parity as $n_2+n_3+n_4$.

2. $a_4(U_i(\mathfrak{p}_i);l_{ij})$ where $\min\{l_{12},l_{34}\}=1$. Similar to the above, we deduce that $1+|n_2+n_3-n_4-1|\leq n_1\leq n_2+n_3+n_4-2$ where n_1 has the same parity as $n_2+n_3+n_4$.

3. $a_4(U_i(\mathfrak{p}_i);l_{ij},(123))$ where $l_{34}=0$. We solve that $l_{13}=n_3-1$, and

$$l_{12}=\frac{n_1+n_2-n_3-n_4-1}{2}, \quad l_{24}=\frac{n_2+n_3+n_4-n_1-1}{2}, \quad l_{14}=\frac{n_1+n_4-n_2-n_3+1}{2}.$$

   It yields

$$n_1\geq n_3+n_4-n_2+1, \quad n_1\leq n_2+n_3+n_4-1, \quad n_1\geq n_2+n_3-n_4-1.$$

4. $a_4(U_i(\mathfrak{p}_i);l_{ij},(124))$ where $l_{34}=0$. We solve that $l_{13}=n_3$, and

$$l_{12}=\frac{n_1+n_2-n_3-n_4-1}{2},\quad l_{24}=\frac{n_2+n_3+n_4-n_1-1}{2},\quad l_{14}=\frac{n_1+n_4-n_2-n_3-1}{2}.$$

It yields

$$n_1\geq n_3+n_4-n_2+1,\quad n_1\leq n_2+n_3+n_4-1,\quad n_1\geq n_2+n_3-n_4+1.$$

5. $a_4(U_i(\mathfrak{p}_i);l_{ij},(134))$ where $l_{12}=0$. We solve that $l_{24}=n_2$, and

$$l_{34}=\frac{n_3+n_4-n_1-n_2-1}{2},\quad l_{24}=\frac{n_1+n_2+n_3-n_4-1}{2},\quad l_{14}=\frac{n_1+n_4-n_2-n_3-1}{2}.$$

It yields

$$n_1\leq n_3+n_4-n_2-1,\quad n_1\geq n_4-n_2-n_3+1,\quad n_1\geq n_2+n_3-n_4+1.$$

6. $a_4(U_i(\mathfrak{p}_i);l_{ij},(234))$ where $l_{12}=0$. We solve that $l_{24}=n_2-1$, and

$$l_{34}=\frac{n_3+n_4-n_1-n_2-1}{2},\quad l_{24}=\frac{n_1+n_2+n_3-n_4-1}{2},\quad l_{14}=\frac{n_1+n_4-n_2-n_3-1}{2}.$$

It yields

$$n_1\leq n_3+n_4-n_2-1,\quad n_1\geq n_4-n_2-n_3+1,\quad n_1\geq n_2+n_3-n_4-1.$$

In cases 3 to 6, n_1 has the different parity from $n_2+n_3+n_4$. Combine case 3 and case 6. If $n_2>n_4$, then case 6 is empty, and we have $n_2+n_3-n_4-1\leq n_1\leq n_2+n_3+n_4-1$. If $n_2\leq n_4$, then case 6 is $|n_2+n_3-n_4-1|\leq n_1\leq n_3+n_4-n_2-1$, and case 3 is $n_3+n_4-n_2+1\leq n_1\leq n_2+n_3+n_4-1$. So, we arrive at $|n_2+n_3-n_4-1|\leq n_1\leq n_2+n_3+n_4-1$. Similarly, we combine case 4 and case 5 to have $|n_2+n_3-n_4|+1\leq n_1\leq n_2+n_3+n_4-1$.

So, let us combine cases 1, 4 and 5. The range of n_1 is $|n_2+n_3-n_4|\leq n_1\leq n_2+n_3+n_4$. The cases 2, 3 and 6 lead to $|n_2+n_3-n_4-1|\leq n_1\leq n_2+n_3+n_4-1$. Thus, the number of terms is

$$\begin{aligned}&\sum_{r=|n_2+n_3-n_4|}^{n_2+n_3+n_4}(2r+1)+\sum_{r=|n_2+n_3-n_4-1|}^{n_2+n_3+n_4-1}(2r+1)\\ =&4(n_2+n_3)(2n_4+1)\\ =&(2n_2+1)(2n_3+1)(2n_4+1)-(2n_2-1)(2n_3-1)(2n_4+1).\end{aligned}$$

This concludes the proof. □

The theorem indicates that (D.6) and (D.8) give all the linear relations without missing anything. Now, we consider (C.16) where label permutations are taken into consideration. As we have discussed in the main text, once the tensors appearing in a_4 are chosen, we can arrange them in the order we want. When U_i are mutually unequal, the conditions (D.7) and (D.9) are just those in the Table 1. However, these conditions are not suitable if some of U_i are equal.

We omit the case where $U_1=U_2\neq U_3,U_4$, and only examine the case $U_1=U_2=U_3$.

Problem 1: Consider (C.16a) where $U_1=U_2=U_3$. It is equivalent to consider the linearly independent terms of $a_4(U_1,U_1,U_1,U_4;l_{ij})$. The relation (C.15) between l_{ij} can be rewritten as

$$\begin{aligned}&2(l_{12}-l_{34})=2(l_{13}-l_{24})=2(l_{23}-l_{14})=n_1-n_4,\\&l_{14}+l_{24}+l_{34}=n_4.\end{aligned}$$

Thus, we define $(d_1,d_2,d_3)=(l_{12},l_{13},l_{23})$ if $n_1\leq n_4$, and $(d_1,d_2,d_3)=(l_{34},l_{24},l_{14})$ if $n_1\geq n_4$. We have $d_1+d_2+d_3=\min\{(3n_1-n_4)/2,n_4\}\triangleq d$ is a constant determined by n_1 and n_4. Define $\psi(d_1,d_2,d_3)=a_4(U_1,U_1,U_1,U_4;l_{ij})$. Similar to (C.9), we have $\psi(d_1,d_2,d_3)=\psi(d_{\sigma(1)},d_{\sigma(2)},d_{\sigma(3)})$ for any permutation σ. The linear relation (D.6) is then written as

$$\begin{aligned}&\psi(d_1+2,d_2,d_3)+\psi(d_1,d_2+2,d_3)+\psi(d_1,d_2,d_3+2)\\=&2\psi(d_1+1,d_2+1,d_3)+2\psi(d_1+1,d_2,d_3+1)+2\psi(d_1,d_2+1,d_3+1).\end{aligned}$$

According to the conditions in Table 1, we need to show that $\psi(i,i,d-2i)$ for $3i\leq d$ are linearly independent and can linearly express others. We use induction on d. For $d=0,1,2$ we verify directly. When $d=0$, there is only one term $\psi(0,0,0)$. When $d=1$, by the permutational symmetry there is only one term $\psi(0,0,1)$. When $d=2$, we have

$$\begin{aligned}3\psi(0,0,2)&=\psi(2,0,0)+\psi(0,2,0)+\psi(0,0,2)\\&=2\psi(1,1,0)+2\psi(1,0,1)+2\psi(0,1,1)=6\psi(1,1,0).\end{aligned}$$

Thus, there is only one linearly independent term $\psi(0,0,2)$.

Assume $d\geq 3$. The linear relations between ψ where $d_i\geq 1$ are identical to $\psi(d_1-1,d_2-1,d_3-1)$ for $d-3$. By the assumption of induction, $\psi(i,i,d-2i)$ for $1\leq i\leq d-2i$ give the linearly independent terms. Thus, let us assume that $\psi(d_1,d_2,d_3)$ are all known when $d_i\geq 1$, and solve ψ when some d_i are zero. Now let $d_1=0$. If $d_2,d_3\geq 1$, then

$$\begin{aligned}&\psi(0,d_2+2,d_3)-2\psi(0,d_2+1,d_3+1)+\psi(0,d_2,d_3+2)\\=&2\psi(1,d_2+1,d_3)+2\psi(1,d_2,d_3+1)-\psi(2,d_2,d_3)\end{aligned}$$

is known. For $d_2=0$, we have

$$\psi(0,2,d-2)-2\psi(0,1,d-1)+\psi(0,0,d)=2\psi(1,1,d-2)+2\psi(1,0,d-1)-\psi(2,0,d-2).$$

Use invariance under permutation, we get

$$-\psi(0,2,d-2)+2\psi(0,1,d-1)=-\psi(1,1,d-2)+\frac{1}{2}\psi(0,0,d).$$

Define a vector $\boldsymbol{z}$ where $z_i=\psi(0,i,d-i)$ for $i=1,\cdots,d-1$. The above linear equations can be written as

$$\begin{pmatrix} 2 & -1 & & \\ -1 & 2 & \ddots & \\ & \ddots & \ddots & -1 \\ & & -1 & 2 \end{pmatrix} \boldsymbol{z}=\boldsymbol{b}+\begin{pmatrix} \frac{1}{2}\psi(0,0,d) \\ 0 \\ \vdots \\ 0 \\ \frac{1}{2}\psi(0,0,d) \end{pmatrix},$$

where $\boldsymbol{b}$ satisfies $b_i=b_{d-i}$ that is given by $\psi(d_1,d_2,d_3)$ with $d_i\geq 1$. Hence, the value of $\psi(0,0,d)$ is needed to fully determine $\psi(0,d_2,d_3)$, and the solution also satisfies $z_i=z_{d-i}$.

Problem 2: Consider (C.16b) where $U_1=U_2=U_3$. Again, we shall consider the linearly independent terms of $a_4(U_1,U_1,U_1,U_4;l_{ij},(\tau_1\tau_2\tau_3))$. Using arguments similar to (C.9), we can deduce that

$$\begin{aligned}
&a_4(U_1,U_1,U_1,U_4;l_{12},l_{13},l_{14},l_{23},l_{24},l_{34},(124))\\
&\qquad =a_4(U_1,U_1,U_1,U_4;l_{12},l_{23},l_{24},l_{13},l_{14},l_{34},(214))\\
&\qquad =-a_4(U_1,U_1,U_1,U_4;l_{12},l_{23},l_{24},l_{13},l_{14},l_{34},(124)),\\
&a_4(U_1,U_1,U_1,U_4;l_{12},l_{13},l_{14},l_{23},l_{24},l_{34},(134))\\
&\qquad =a_4(U_1,U_1,U_1,U_4;l_{13},l_{12},l_{14},l_{23},l_{34},l_{24},(124)),\\
&a_4(U_1,U_1,U_1,U_4;l_{12},l_{13},l_{14},l_{23},l_{24},l_{34},(234))\\
&\qquad =-a_4(U_1,U_1,U_1,U_4;l_{23},l_{13},l_{34},l_{12},l_{24},l_{14},(124)).
\end{aligned}$$

Thus, it allows us not to consider the terms with $(\tau_1\tau_2\tau_3)=(134),(234)$. When $(\tau_1\tau_2\tau_3)=(124)$, the relations between l_{ij} require

$$\begin{aligned}
&2(l_{12}-l_{34}+1)=2(l_{13}-l_{24})=2(l_{23}-l_{14})=n_1-n_4+1,\\
&l_{14}+l_{24}+l_{34}=n_4-1.
\end{aligned}$$

Thus, we define $(d_1,d_2,d_3)=(l_{12},l_{13},l_{23})$ if $n_1\leq n_4-1$, and $(d_1,d_2,d_3)=(l_{34},l_{24},l_{14})$ if $n_1\geq n_4+1$. We have $d_1+d_2+d_3=\min\{n_4-1,(3n_1-n_4-1)/2\}=d$. To simplify the presentation, we only discuss the case $n_1\leq n_4-1$. Define $\varphi(d_1,d_2,d_3)=a_4(U_i^{n_i};l_{ij},(124))$. Then we have

$$\varphi(d_1,d_2,d_3)=-\varphi(d_1,d_3,d_2). \tag{D.10}$$

Use permutational symmetry on $a_4(U_1,U_1,U_1,U_4;l_{ij},(123))$, the first three equations in (D.8) become

$$\begin{aligned}&\varphi(d_1,d_2,d_3+1)-\varphi(d_3,d_2,d_1+1)\\=&-\varphi(d_1,d_3,d_2+1)+\varphi(d_2,d_3,d_1+1)\\=&\varphi(d_3,d_1,d_2+1)-\varphi(d_2,d_1,d_3+1)\\=&a_4(U_1,U_1,U_1,U_4;d_1,d_2,d_3+c,d_3,d_2+c,d_1+c,(123)),\quad c=\frac{n_4+1-n_1}{2}.\end{aligned}\tag{D.11}$$

The fourth becomes

$$\varphi(d_1,d_2,d_3)+\varphi(d_2,d_3,d_1)+\varphi(d_3,d_1,d_2)=0.\tag{D.12}$$

Our goal is to verify that $\varphi(i,i,d-2i)$ for $3i<d$ give all the linearly independent terms. Use induction on d. When $d=0$, we have $\varphi(0,0,0)=0$. When $d=1$, we have $\varphi(1,0,0)=0$ and $\varphi(0,1,0)=-\varphi(0,0,1)$. So, there is only one linearly independent term $\varphi(0,0,1)$. When $d=2$, we have $\varphi(2,0,0)=\varphi(0,1,1)=0$, and

$$\varphi(0,0,2)-\varphi(1,0,1)=-\varphi(0,1,1)+\varphi(0,1,1)=\varphi(1,0,1)-\varphi(0,0,2).$$

Together with $\varphi(0,2,0)=-\varphi(0,0,2)$, $\varphi(1,1,0)=-\varphi(1,0,1)$, we find that there is only one linearly independent term $\varphi(0,0,2)$.

Now consider $d\geq 3$. The linear relations between φ for $d_i\geq 1$ are identical to the case $d-3$. By the assumption of induction, in these terms the linearly independent ones can be given by $\varphi(i,i,d-2i)$ with $1\leq i<d-2i$. We assume that $\varphi(d_1,d_2,d_3)$ are known for $d_i\geq 1$ and solve those with some $d_i=0$. If two of d_i are zero, the linear relations yield

$$\varphi(d,0,0)=0,\varphi(0,0,d)=-\varphi(0,d,0).$$

Below, we consider ψ with exactly one d_i zero, to show that they can be solved from $\varphi(0,0,d)$ and $\varphi(d_1,d_2,d_3)$ where $d_i\geq 1$.

In (D.11), let $d_3=0$, $d_1+d_2=d-1$, where $1\leq d_1\leq d_2\leq d-2$. Then, the first and third lines give

$$\varphi(0,d_1,d_2+1)+\varphi(0,d_2,d_1+1)=\varphi(d_1,d_2,1)+\varphi(d_2,d_1,1),$$

where the right-hand side is known. Together with $\varphi(0,d_1,d_2)=-\varphi(0,d_2,d_1)$, we can solve $\varphi(0,d_1,d_2)$ for $1\leq d_1,d_2\leq d-1$.

Next, we deal with $\varphi(d_1,0,d_2)$ where $d_1,d_2\geq 1$. Using the second line in (D.11), we obtain

$$\varphi(d_2,0,d_1+1)-\varphi(d_1,0,d_2+1)=\varphi(d_1,d_2,1)-\varphi(0,d_2,d_1+1),\tag{D.13}$$

where the right-hand side is already obtained above. Note that switching d_1 and d_2 leads to the same equation, and $d_1=d_2$ gives nothing. So, we require $0\le d_1<d_2\le d-1$. Here, $d_1=0$ gives $\varphi(0,0,d)=\varphi(d-1,0,1)$. Then, by (D.10) and (D.12), we deduce that

$$\varphi(d_2,0,d_1)=-\varphi(d_1,d_2,0)-\varphi(0,d_1,d_2)=\varphi(d_1,0,d_2)-\varphi(0,d_1,d_2), \tag{D.14}$$

where $1\le d_1<d_2\le d-1$. (D.13) and (D.14) give $d-1$ equations in total for $\varphi(d_1,0,d_2)$ where $d_1,d_2\ge 1$. They can indeed be solved by rewriting the left-hand side of (D.13) as

$$\varphi(d_2,0,d_1+1)-\varphi(d_1,0,d_2+1)=\varphi(d_1+1,0,d_2)-\varphi(d_1,0,d_2+1)-\varphi(0,d_1+1,d_2),$$

leading to

$$\varphi(d_1+1,0,d_2)-\varphi(d_1,0,d_2+1)=\varphi(d_1,d_2,1).$$

Finally, we use $\varphi(d_1,d_2,0)=-\varphi(d_1,0,d_2)$ for $1\le d_1,d_2\le d-1$ to finish the induction.

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