Hamiltonians and order parameters for crystals of orientable molecules

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Abstract

Many modern functional materials exhibit microscopic degrees of freedom that are difficult to describe mathematically or do not conform to conventional models in solid state physics. In this paper, we consider crystals containing orientable molecular species, which encompass the class of promising photovoltaic materials $CH_3NH_3PbX_3$. Abstracting these materials as crystals of orientable rigid rotors, we develop an effective Hamiltonian that expresses the crystal potential energy in terms of collective orientations of interacting rigid rotors. The approach is motivated by the cluster expansion framework from alloy theory and is appropriate for describing both chiral and achiral molecules. This framework utilizes a quaternion parameterization of molecular orientation and makes full use of the symmetry both of the rotors and of the crystal in order to constrain the functional form of the final Hamiltonian expression. The resulting Hamiltonian is compact, systematically improvable, and is suitable for Monte Carlo or molecular dynamics simulation. We apply this formalism to $CH_3NH_3PbI_3$ and report symmetry-adapted basis functions that can be used to construct order parameters or Hamiltonians that describe orientational correlation of methylammonium ions in hybrid organic-inorganic halide perovskite materials.

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I. INTRODUCTION

The properties of many materials depend sensitively on temperature as a result of atomic-scale excitations and disorder.[1–4] Most materials of technological relevance are characterized by configurational disorder due to alloying and many high temperature phases are dynamically stabilized by large anharmonic vibrational excitations[5–9]. Thermal excitations are especially intriguing in molecular crystals (also sometimes called plastic crystals) and in hybrid organic-inorganic crystals where molecular orientational degrees of freedom can become activated. At elevated temperatures, molecular orientational excitations may become large enough to entropically stabilize a high symmetry phase with dynamic orientational disorder, which, upon cooling, either becomes fixed in a statically disordered orientational glass or equilibrates to an orientationally ordered low-symmetry phase.

There is currently much interest in understanding the thermodynamic and electronic properties of molecular crystals due to the exceptional functional properties of hybrid organic/inorganic perovskites[10–18] that have recently led to impressive achievements in adapting them for photovoltaic applications. A unique feature of hybrid perovskites is the presence of molecular interstitial cations, such as $CH_3NH_3^+$, that can rotate within the cuboctahedral interstitial sites of a halide based perovskite host[19–22]. The molecular cations of hybrid perovskites are observed to undergo orientational order-disorder transformations that couple with the structural transitions of the host[23, 24]. In the low temperature orthorhombic phase of $CH_3NH_3PbI_3$, for example, molecular orderings favor an orientationally locked head-to-tail arrangement with rotational fluctuations occurring only along the high symmetry axis of the $CH_3NH_3^+$ ion. In the higher temperature tetragonal and cubic phases, in contrast, the molecules can undergo orientational fluctuations in the orientation of the high symmetry axis, as well as in the rotation of the molecules about its high symmetry axis[25–28].

The molecules of a plastic crystal or within an inorganic host may undergo significant reorientation at elevated temperature, to the point that it may transition between distinct low-energy orientations. In these instances, small-displacement or small-angle approximations (harmonic theories) are inadequate to accurately describe the structural dynamics. To describe large orientational fluctuations, theoretical descriptions must treat all possible orientations on an equal footing. Although approaches based on Heisenberg-like Hamiltonians

have been employed to determine equilibrium molecular orientations, such models can only describe crystals of dimers (or other linear molecules). Analytic descriptions of molecular motion within a plastic crystal or inorganic host must make use of functions of rotational variables that can describe any full rigid-body orientation and that also respect all molecular and crystal symmetries.

In this paper, we extend the cluster expansion methodology[1, 3, 29, 30] to represent the crystal potential energy in terms of the collective orientations of interacting rigid rotors arranged on the sites of a crystal. The resulting model, which we refer to as the *rigid rotor cluster expansion*, fully generalizes classical orientational Hamiltonians to describe interactions due to relative orientations in a crystal of *arbitrary* orientable species in three dimensions, a class that encompasses any molecular species. These orientations are three-dimensional degrees of freedom (which can be expressed as a set of three angles, or as a unit quaternion).

Because the rigid rotor cluster expansion is a Hamiltonian expressed in terms of a unit-quaternion description of molecular orientation, it can be classified as a particular realization of the spin cluster expansion[3] for a four-dimensional spin variable. However, the fact that the unit quaternion 'spin' in the rigid rotor cluster expansion corresponds to the orientation of an arbitrary orientable species is an essential distinction. Unlike a simple spin vector, a $3D$ orientable species can have nontrivial point symmetries, and we demonstrate that these symmetries constrain the functional form of the Hamiltonian in subtle and qualitatively distinct ways that have no analogue in existing lattice models. Moreover, we emphasize that existing lattice models of orientable species (e.g., magnetic spins or dimer molecules), are only suitable for objects whose orientations can be fully specified by a three-component unit vector, having two degrees of freedom that specify the directional alignment of its axis (sometimes defined via the polar and azimuthal angles θ and ϕ).

The general approach consists of constructing a complete set of site basis functions for each oriented rotor as a tensor product comprising one site basis function from each site of the crystal. In the context of a crystal of rigid rotors, the site basis functions take full consideration of point-group symmetries of the molecule, while the crystal basis functions are invariant to all molecular symmetries, as well as all space-group symmetries of the crystal. In this way, the Hamiltonian of a molecular crystal due to molecular orientations can be expanded to arbitrary order in terms of polynomials of rotation parameters for singlets,

pairs, triplets etc. of molecular clusters. Moreover, the generalized rigid rotor Hamiltonians can be parameterized by fitting to first principles calculations, and finite temperature thermodynamic properties are accessible through Monte Carlo simulations. The paper is structured as follows: Sec. II describes important considerations for applying intrinsic point symmetries and global crystal symmetries to molecular orientations, represented either as rotation matrices or as unit a; Sec. III and Sec. IV present the main results of the paper, with Sec. IV describing order parameters and Hamiltonian basis functions for the orientations of the $CH_3NH_3^+$ ions in $CH_3NH_3PbI_3$.

II.   MOLECULAR ROTATION AS A DEGREE OF FREEDOM

We begin by describing molecular orientation mathematically as a microscopic degree of freedom in a crystal of rigid rotors. We consider symmetry properties of the rigid rotors and demonstrate that these give rise to sets of equivalent rotor orientations that are physically indistinguishable. We additionally consider symmetry properties of an entire crystal of rigid rotors and relations describing how these give rise to symmetrically equivalent orientational microstates of the crystal of rigid rotors. We then introduce a compact representation of these symmetry relations using a parameterization of rigid-rotor orientation in terms of unit quaternions.

A.   Symmetry properties of an oriented molecule in free space

The positions of the ions of a molecule can be represented as a $3 \times n$ matrix

$$\mathbf{R} = \left(\vec{r}^{(1)} | \dots | \vec{r}^{(n)} \right), \tag{1}$$

where n is the number of ions in the molecule and each column vector $\vec{r}^{(i)}$ refers to the coordinates of the ith ion of the molecule. It is convenient to express $\mathbf{R}$ as a rotated reference molecule whose geometric center has been translated to a position $\vec{r}$ according to

$$\mathbf{R} = \mathbf{Q}\,\mathbf{m} + \vec{r}\,\mathbf{1}^{(1 \times n)}, \tag{2}$$
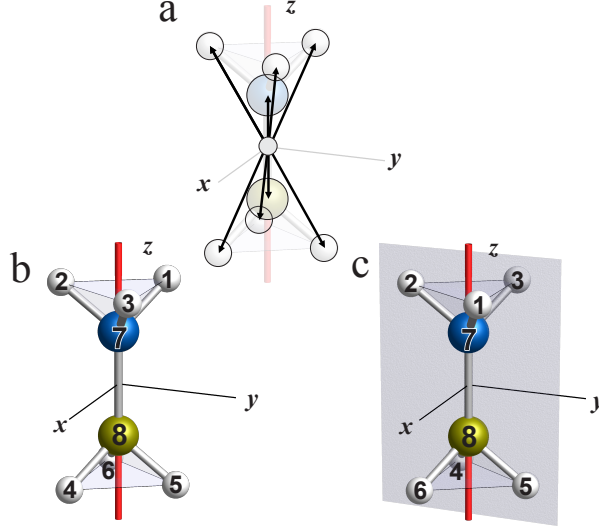
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FIG. 1. Depictions of the $CH_3NH_3^+$ molecular ion referred to in this work. The reference coordinates of the molecule are recorded as columns of the $3 \times n$ matrix $\mathbf{m}$, with the jth column of $\mathbf{m}$ recording the position of the jth atom of the molecule, relative to the geometric center of the molecule, as depicted by the vectors in (a). The numbered atoms in (b) define the orientation and atomic labeling the reference $CH_3NH_3^+$ molecule used throughout this work. (c) The mirror plane normal to x yields a new reference molecule, $\mathbf{m}_\star$, which is indistinguishable from $\mathbf{m}$, but reorders the atomic positions in a way that is inconsistent with a rigid rotation.

The geometric center, $\vec{r}$, is simply the average over the positions of the constituent ions of the molecule, while $\mathbf{1}^{(1 \times n)}$ indicates a $(1 \times n)$ matrix of ones. We refer to the $3 \times n$ matrix $\mathbf{m}$ as the *reference molecule*. Its columns are vectors from the geometric center of the molecule to each ion within the molecule in a particular reference state, as depicted in Figs. 1(a) and (b) for the $CH_3NH_3^+$ molecular ion. The 3×3 rotation matrix $\mathbf{Q}$ then describes any change in orientation of the molecule represented by $\mathbf{R}$ relative to its reference coordinates. $\mathbf{Q}$ is a rotation matrix satisfying $\mathbf{Q}^{-1} = \mathbf{Q}^\top$ and $\det(\mathbf{Q}) = +1$. As such, Eq. (2) indicates that, while the molecule may undergo a change in rigid orientation, it does not deform. A discussion of how this rigidity assumption may be relaxed can be found in Sec. V.

The various symmetries exhibited by a molecule (i.e., rotation, reflection, inversion, and/or rotoinversion) comprise the molecular point group P. A point-group operator $\hat{p}$ belonging to P can be *represented* as either a permutation matrix $\mathbf{W}(\hat{p})$ or a 3×3 orthogonal matrix $\mathbf{S}(\hat{p})$, describing the equivalent transformation of the molecular coordinates according to

$$\hat{p}[\mathbf{m}] = \mathbf{S}(\hat{p})\,\mathbf{m} = \mathbf{m}\,\mathbf{W}(\hat{p})^\top. \tag{3}$$

The permutation matrix, $\mathbf{W}(\hat{p})$, is a $n \times n$ orthogonal matrix consisting of ones and zeros whose transpose permutes the columns of $\mathbf{m}$. As such, Eq. (3) defines the point-group operation $\hat{p}$ as a rigid-body spatial transformation of the molecule that is indistinguishable from a permutation of its atoms.

A point-group operation $\hat{p}$ is classified as either *proper* or *improper*, depending on the sign of its action, defined as $\text{sgn}(\hat{p}) \equiv \det(\mathbf{S}(\hat{p}))$. Proper operations, having $\text{sgn}(\hat{p}) = +1$, comprise rotation operations and the identity operation. Conversely, improper operations, having $\text{sgn}(\hat{p}) = -1$, comprise inversion, reflection, and rotoinversion operations. Where necessary, we use the notation $\hat{p}_\circ$ to specify that an operation is proper and $\hat{p}_\star$ to specify that it is improper. Due to the closure property of P, and the fact that $\text{sgn}(\hat{p}_1 \circ \hat{p}_2) = \text{sgn}(\hat{p}_1)\,\text{sgn}(\hat{p}_2)$, the point group of an achiral molecule contains an equal number of proper and improper operations, with the proper operations, taken together, forming the normal subgroup $P_\circ$.

The distinction between proper and improper point-group operations makes it possible to differentiate between two general classes of molecules. A *chiral* molecule is a molecule whose point group contains only proper operations, while the point group of an *achiral* molecule contains both proper and improper operations. Application of an improper spatial transformation, such as a reflection, to the chiral molecule transforms it into a different enantiomer. A chiral molecule has two distinct enantiomers that cannot be related by any combination of rigid rotation or permutation of atoms [31]. As we shall demonstrate, this distinction has important consequences when applying a symmetry operation of a crystal to a molecule.

An essential trait of chiral molecules is that $\mathbf{m}$ and its inverse $\mathbf{m}_\star = -\mathbf{m}$ represent two entirely distinct reference molecules. We distinguish between these two *enantiomers* via the variable $\chi \in \{-1, +1\}$, with $\chi = -1$ indicating the reference state $\mathbf{m}_\star$ and $\chi = +1$ indicating the reference state $\mathbf{m}$. The equivalent expression to Eq. (2) for the coordinates of a chiral molecule is then

$$\mathbf{R} = \chi\, \mathbf{Q}\, \mathbf{m} + \vec{r}\, \mathbf{1}^{(1 \times n)}, \tag{4}$$

where the selected value of χ specifies which enantiomer serves as the reference molecule.

Equation (3) shows how a molecular point-group operation acts on the molecule in its reference state (relative to which the $\mathbf{S}(\hat{p})$ point-group representations are defined). We

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also seek expressions for the application of symmetry operations to the molecule in an oriented state and, in particular, expressions for the action of a point-group operation on the rotation matrix $\mathbf{Q}$ introduced in Eq. (2). To this end, we first consider the effect of molecular symmetry on an oriented chiral molecule, utilizing the fundamental point-group relations of Eq. (3). In doing so, we emphasize that, as for the ideal molecule, the oriented molecule is indistinguishable under a permutation of its sites. Applying a proper operation to the oriented molecule $\mathbf{R} = \mathbf{Q}\,\mathbf{m}$ yields[32]

$$
\begin{aligned}
\mathbf{R}\,\mathbf{W}(\hat{p}_\circ)^\top &= \mathbf{Q}\,\mathbf{m}\,\mathbf{W}(\hat{p}_\circ)^\top \\
&= \mathbf{Q}\,\mathbf{S}(\hat{p}_\circ)\,\mathbf{m} \\
&= \hat{p}_\circ\,[\mathbf{Q}]\,\mathbf{m},
\end{aligned}
\tag{5}
$$

where

$$
\hat{p}_\circ\,[\mathbf{Q}] = \mathbf{Q}\,\mathbf{S}(\hat{p}_\circ)
\tag{6}
$$

defines the effect of operation $\hat{p}_\circ$ on the orientation $\mathbf{Q}$. This operation amounts to a rotation of the reference molecule by $\mathbf{S}(\hat{p}_\circ)$ *before* applying the arbitrary rotation $\mathbf{Q}$.

Although Equation (6) remains valid for the action of a proper operation on an oriented achiral molecule, the effect of improper operations on the oriented achiral molecule and its rotation matrix $\mathbf{Q}$ requires additional consideration. An improper operation is, by its nature, a discontinuous transformation of the molecule. While a rotation can be thought of as comprising arbitrarily many smaller rotations, applied in succession, a reflection or inversion must happen 'all at once' without visiting any intermediate states. The discontinuous nature of an improper transformation, $\hat{p}_\star$, can be thought of as the composition of a discontinuous transformation, which transforms the molecule to a distinct, 'improper' reference state, followed by a continuous transformation, which rotates the new reference state to its transformed orientation.

By analogy to Eq. (5), the effect of applying an improper point-group operation to an achiral molecule can be expressed as

$$
\mathbf{R}\,\mathbf{W}(\hat{p}_\star)^\top = \mathbf{Q}\,\mathbf{m}\,\mathbf{W}(\hat{p}_\star)^\top
\tag{7}
$$

However, before utilizing Eq. (3), we first express $\hat{p}_\star$ as a product of an improper point-

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group operation $\hat{\mathrm{x}}_\star$ and a 'residual' proper point-group operation $\hat{p}'_\circ$ such that $\mathbf{W}(\hat{p}_\star)^\top = \mathbf{W}(\hat{p}'_\circ)^\top \mathbf{W}(\hat{\mathrm{x}}_\star)^\top$. Inserting this factorization into Eq. (7) and using Eq. (3) allows us to write

$$\mathbf{Q}\,\mathbf{m}\,\mathbf{W}(\hat{p}_\star)^\top = \mathbf{Q}\,\mathbf{S}(\hat{p}'_\circ)\,\mathbf{m}\,\mathbf{W}(\hat{\mathrm{x}}_\star)^\top = \mathbf{Q}\,\mathbf{S}(\hat{p}'_\circ)\,\mathbf{m}_\star, \tag{8}$$

where $\mathbf{m}_\star = \mathbf{m}\,\mathbf{W}(\hat{\mathrm{x}}_\star)^\top$. In this relation, we have ascribed the discontinuous portion of the transformation to a 'canonical' improper operator $\hat{\mathrm{x}}_\star$, which we designate from among the improper operations of P. The residual operation, $\hat{p}'_\circ$, describes a proper rotation of the improper reference molecule $\mathbf{m}_\star$. The effect of an improper point-group operation $\hat{p}_\star$ on $\mathbf{Q}$ can, therefore, be expressed as

$$\hat{p}_\star\,[\mathbf{Q}] = \mathbf{Q}\,\mathbf{S}(\hat{p}'_\circ), \tag{9}$$

with the recognition that the symmetry-transformed rotation matrix acts on the *improper* (but indistinguishable) reference molecule $\mathbf{m}_\star$ instead of $\mathbf{m}$. Illustrations of the proper and improper reference molecules for $CH_3NH_3{}^+$ are given by Figs. 1(b) and (c), which are related by the x-normal mirror plane. Although the depicted molecules appear identical, the labeled sites in Figs. 1(b) and (c) cannot be made to coincide with each other by a proper rotation.

We emphasize that for achiral molecules, $\mathbf{m}_\star$ and $\mathbf{m}$ refer to reference molecules that are indistinguishable from each other up to a permutation of the order in which ionic coordinates appear as columns of their respective coordinate matrices. For an initial orientation, $\mathbf{Q}$, of the proper reference coordinates $\mathbf{m}$, the set of proper point-group operations, which together form the proper subgroup, $P_\circ$, of P, generate a set of orientations that are symmetry-equivalent to $\mathbf{Q}$. This set of equivalent orientations is called the *orbit* of $\mathbf{Q}$. The important consequence of Eq. (8) is that the set of improper operations, $\{\hat{p}_\star \in P\}$, generates an identical orbit of equivalent orientations, but these are of the improper reference coordinates, $\mathbf{m}_\star$. Due to this property, the canonical improper operator, $\hat{\mathrm{x}}_\star$, is quite useful for developing the formalism that follows. In particular, the entire point group of an achiral molecule can be formed by taking the union $P = \{P_\circ, \hat{\mathrm{x}}_\star \circ P_\circ\}$. When it is present in P, the inversion operation is a particularly convenient choice for $\hat{\mathrm{x}}_\star$. For achiral molecules without inversion we designate a reflection or rotoinversion operation to serve as $\hat{\mathrm{x}}_\star$.
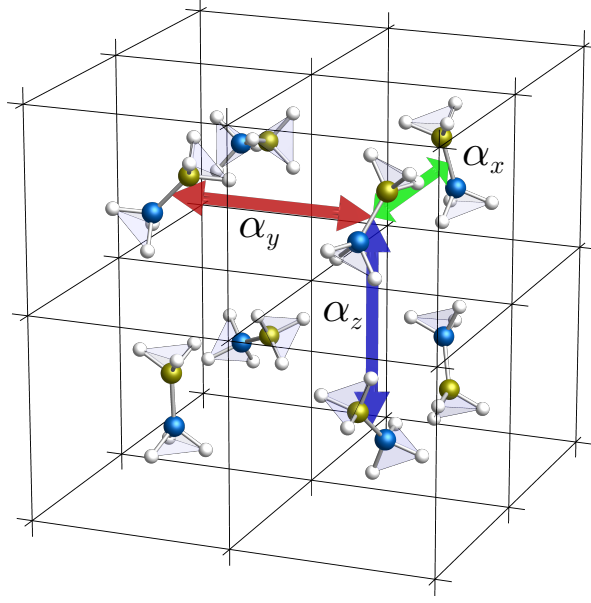
FIG. 2. Illustration of a portion of a crystal of oriented $CH_3NH_3^+$ molecular ions. The geometric centers of the molecules reside on a simple cubic sublattice within the perovskite host (not depicted). Green, red, and blue arrows highlight the x-oriented, y-oriented, and z-oriented nearest-neighbor pair clusters of molecular sites. These three pairs are symmetrically equivalent with respect to the crystal space-group symmetry.

B.   Symmetry properties for a crystal of oriented molecules

We next consider the effect of space-group symmetries of a host crystal applied to oriented molecules residing at well defined sites within the crystal. Such an arrangement is illustrated in Fig. 2 for the lattice of $CH_3NH_3^+$ ions within a $CH_3NH_3PbX_3$ hybrid perovskite. A space-group operation $\hat{s}$ of a crystal acts on a point $\vec{r}$ within the crystal according to

$$\vec{r}\,' = \hat{s}\,[\vec{r}\,] = \mathbf{S}(\hat{s})\vec{r} + \vec{\tau}\,(\hat{s})\,, \tag{10}$$

where $\mathbf{S}(\hat{s})$ and $\vec{\tau}(\hat{s})$ are the orthogonal matrix and translation vector, respectively, that form the Cartesian spatial representation of $\hat{s}$.

The action of a space-group operation on the crystal of oriented molecules alters both the positions and orientations of the molecules within the crystal. A space-group operation $\hat{s}$ that relocates a molecule originally centered at $\vec{r}^{(\eta)}$ to the new position $\vec{r}^{(\nu)}$, also transforms the molecular coordinates according to

$$\mathbf{R}'^{(\nu)} = \mathbf{S}(\hat{s})\mathbf{Q}^{(\eta)}\,\mathbf{m} + \vec{r}^{(\nu)}\,\mathbf{1}^{(1\times n)} \tag{11}$$

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The primed matrix $\mathbf{R}'^{(\nu)}$ in Eq. (11) denotes the molecular coordinates centered at $\vec{r}^{(\nu)}$ after application of operation $\hat{s}$ to the crystal. Because application of $\hat{s}$ to the crystal takes the molecule originally at position $\vec{r}^{(\eta)}$ to position $\vec{r}^{(\nu)}$, the molecular coordinates at site ν after transformation depend explicitly on the orientation state of the molecule that was previously at site η. Using the shorthand notation $\nu = \hat{s}[\eta]$ and $\eta = \hat{s}^{-1}[\nu]$ for the effect of a space-group operation on the crystal site indices, we can rewrite Eq. (11) more formally as

$$\mathbf{R}'^{(\nu)} = \hat{s}\left[\mathbf{R}^{(\nu)}\right] = \mathbf{S}(\hat{s})\mathbf{Q}^{\left(\hat{s}^{-1}[\nu]\right)}\mathbf{m} + \vec{r}^{(\nu)}\mathbf{1}^{(1\times n)}. \tag{12}$$

The unprimed matrix $\mathbf{R}^{(\nu)}$ denotes the molecular coordinates before the application of $\hat{s}$.

In conjunction with a space-group operation, we can also apply a molecular point-group operation $\hat{p}$ to the oriented molecule. The resultant molecular coordinates transform as

$$\mathbf{R}'^{(\nu)} = \mathbf{S}(\hat{s})\,\mathbf{Q}^{(\eta)}\,\mathbf{m}\,\mathbf{W}(\hat{p})^{\top} + \vec{r}^{(\nu)}\mathbf{1}^{(1\times n)} \tag{13}$$

where we have used the permutation representation $\mathbf{W}(\hat{p})$ of the molecular point-group operation.

Equation (13) establishes how a space-group operation and a molecular point-group operation together transform the molecular coordinates $\mathbf{R}^{(\eta)}$ and geometric centers $\vec{r}^{(\eta)}$. By considering Eq. (13), we will construct transformation rules for the molecular orientation under concurrent application of a space-group and molecular point-group operation. These relations will depend on the proper-vs-improper nature of both the point-group and space-group operations and also, therefore, on the chiral nature of the molecule. We shall proceed by establishing how such operations act on the molecular orientation $\mathbf{Q}^{(\eta)}$ in each possible scenario.

1. *Chiral molecules*

First we consider the simplest case of chiral molecules in a host crystal that possesses no improper space-group operations. Starting with Eq. (13) and using Eq. (3) we can express the action of a total crystal operation $\hat{g}$ (i.e. a combination of a space-group operation, $\hat{s}$,

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with molecular point-group operations, $\hat{p}$) on the coordinates of an individual molecule as

$$\mathbf{R}'^{(\nu)} = \hat{g}\left[\mathbf{R}^{(\nu)}\right] = \mathbf{S}(\hat{s})\,\mathbf{Q}^{(\eta)}\,\mathbf{S}(\hat{p})\,\mathbf{m} + \vec{r}^{\,(\nu)}\,\mathbf{1}^{(1\times n)}, \tag{14}$$

where again $\eta = \hat{s}^{-1}[\nu]$. Since $\mathbf{R}'^{(\nu)}$ can also be written as

$$\mathbf{R}'^{(\nu)} = \mathbf{Q}'^{(\nu)}\,\mathbf{m} + \vec{r}^{\,(\nu)}\,\mathbf{1}^{(1\times n)}, \tag{15}$$

we can infer by comparing the two relations that the effect of $\hat{g}$ on $\mathbf{Q}^{(\nu)}$ takes the form

$$\mathbf{Q}'^{(\nu)} = \hat{g}\left[\mathbf{Q}^{(\nu)}\right] = \mathbf{S}(\hat{s})\,\mathbf{Q}^{(\eta)}\,\mathbf{S}(\hat{p}). \tag{16}$$

This relation can be interpreted as a rotation by $\mathbf{S}(\hat{p})$ before, and a rotation by $\mathbf{S}(\hat{s})$ after, the application of the orientational transformation $\mathbf{Q}^{(\eta)}$.

When the crystal hosting chiral molecules has both proper and improper space-group operations, it is necessary to explicitly consider the effect of symmetry on the chirality variables $\chi^{(\nu)}$ introduced in Eq. (4). Indeed, the application of an improper space-group operation to a chiral molecule will switch it to its enantiomer. As such, in addition to an improper space-group operation acting on $\mathbf{Q}^{(\nu)}$, it also acts on the chirality variable $\chi^{(\nu)}$ according to

$$\hat{g}\left[\chi^{(\nu)}\right] = \operatorname{sgn}(\hat{s})\,\chi^{(\eta)}, \tag{17}$$

where the value $\operatorname{sgn}(\hat{s}) = \pm 1$, as before, indicates whether $\hat{s}$ is proper or improper. The transformation rule for the orientation of the chiral molecule is thus

$$\hat{g}\left[\mathbf{Q}^{(\nu)}\right] = \tilde{\mathbf{S}}(\hat{s})\,\mathbf{Q}^{(\eta)}\,\mathbf{S}(\hat{p}), \tag{18}$$

where $\tilde{\mathbf{S}}(\hat{s}) = \operatorname{sgn}(\hat{s})\,\mathbf{S}(\hat{s})$ is a proper rotation.

2. Achiral molecules

Application of symmetry to the orientations, $\mathbf{Q}^{(\nu)}$, of achiral molecules in a crystal having both proper and improper space-group operations is more subtle than for chiral molecules in a crystal. Equation (16) remains valid for achiral molecules when applying a proper space-

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group operation of the crystal. The application of an improper space-group or improper molecular point-group operation to an achiral molecule, however, will result in molecular coordinates $\mathbf{R}'^{(\nu)}$ that are not a rigid re-orientation of the original reference molecule $\mathbf{m}$. Instead, the transformed coordinates must be mapped onto the improper reference molecule $\mathbf{m}_\star = \mathbf{m}\,\mathbf{W}(\hat{x}_\star)^\top$. As an example, the application of an improper molecular point-group operation, $\hat{p}_\star$, concurrently with a proper space-group operation, $\hat{s}_\circ$, is given by

$$\mathbf{R}'^{(\nu)} = \mathbf{S}(\hat{s}_\circ)\,\mathbf{Q}^{(\eta)}\,\mathbf{S}(\hat{p}'_\circ)\,\mathbf{m}\,\mathbf{W}(\hat{x}_\star)^\top + \vec{r}^{(\nu)}\,\mathbf{1}^{(1\times n)}, \tag{19}$$

where, as before, we use the canonical improper operator $\hat{x}_\star$ to write $\hat{p}_\star = \hat{p}'_\circ \circ \hat{x}_\star$. With $\mathbf{m}_\star = \mathbf{m}\,\mathbf{W}(\hat{x}_\star)^\top$, Eq. (19) can also be expressed as

$$\mathbf{R}'^{(\nu)} = \mathbf{Q}'^{(\nu)}\,\mathbf{m}_\star + \vec{r}^{(\nu)}\,\mathbf{1}^{(1\times n)}, \tag{20}$$

provided

$$\mathbf{Q}'^{(\nu)} = \hat{g}\left[\mathbf{Q}^{(\nu)}\right] = \mathbf{S}(\hat{s}_\circ)\,\mathbf{Q}^{(\eta)}\,\mathbf{S}(\hat{p}'_\circ). \tag{21}$$

The transformed orientation, $\mathbf{Q}'^{(\nu)}$, however, now acts on the improper reference molecule $\mathbf{m}_\star$.

The application of an improper space-group operation, $\hat{s}_\star$, with an improper molecular point-group operation, $\hat{p}_\star$, also requires special attention. We again rely on the canonical improper operator to factor the improper point-group operation as $\hat{p}_\star = \hat{x}_\star \circ \hat{p}''_\circ$. Using Eq. (3), the effect of both operations on $\mathbf{R}^{(\nu)}$ can be written as

$$\mathbf{R}'^{(\nu)} = \mathbf{S}(\hat{s}_\star)\,\mathbf{Q}^{(\eta)}\,\mathbf{S}(\hat{x}_\star)\,\mathbf{S}(\hat{p}''_\circ)\,\mathbf{m} + \vec{r}^{(\nu)}\,\mathbf{1}^{(1\times n)}, \tag{22}$$

such that

$$\mathbf{Q}'^{(\nu)} = \hat{g}\left[\mathbf{Q}^{(\nu)}\right] = \mathbf{S}(\hat{s}_\star)\,\mathbf{Q}^{(\eta)}\,\mathbf{S}(\hat{x}_\star)\,\mathbf{S}(\hat{p}''_\circ). \tag{23}$$

Expressed in this form, it is evident that $\mathbf{Q}'^{(\nu)}$ is a proper rotation matrix and therefore acts on the original molecular reference $\mathbf{m}$. This can be verified via the mathematical equivalence

$$\mathbf{S}(\hat{s}_\star)\,\mathbf{Q}^{(\eta)}\,\mathbf{S}(\hat{x}_\star) = \tilde{\mathbf{S}}(\hat{s}_\star)\,\mathbf{Q}^{(\eta)}\,\tilde{\mathbf{S}}(\hat{x}_\star), \tag{24}$$

where the notation $\tilde{\mathbf{S}}(\hat{s}_\star)$ denotes the proper rotation $\tilde{\mathbf{S}}(\hat{s}_\star) = -\mathbf{S}(\hat{s}_\star)$.

The final symmetry transformation to consider for an achiral molecule is that of an improper space-group operation, $\hat{s}_\star$, applied in conjunction with a proper molecular point-group operation $\hat{p}_\circ$. Utilizing the decomposition $\hat{p}_\circ = \hat{x}_\star^{-1} \hat{p}_\circ''' \circ \hat{x}_\star$, this transformation of $\mathbf{R}^{(\nu)}$ becomes

$$\mathbf{R}'^{(\nu)} = \mathbf{S}(\hat{s}_\star)\, \mathbf{Q}^{(\eta)}\, \mathbf{S}(\hat{x}_\star^{-1})\, \mathbf{S}(\hat{p}_\circ''')\, \mathbf{m}\, \mathbf{W}(\hat{x}_\star)^\top + \vec{r}^{\,(\nu)}\, \mathbf{1}^{(1\times n)}. \tag{25}$$

Recognizing, as before, that $\mathbf{m}_\star = \mathbf{m}\mathbf{W}(\hat{x}_\star)^\top$, it is evident that Eq. (25) thus acts on the improper reference molecule, $\mathbf{m}_\star$, and that the transformed molecular orientation is

$$\mathbf{Q}'^{(\nu)} = \hat{g}\left[\mathbf{Q}^{(\nu)}\right] = \mathbf{S}(\hat{s}_\star)\, \mathbf{Q}^{(\eta)}\, \mathbf{S}(\hat{x}_\star^{-1})\, \mathbf{S}(\hat{p}_\circ'''), \tag{26}$$

which is a proper rotation matrix.

C. The total crystal rotor group

Application of a space-group operation of the host crystal (i.e. without molecules) to the same crystal containing an arrangement of oriented molecules generates a distinct, but symmetrically equivalent, arrangement of oriented molecules. Rotationally-invariant properties of the crystal, such as the total energy, are therefore be identical for both arrangements. Similarly, scalar properties of the crystal will be unaffected when applying molecular point-group operations to one or more of the molecules in the crystal in conjunction with a space-group operation. A Hamiltonian of the crystal should thus predict the same energy for all molecular orientations that are equivalent due to molecular or crystal symmetries. As such, we proceed by finding the collection of symmetry operations that, given an arrangement of oriented molecules, generates all symmetrically equivalent arrangements.

The most general symmetry operation of a crystal of oriented molecules consists of a space-group operation applied to the entire crystal, composed with any combination of molecular point-group operations applied to the individual molecules. We specify this composite operation as $\hat{g} = \left(\hat{s}, \hat{p}^{(1)}, \ldots, \hat{p}^{(\nu)}, \ldots, \hat{p}^{(N)}\right)$, which is an ordered tuple formed by one space-group operation $\hat{s}$ of the crystal and one point-group operation $\hat{p}^{(\nu)}$ of each molecule ν[33]. The set of all possible operators $\hat{g}$ form the total crystal rotor group, G. By convention, we apply an operator $\hat{g}$ by first applying its constituent point-group operations to

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the molecules, followed by applying the space-group operation to the crystal and molecules together. Given this convention, the total group is closed under both composition and inversion of its elements, according to the relations

$$\hat{g}_2 \circ \hat{g}_1 = \left(\hat{s}_2 \circ \hat{s}_1, \hat{p}_2^{\hat{s}_1[1]} \circ \hat{p}_1^{(1)}, \ldots, \hat{p}_2^{\hat{s}_1[N]} \circ \hat{p}_1^{(N)} \right). \tag{27}$$

and

$$\hat{g}^{-1} = \left(\hat{s}^{-1}, \hat{p}^{\left(\hat{s}^{-1}[1]\right)-1}, \ldots, \hat{p}^{\left(\hat{s}^{-1}[N]\right)-1} \right), \tag{28}$$

respectively. These relations account for both the permutation of molecules due to the space-group operations and composition of the constituent point-group operations.

Based on the symmetry relations developed in Sec. II B, it is sufficient to consider only operations in the *fully proper* total rotor group, $G_\circ$, for a crystal containing only achiral molecules. A fully proper total rotor group operation consists of either a proper space-group operation composed with only proper molecular point-group operations, or an improper space-group operation composed with only improper molecular point-group operations. Any partially or fully improper total rotor group operation will convert the reference molecule of one or more molecules to its improper reference, $\mathbf{m}_\star$; however, its effect on the combined molecular orientations will be identical to exactly one element of $G_\circ$.

Motivated by this observation, we partition the fully proper total rotor group as $G_\circ = A \otimes P_\circ^{(1)} \otimes \cdots \otimes P_\circ^{(N)}$, where A is the *augmented space group*. Each element $\hat{a}$ of A is associated with a space-group element: an augmented operation is defined as

$$\hat{a} \equiv (\hat{s}_\circ, \hat{e}, \ldots, \hat{e}) \tag{29}$$

for a proper space-group operation $\hat{s}_\circ$, where the identity elements, $\hat{e}$, act on each molecule individually, and as

$$\hat{a} \equiv (\hat{s}_\star, \hat{x}_\star, \ldots, \hat{x}_\star), \tag{30}$$

where the canonical improper operators, $\hat{x}_\star$ act on each molecule individually. This partition is a natural generalization of the partition of the point group of an individual achiral molecule, described in Sec. II A, based on the canonical improper operator.

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D. Expressing molecular orientation in terms of unit quaternions

Expressing functions of the molecular orientation $\mathbf{Q}^{(\nu)}$ is complicated by the fact that, while a rotation matrix consists of nine entries, its degrees of freedom are restricted by the constraints that it be orthogonal (i.e., $\mathbf{Q}^{(\nu)\top}\mathbf{Q}^{(\nu)} = \mathbf{I}$) and preserve handedness (i.e., $\det \mathbf{Q}^{(\nu)\top} = +1$). These constraints reduce the number of degrees of freedom to three, which are analogous to the three Euler angles.

An alternative interpretation of the rotation matrix, due to Euler's rotation theorem, is that it encodes a rotation axis (represented by a three-dimensional unit vector $\hat{u}$) and a rotation angle θ about that axis[34]. This interpretation allows a powerful correspondence between the rigid-body rotation $\mathbf{Q}$ and the four-dimensional vector

$$\vec{q}(\mathbf{Q}) = \left[\cos\left(\frac{\theta}{2}\right), u_x \sin\left(\frac{\theta}{2}\right), u_y \sin\left(\frac{\theta}{2}\right), u_z \sin\left(\frac{\theta}{2}\right)\right]^\top, \tag{31}$$

which satisfies the constraint $q_1^2 + q_2^2 + q_3^2 + q_4^2 = 1$, indicating that $\vec{q}$ describes a point on the three-dimensional spherical surface of a four-dimensional unit ball.

The unit quaternion parameterization of molecular rotations exhibits several mathematical conveniences that facilitate our development of the rigid rotor cluster expansion. A brief overview of these properties is provided in App. C. A particular advantage of the unit quaternion parameterization is that a composite rotation such as $\mathbf{Q}' = \mathbf{Q}_3\,\mathbf{Q}_2\,\mathbf{Q}_1$, when written in terms of quaternions, can be expressed as either $\mathbf{Q}' = \mathbf{M}^{(L)}(\mathbf{Q}_3)\,\mathbf{M}^{(R)}(\mathbf{Q}_1)\,\vec{q}(\mathbf{Q}_2)$ or $\mathbf{Q}' = \mathbf{M}^{(R)}(\mathbf{Q}_1)\,\mathbf{M}^{(L)}(\mathbf{Q}_3)\,\vec{q}(\mathbf{Q}_2)$, where $\vec{q}(\mathbf{Q}_2)$ is the unit quaternion corresponding to $\mathbf{Q}_2$, $\mathbf{M}^{(L)}(\mathbf{Q}_3)$ is a 4×4 transformation matrix describing left-sided application of $\mathbf{Q}_3$, and $\mathbf{M}^{(R)}(\mathbf{Q}_1)$ is a 4×4 transformation matrix describing right-sided application of $\mathbf{Q}_1$. Because $\mathbf{M}^{(R)}(\mathbf{Q}_1)$ and $\mathbf{M}^{(L)}(\mathbf{Q}_3)$ are commuting matrices, the unit quaternion parameterization of rotation removes any ambiguity in how pre-rotation symmetries (i.e., arising from the molecular point group) and post-rotation symmetries (i.e., arising from the crystal space group) should behave when considered simultaneously. The utilization of this property to describe the action of symmetries on the quaternion $\vec{q}^{(\nu)}$, which describes the orientation of a particular molecule in the crystal, is given in App. B. In particular, the transformation rule due to application of the total crystal operation $\hat{g}_\circ$, which acts on $\vec{q}^{(\nu)}$ via post-rotation by space-group operation $\hat{s}_\circ$ and pre-rotation by molecular point-group operation $\hat{p}_\circ^{(\nu)}$, is

expressed as the single quaternion transformation

$$\hat{g}_\circ\left[\vec{q}^{(\nu)}\right] = \mathbf{M}^{(L)}(\hat{s}_\circ)\,\mathbf{M}^{(R)}\big(\hat{p}_\circ^{(\eta)}\big)\,\vec{q}^{(\eta)}. \tag{32}$$

Note that, as before, ν and η are related via $\eta = \hat{s}^{-1}[\nu]$.

III.   HAMILTONIANS FOR CRYSTALS OF RIGID ROTORS

In this section, we develop a generalized effective Hamiltonian for interacting rigid rotors occupying sites of a crystal in terms of the unit quaternions $\{\vec{q}^{(\nu)}\}$ describing the orientation of the rotor at each site ν:

$$H = H\left(\vec{q}^{(1)}, \ldots, \vec{q}^{(\nu)}, \ldots, \vec{q}^{(N)}\right) \tag{33}$$

We follow the cluster expansion approach first introduced by Sanchez *et al.* [1, 29, 30] for configurational alloy Hamiltonians, adapting it to systematically construct a complete and orthonormal set of crystal basis functions with which to expand any property of the crystal that depends on molecular orientational degrees of freedom. A key ingredient of this approach is the exploitation of symmetry to simplify and minimize the number of expansion coefficients.

The first step of this procedure is to identify a set of site basis functions $\{\varphi_b(\vec{q}^{(\nu)})\}$ that only depend on the orientational degree of freedom, $\vec{q}^{(\nu)}$, at a particular site ν. Site basis functions should form a complete and orthogonal basis set in which to represent any function of the single-site molecular orientation $\vec{q}^{(\nu)}$. Since a molecular orientation is a continuous degree of freedom, infinitely many functions are necessary to form a complete site basis set.

The unit quaternions correspond to points on the unit 3-sphere (i.e., the three-dimensional surface of a four-dimensional unit ball). A set of basis functions that are orthogonal on the surface of the unit 3-sphere are the hyperspherical harmonics, which are four-dimensional analogues of the spherical harmonics in three dimensions[35]. Following this analogy, we distinguish the hyperspherical harmonics $X_l^m(\vec{q})$ by their degree l and their order m, with m taking an integer value between 0 and $l(l+2)$, inclusive. The degree l is simply the polynomial degree of the function, in terms of the elements of $\vec{q}$, while m is used here simply to distinguish functions of the same degree.[36] Any function, f, that only depends

on a particular $\vec{q}^{(\nu)}$ can then be expanded in terms of the hyperspherical harmonic basis functions according to

$$f\left(\vec{q}^{(\nu)}\right) = \sum_{l=0}^{\infty} \sum_{m=0}^{l(l+2)} \kappa_{l,m} X_l^m \left(\vec{q}^{(\nu)}\right), \tag{34}$$

where the $\kappa_{l,m}$ are constant expansion coefficients. For practical applications, the expansion is truncated above some maximum harmonic degree L. The harmonic functions $X_l^m \left(\vec{q}^{(\nu)}\right)$ serve as the local *site basis set* of the orientation of the molecule at site ν. An important property of the hyperspherical harmonics is that the first harmonic, which is of degree zero ($l = 0$), is $X_0^0(\vec{q}^{(\nu)}) = 1$.

Only hyperspherical harmonics with even l are needed to describe any property that depends on the orientation of a particular molecule. Each Cartesian rotation matrix can be represented as either $\vec{q}$ or $-\vec{q}$, which differ only by the addition of a phase angle of 2π to the rotation angle θ, according to Eq. (31). As such, any function $f(\vec{q})$ of a unit quaternion $\vec{q}$ must be even-ordered [i.e., $f(\vec{q}) = f(-\vec{q})$] if $\vec{q}$ is meant to correspond to the orientation of a rigid body. This constraint is satisfied in Eq. (34) if $\kappa_{l,m} = 0$ when l is odd such that the site basis set only needs to consist of even-degree hyperspherical harmonic functions.

Having specified an appropriate site basis at each site of the crystal, it becomes possible to construct crystal basis functions $\{\Phi_{\vec{b}}\left(\ldots, \vec{q}^{(\nu)}, \ldots, \right)\}$ via a tensor product over all M sites in the crystal. Denoting the site basis functions at site ν as $\varphi_b\left(\vec{q}^{(\nu)}\right)$, specified by the single index b, the crystal basis functions can be expressed as

$$\Phi_{\vec{b}}\left(\ldots, \vec{q}^{(\nu)}, \ldots\right) = \prod_{\nu=1}^{M} \varphi_{b_\nu}\left(\vec{q}^{(\nu)}\right). \tag{35}$$

In practice, the $\varphi_{b_\nu}\left(\vec{q}^{(\nu)}\right)$ correspond to the hyperspherical harmonics $X_l^m\left(\vec{q}^{(\nu)}\right)$, sorted in increasing polynomial order (i.e. $b_\nu = 0$ corresponds to $l=0$ and $m = 0$). The *crystal basis functions* of Eq. (35) are products composed of exactly one site basis function from each molecule of the crystal. The labels associated with the constituent site basis functions comprise the N-element vector $\vec{b}$ with each element b_ν specifying the site basis function from site ν that is included in the product of Eq. (35). It can be shown[3, 29] that if the site basis functions are complete and orthonormal, then the crystal basis functions defined in Eq. (35) also form a complete and orthonormal basis over the domain of all orientational microstates of the crystal. Hence any function that depends on the molecular orientations

in the crystal, such as the formation energy, can be expressed as a linear combination of these basis functions, as

$$H\left(\ldots,\vec{q}^{(\nu)},\ldots\right) = \sum_{\vec{b}} V_{\vec{b}}\, \Phi_{\vec{b}}\left(\ldots,\vec{q}^{(\nu)},\ldots\right). \tag{36}$$

The fact that we have defined $\varphi_0\left(\vec{q}^{(\nu)}\right) = 1$ enables a dramatic simplification of low-order crystal basis functions. For a low-order crystal function $\Phi_{\vec{b}}$ defined by Eq. (35), many terms in the product correspond to the unit basis function [i.e., $b_\nu = 0$ and thus $\varphi_{b_\nu}(\vec{q}^{(\nu)}) = 1$]. In the simplest case all elements of the label $\vec{b}$ are zero, resulting in a crystal basis function, $\Phi_{\vec{0}}\left(\ldots,\vec{q}^{(\nu)},\ldots\right) = 1$, that coincides with the constant unit function. Other examples of simple crystal functions occur when only a single element of $\vec{b}$ is nonzero, leading to $\Phi_{\vec{b}}\left(\ldots,\vec{q}^{(\nu)},\ldots\right) = \varphi_{b_\nu}\left(\vec{q}^{(\nu)}\right)$, for a particular site ν. When two elements of $\vec{b}$ are nonzero, the crystal basis function takes the form $\Phi_{\vec{b}}\left(\ldots,\vec{q}^{(\nu)},\ldots\right) = \varphi_{b_\nu}\left(\vec{q}^{(\nu)}\right)\varphi_{b_\eta}\left(\vec{q}^{(\eta)}\right)$ and can be viewed as a basis function associated with a pair cluster of sites $\{\nu,\eta\}$. Figure 2 depicts three nearest-neighbor pair clusters of $CH_3NH_3^+$ ions in a hybrid perovskite crystal.

By considering increasingly more complex basis functions in this fashion, we associate each crystal basis function with a *cluster* of sites, denoted $\alpha\left(\vec{b}\right)$, which are sites of the crystal corresponding to nonzero elements of the indexing vector $\vec{b}$. In terms of the cluster $\alpha\left(\vec{b}\right)$, we can write the tensor product of Eq. (35) equivalently as

$$\Phi_{\vec{b}}\left(\ldots,\vec{q}^{(\nu)},\ldots\right) = \prod_{i\in\alpha(\vec{b})} \varphi_{b_i}\left(\vec{q}^{(i)}\right), \tag{37}$$

where the product is only over the sites belonging to the cluster $\alpha\left(\vec{b}\right)$. In this way, the crystal basis functions can be categorized first by a cluster of sites, $\alpha\left(\vec{b}\right)$, and then by the particular site basis functions $\varphi_{b_i}\left(\vec{q}^{(i)}\right)$ associated with those sites of the cluster.

A. Symmetry invariance of crystal basis functions

The Hamiltonian of Eq. (36) must evaluate to the same value for any two microstates of molecular orientations, $\{\ldots,\vec{q}^{(\nu)},\ldots\}$ and $\{\ldots,\vec{q}'^{(\nu)},\ldots\}$, that map onto each other by an operation in the total crystal rotor group. The total crystal rotor group must therefore

impose constraints on the expansion coefficients, $\{V_{\vec{b}}\}$, of Eq. (36). The space of symmetry-allowed scalar functions of the orientational degrees of freedom resides in a subspace of the full space spanned by $\{\Phi_{\vec{b}}\}$. One approach to enforcing the invariance of the Hamiltonian Eq. (36) to the total crystal rotor group is to construct a set of invariant basis functions $\{\tilde{\Phi}_{\vec{b}}\}$ that span the symmetry-allowed subspace of $\{\Phi_{\vec{b}}\}$. A well established procedure for constructing such symmetry invariant basis functions is to apply the Reynold's operator to each basis function $\{\Phi_{\vec{b}}\}$.[37–39] In the present context, the Reynold's operator is defined as an average over the group action of all operations in the total crystal rotor group G according to

$$\hat{\mathcal{R}}^{(G)}[F] = \frac{1}{|G|} \sum_{\hat{g} \in G} \hat{g}[F], \tag{38}$$

where $|G|$ denotes the *order* of G (i.e., the number of elements in the group), and F is an arbitrary function of the crystal microstate. If we consider an arbitrary function F as being composed of a symmetry-invariant component $F^{(sym)}$ and a residual component $F^{(nonsym)}$, such that $F = F^{(sym)} + F^{(nonsym)}$, then the Reynold's operator performs the projection $F^{(sym)} = \hat{\mathcal{R}}^{(G)}\left[F^{(sym)}\right] = \hat{\mathcal{R}}^{(G)}[F]$.

We shall focus on the case of a crystal possessing improper symmetries and containing achiral molecules. As described in Sec. II B, it is sufficient in this situation to consider only the fully proper subgroup, $G_\circ$, of the total crystal rotor group. Application of $\hat{\mathcal{R}}^{(G_\circ)}$ to a particular $\Phi_{\vec{b}}$ of the form in Eq. (35) can be expanded as the nested sum

$$\Phi_{\vec{b}}^{(sym)} = \frac{1}{|G_\circ|} \sum_{\hat{a} \in A} \sum_{\hat{p}^{(1)} \in P_\circ^{(1)}} \cdots \sum_{\hat{p}^{(N)} \in P_\circ^{(N)}} \hat{a}\left[\Phi_{\vec{b}}\left(\ldots, \hat{p}^{(\nu)-1}\left[\vec{q}^{(\nu)}\right], \ldots\right)\right], \tag{39}$$

which utilizes the augmented space-group operation, $\hat{a}$, defined in Sec. II C. From the nested sum expressed in Eq. (39), it is apparent that each internal sum running over the proper point group of each molecule ν is independent of the particular operation $\hat{a}$ operating in the outer sum over the augmented space group A. Employing the simple associative identity $\sum_i \sum_j f_i g_j = \left(\sum_i f_i\right)\left(\sum_j g_j\right)$, Eq. (39) is equivalent to

$$\Phi_{\vec{b}}^{(sym)} = \frac{1}{|A|} \sum_{\hat{a} \in A} \hat{a}\left[\prod_{(\nu)} \hat{\mathcal{R}}^{\left(P_\circ^{(\nu)}\right)}\left[\varphi_{b_\nu}\left(\vec{q}^{(\nu)}\right)\right]\right], \tag{40}$$

which reveals the important result that each site basis function $\varphi_{b_\nu}\left(\vec{q}^{(\nu)}\right)$ can be symmetrized with respect to the proper point group $P_\circ^{(\nu)}$ independently of the other site basis functions or any crystal basis function to which it contributes. Denoting these symmetry-invariant functions as $\{\tilde{\varphi}_b\}$, $\Phi_{\vec{b}}^{(sym)}$ becomes

$$\tilde{\Phi}_{\vec{b}}^{(sym)} = \frac{1}{|A|} \sum_{\hat{a} \in A} \prod_{\nu=1}^{N} \hat{a} \left[\tilde{\varphi}_{b_\nu} \left(\vec{q}^{(\nu)} \right) \right] . \tag{41}$$

Thus, once the $\{\tilde{\varphi}_b\}$ have been constructed, we no longer need to explicitly consider molecular point-group symmetries.

The sum in Eq. (41) over all $\hat{a}$ belonging to the augmented space group, A, can proceed in two steps. As described in the lead up to Eq. (37), each unsymmeterized starting crystal basis function corresponds to the product of site basis functions belonging to sites of a cluster α. It proves convenient to factor the symmetry operations $\hat{a}$ into those symmetry operations that map α onto itself and those that map the cluster onto symmetrically equivalent clusters β within the crystal. As an example, the three different nearest-neighbor pairs highlighted in Fig. 2 have distinct orientations, but all three are equivalent with respect to the space-group of the crystal. This procedure is described in more detail in App. C.

Finally, we stress that when the Reynolds operator is applied to a set of unsymmetrized basis functions, either for a molecule or the entire crystal, the resulting symmetrized functions nearly always span a subspace of much lower dimension than the starting basis set. As such, an orthogonalization procedure should be performed after symmetrization to ensure that there are no linear dependencies among the symmetrized basis functions. The details of this orthogonalization can be found elsewhere[39, 40].

B. Considerations for chiral rotors

The Hamiltonian of a crystal containing the two enantiomers of a chiral molecule depends not only on the orientational degrees of freedom, $\vec{q}^{(\nu)}$, but also on the chirality variables $\chi^{(\nu)}$, introduced in Sec. II A, which take a value of $+1$ when the 'A-type' enantiomer is present and -1 when the 'B-type' enantiomer is present. The chirality variable, $\chi^{(\nu)}$, serves a similar role as an Ising occupation variable for a binary alloy, with A- and B-type enantiomers playing the role of the A and B alloy species. The site basis functions $\varphi_0^{(\nu)}(\chi^{(\nu)}) = 1$ and
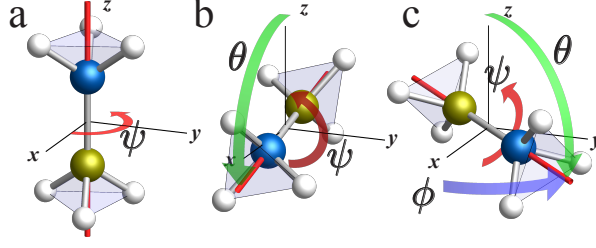
FIG. 3. Illustration of the effect of the three Euler angles $(\psi, \theta \phi)$ on the reference molecule depicted in Fig. 1. (a) The primary Euler angle, ψ, is about the z axis, (b) the second Euler angle, θ, is about the y axis, (c) and the final Euler angle, ϕ, is about the z axis once again.

$\varphi_1^{(\nu)}(\chi^{(\nu)}) = \chi^{(\nu)}$ together form a complete basis with which to describe any function that depends only on site occupation (i.e. whether the site is occupied by the 'A-type' enantiomer or the the 'B-type' enantiomer). A function that depends on both enantiomer occupation and enantiomer orientation can be written as a linear combination of basis functions formed as the tensor product of the occupational basis set $\{1, \chi^{(\nu)}\}$ with the orientational basis set $\{\varphi_{b_\nu}(\vec{q}^{(\nu)})\}$, expressed in terms of the quaternion orientation $\vec{q}^{(\nu)}$. The resulting set of functions $\{\varphi_{b_\nu}(\vec{q}^{(\nu)}), \chi^{(\nu)}\varphi_{b_\nu}(\vec{q}^{(\nu)})\}$ constitutes a complete basis set with respect to the orientation (represented as a proper rotation) and chirality of a single chiral molecule.

As in the case of the achiral molecule, crystal basis functions can be constructed within the cluster expansion formalism, by forming tensor products of the site basis sets for progressively larger and more complex clusters. The crystal basis functions may then be symmetrized as described in the previous section for a crystal of achiral molecules, using the symmetry representation in App. II D. In the case of the chiral molecule, we must consider the full total crystal rotor group, G, including all improper operations, if they exist.

IV. APPLICATION TO CH$_3$NH$_3$PBI$_3$

As an illustration, we develop a rigid rotor cluster expansion Hamiltonian for the hybrid organic–inorganic CH$_3$NH$_3$PbX$_3$ perovskite. The CH$_3$NH$_3$PbX$_3$ perovskite is a very promising materials for photovoltaic energy conversion that consists of an inorganic lead-halide perovskite structure containing CH$_3$NH$_3{}^+$ molecular ions at its octahedral sites[19–22]. While the idealized perovskite host crystal has cubic space-group symmetry ($Pm\bar{3}m$) at elevated temperature[41], the methylammonium ions have C_{3v} trigonal point symmetry. This, coupled with the fact that the methylammonium ions dynamically reorient within the crystal at

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elevated temperature[23, 24, 26], make it a fascinating and technologically important case study. There is one $CH_3NH_3^+$ ion per $CH_3NH_3PbX_3$ unit cell, which we treat as a rigid rotor and imbue with an orientational degree of freedom, represented by a unit quaternion variable.

A. Description of site basis functions

The C_{3v} point-group symmetry of $CH_3NH_3^+$ results in three symmetry-invariant site basis functions at 2nd order and five symmetry-invariant site basis functions at 4th order. These site basis functions are tabulated in Tables I and II. There are 21 and 27 site basis functions at 6th and 8th order, respectively, which are tabulated in the supplementary information. As described in Sec. III, odd-order site basis functions are not allowed, due to the mathematical equivalence of $\vec{q}^{\lambda}$ and $-\vec{q}^{\lambda}$. We performed group-theoretical analyses and constructed invariant basis functions using algorithms implemented in the Clusters Approach to Statistical Mechanics (CASM) library[8, 43–45].

It is possible to visualize functions of unit quaternions as a sequence of two-dimensional surfaces. A four-dimensional unit quaternion is constrained to the three-dimensional surface of a four-dimensional hypersphere. One way to parameterize points on this three-dimensional surface is via the three independent extrinsic Euler angles, (ψ, θ, ϕ). These angles are extrinsic in that they specify rotations relative to the fixed coordinate system of the crystal. For the methylammonium ion, we define the primary Euler angle ψ about the high-symmetry three-fold axis, which is oriented along the z axis in the reference molecule. The secondary Euler angles θ and ϕ describe subsequent rotations about the y and z axes, respectively. This is the extrinsic Euler z-y-z convention, and the quaternion corresponding to this rotation is given by $\vec{q}_{zyz}(\psi, \theta, \phi) = \vec{q}_z(\phi)\vec{q}_y(\theta)\vec{q}_z(\psi)$. Thus, a unit quaternion is a function $\vec{q}(\psi, \theta, \phi)$ on the domain of unique orientations specified by $\psi \in [0, 2\pi]$, $\theta \in [0, \pi]$ and $\phi \in [0, 2\pi]$. In this work, we visualize functions of a unit quaternion in terms of (ψ, θ, ϕ) by taking snapshots at several fixed values of the primary rotation ψ. For each snapshot, we plot the remaining two angles (θ, ϕ) as radial and angular coordinates, respectively, of a polar coordinate system.

Using this convention, we depict several of the C_{3v}-invariant site basis functions for the oriented $CH_3NH_3^+$ ion in Fig. 4. The three second-order site basis functions have no dependence on primary rotation angle ψ and correspond to the p_x, p_y, and p_z spherical harmonics,
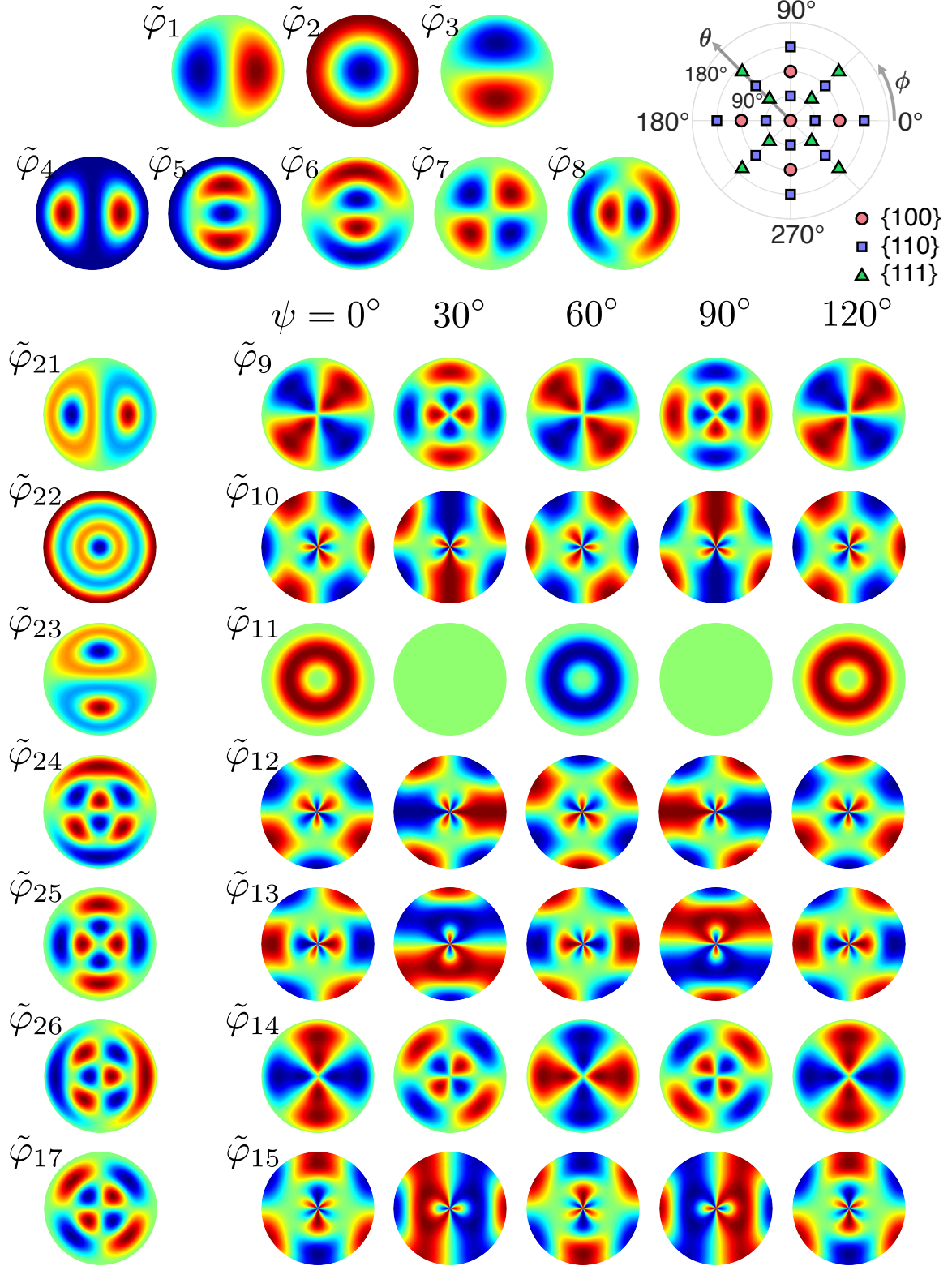
22

FIG. 4. Site basis functions of orientations of the methylammonium ion in $CH_3NH_3PbI_3$, at 2nd, 4th, and 6th orders. For basis functions that depend in the intrinsic rotation angle ψ, snapshots are taken at several values of ψ, as indicated by the highlighted value on the number line. Only a subset of 6th-order site basis functions are depicted. Formulae for 6th-order site basis functions are provided in the supporting information[42].

as suggested by their antisymmetry in (θ, ϕ) and presence of a single nodal plane. The five fourth-order site basis functions likewise lack any dependence on ψ and correspond to d-type spherical harmonics, having two intersecting nodal surfaces. These ψ-independent functions have even higher symmetry than required by the C_{3v} molecular symmetry of CH_3NH_3. In fact, because these basis functions depend only on the direction of the three-fold axis of the molecule, they are consistent with molecules having any order of rotational symmetry, including the $C_{\infty v}$ continuous rotational symmetry of a polar dimer, and thus correspond to basis functions of an anisotropic Heisenberg model[3].

At sixth-order we are able to construct C_{3v}-invariant site basis functions that do depend on the primary Euler angle ψ, in addition to the seven f-type basis functions of the classical Heisenberg model. 14 of the 21 distinct sixth-order site basis functions are depicted in Fig. 4. The first seven, corresponding to f-type spherical harmonics, do not depend on ψ, while the remaining seven do have a dependence on ψ, exhibiting the requisite periodicity $2\pi/3$ in ψ. Because of this periodicity, $\psi - dependent$ functions are only depicted on the interval $\psi \in [0, 2\pi/3]$. Formulae for all 21 6th-order site basis functions are provided as Supplemental Material[42].

B. Description of crystal basis functions

Crystal basis functions can be formed as the tensor product of the site basis functions belonging to different sites of the crystal, where each site basis function has been made invariant to the molecular point group of $CH_3NH_3{}^+$. The resulting crystal basis functions must be made invariant to the space group of the crystal, which for a particular crystal basis function associated with a cluster of sites α can be achieved by applying the Reynolds operator for the cluster point group that maps the cluster α onto itself. The first non-unity symmetry-invariant basis functions of the 1-site cluster appear at eighth order in the unit quaternion. The first of these is ψ-independent and corresponds to the lowest-order spherical harmonic that is invariant to O_h point symmetry, after the spherically-symmetric s-type harmonic. The other eighth-order 1-site cluster function does depend on ψ. These two single-site crystal basis functions at 8th order are depicted in Fig. 5. Any site or crystal basis functions that is not invariant to ψ must be periodic in ψ with a period of $2\pi n/3$, for integer n, due to the three-fold rotational symmetry of CH_3NH_3.
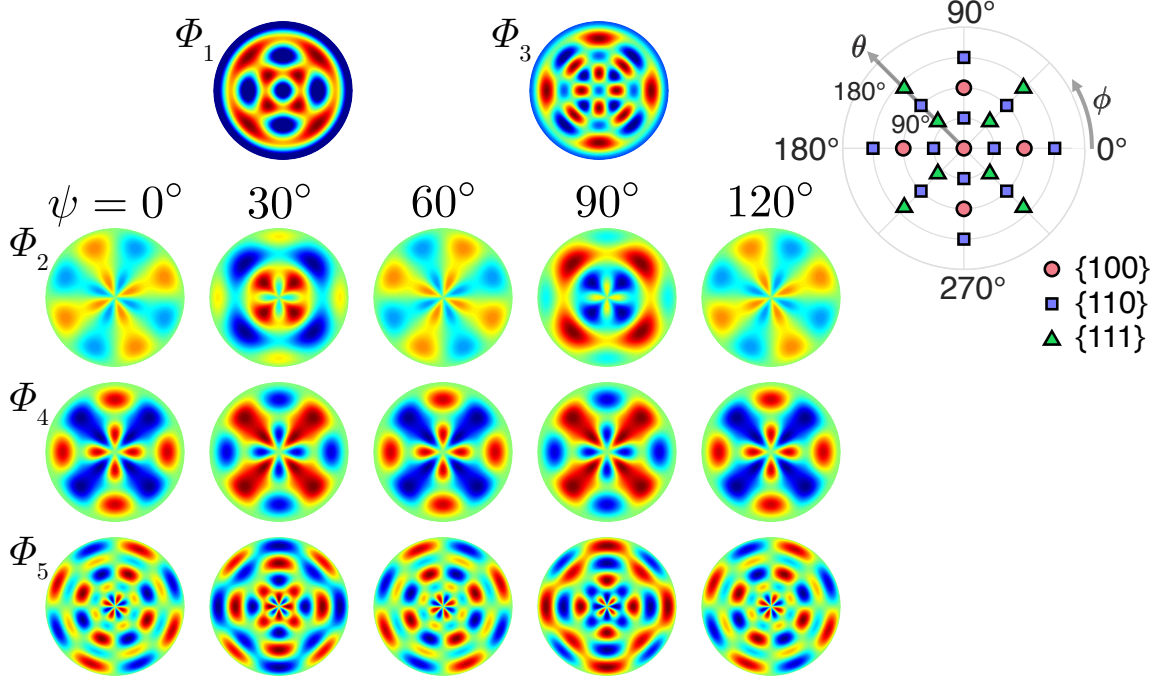
24

FIG. 5. Depictions of the first five non-trivial crystal basis functions for the single-site cluster in $CH_3NH_3PbI_3$. The first two are found at 8th order, and three more occur at 12th order. Snapshots are taken at several values of the intrinsic rotation angle ψ, as indicated by the highlighted value on the number line. Formulae for single-site cluster basis functions are provided as Supplemental Material[42].

The simplest interactions between molecular orientations is captured by the nearest-neighbor pair cluster. In the perovskite structure, there are three equivalent nearest-neighbor pair interactions, aligned along [100] (x), [010] (y), and [001] (z), as illustrated in Fig. 2. From the tensor product formed by the second- and fourth-order site basis functions at the two constituent sites of the pair, there are eight pair basis functions that are invariant to the cluster point-group symmetry. Although the site basis functions at every site have identical functional forms, each equivalent orientation of the nearest-neighbor pair has a basis set with a distinct functional form. These three equivalent basis sets, which are expressed as monomials of the site basis functions at the constituent sites of the pair, are tabulated in Tables III, IV, and V. The basis functions for the equivalent pair orientations are related by symmetry, such that basis functions with the same index for different pair orientations must have the same interaction parameter in the full Hamiltonian.

TABLE I. Site basis functions at 2$^{\text{nd}}$ order

Function	Formula	irrep
$\tilde{\varphi}_1$	$(q_1 q_3 + q_2 q_4)$	T_{1u}
$\tilde{\varphi}_2$	$-1/2(q_1^2 - q_2^2 - q_3^2 + q_4^2)$	T_{1u}
$\tilde{\varphi}_3$	$(q_1 q_2 - q_3 q_4)$	T_{1u}

TABLE II. Site basis functions at 4$^{\text{th}}$ order

Function	Formula	irrep
$\tilde{\varphi}_4$	$-1/8(q_1^4 + 2q_1^2 q_2^2 - 10q_1^2 q_3^2 + 2q_1^2 q_4^2 - 24q_1 q_2 q_3 q_4 + q_2^4 + 2q_2^2 q_3^2 - 10q_2^2 q_4^2 + q_3^4 + 2q_3^2 q_4^2 + q_4^4)$	E_g
$\tilde{\varphi}_5$	$-\sqrt{3/64}(q_1^4 - 6q_1^2 q_2^2 - 2q_1^2 q_3^2 + 2q_1^2 q_4^2 + 8q_1 q_2 q_3 q_4 + q_2^4 + 2q_2^2 q_3^2 - 2q_2^2 q_4^2 + q_3^4 - 6q_3^2 q_4^2 + q_4^4)$	E_g
$\tilde{\varphi}_6$	$\sqrt{3/4}(q_1^3 q_2 - q_1^2 q_3 q_4 - q_1 q_2^3 - q_1 q_2 q_3^2 + q_1 q_2 q_4^2 + q_2^2 q_3 q_4 + q_3^3 q_4 - q_3 q_4^3)$	T_{2g}
$\tilde{\varphi}_7$	$-\sqrt{3}(q_1^2 q_2 q_3 + q_1 q_2^2 q_4 - q_1 q_3^2 q_4 - q_2 q_3 q_4^2)$	T_{2g}
$\tilde{\varphi}_8$	$-\sqrt{3/4}(q_1^3 q_3 + q_1^2 q_2 q_4 - q_1 q_2^2 q_3 - q_1 q_3^3 + q_1 q_3 q_4^2 - q_2^3 q_4 - q_2 q_3^2 q_4 + q_2 q_4^3)$	T_{2g}

V. DISCUSSION

We have introduced a framework with which to formulate effective Hamiltonians for interacting molecules with orientational degrees of freedom (i.e., rigid rotors) within a host crystal. The Hamiltonian is expressed in terms of a complete and orthonormal set of crystal basis functions and is capable of describing an arbitrary energy surface as a function of all orientational degrees of freedom of rigid rotors within the crystal. Similar to the alloy cluster expansion Hamiltonians formalized by Sanchez *et al.* [29, 30], the crystal basis functions introduced here can be associated with clusters of sites and thereby have a natural hierarchy in which the lowest order crystal basis functions depend only on the orientational state of small and compact clusters comprising one, two, or three rotors. We, therefore, refer to

TABLE III. Cluster basis functions for x-oriented nearest neighbor

Function	Formula
$\Phi_1^{(\alpha_x)}$	$\sqrt{2}\tilde{\varphi}_1^{(1)}\tilde{\varphi}_1^{(2)}$
$\Phi_2^{(\alpha_x)}$	$(\tilde{\varphi}_4^{(1)}\tilde{\varphi}_1^{(2)} - \tilde{\varphi}_1^{(1)}\tilde{\varphi}_4^{(2)})$
$\Phi_3^{(\alpha_x)}$	$(\tilde{\varphi}_2^{(1)}\tilde{\varphi}_2^{(2)} + \tilde{\varphi}_3^{(1)}\tilde{\varphi}_3^{(2)})$
$\Phi_4^{(\alpha_x)}$	$\sqrt{1/2}(\tilde{\varphi}_8^{(1)}\tilde{\varphi}_2^{(2)} - \tilde{\varphi}_7^{(1)}\tilde{\varphi}_3^{(2)} + \tilde{\varphi}_3^{(1)}\tilde{\varphi}_7^{(2)} - \tilde{\varphi}_2^{(1)}\tilde{\varphi}_8^{(2)})$
$\Phi_5^{(\alpha_x)}$	$\sqrt{2}\tilde{\varphi}_4^{(1)}\tilde{\varphi}_4^{(2)}$
$\Phi_6^{(\alpha_x)}$	$\sqrt{2}\tilde{\varphi}_5^{(1)}\tilde{\varphi}_5^{(2)}$
$\Phi_7^{(\alpha_x)}$	$\sqrt{2}\tilde{\varphi}_6^{(1)}\tilde{\varphi}_6^{(2)}$
$\Phi_8^{(\alpha_x)}$	$(\tilde{\varphi}_7^{(1)}\tilde{\varphi}_7^{(2)} + \tilde{\varphi}_8^{(1)}\tilde{\varphi}_8^{(2)})$

TABLE IV. Cluster basis functions for y-oriented nearest neighbor

Function	Formula
$\Phi_1^{(\alpha_y)}$	$\sqrt{2}\tilde{\varphi}_3^{(1)}\tilde{\varphi}_3^{(2)}$
$\Phi_2^{(\alpha_y)}$	$-\sqrt{3/4}(\tilde{\varphi}_3^{(1)}\tilde{\varphi}_5^{(2)} - \tilde{\varphi}_5^{(1)}\tilde{\varphi}_3^{(2)} - \sqrt{1/3}\tilde{\varphi}_3^{(1)}\tilde{\varphi}_4^{(2)} + \sqrt{1/3}\tilde{\varphi}_4^{(1)}\tilde{\varphi}_3^{(2)})$
$\Phi_3^{(\alpha_y)}$	$(\tilde{\varphi}_1^{(1)}\tilde{\varphi}_1^{(2)} + \tilde{\varphi}_2^{(1)}\tilde{\varphi}_2^{(2)})$
$\Phi_4^{(\alpha_y)}$	$-\sqrt{1/2}(\tilde{\varphi}_6^{(1)}\tilde{\varphi}_2^{(2)} + \tilde{\varphi}_7^{(1)}\tilde{\varphi}_1^{(2)} - \tilde{\varphi}_1^{(1)}\tilde{\varphi}_7^{(2)} - \tilde{\varphi}_2^{(1)}\tilde{\varphi}_6^{(2)})$
$\Phi_5^{(\alpha_y)}$	$\sqrt{9/8}(\tilde{\varphi}_5^{(1)}\tilde{\varphi}_5^{(2)} - \sqrt{1/3}\tilde{\varphi}_4^{(1)}\tilde{\varphi}_5^{(2)} - \sqrt{1/3}\tilde{\varphi}_5^{(1)}\tilde{\varphi}_4^{(2)} + 1/3\tilde{\varphi}_4^{(1)}\tilde{\varphi}_4^{(2)})$
$\Phi_6^{(\alpha_y)}$	$\sqrt{9/8}(\tilde{\varphi}_4^{(1)}\tilde{\varphi}_4^{(2)} + \sqrt{1/3}\tilde{\varphi}_4^{(1)}\tilde{\varphi}_5^{(2)} + \sqrt{1/3}\tilde{\varphi}_5^{(1)}\tilde{\varphi}_4^{(2)} + 1/3\tilde{\varphi}_5^{(1)}\tilde{\varphi}_5^{(2)})$
$\Phi_7^{(\alpha_y)}$	$\sqrt{2}\tilde{\varphi}_8^{(1)}\tilde{\varphi}_8^{(2)}$
$\Phi_8^{(\alpha_y)}$	$(\tilde{\varphi}_6^{(1)}\tilde{\varphi}_6^{(2)} + \tilde{\varphi}_7^{(1)}\tilde{\varphi}_7^{(2)})$

TABLE V. Cluster basis functions for z-oriented nearest neighbor

Function	Formula
$\Phi_1^{(\alpha_z)}$	$\sqrt{2}\tilde{\varphi}_2^{(1)}\tilde{\varphi}_2^{(2)}$
$\Phi_2^{(\alpha_z)}$	$-\sqrt{3/4}(\tilde{\varphi}_5^{(1)}\tilde{\varphi}_2^{(2)} + \sqrt{1/3}\tilde{\varphi}_4^{(1)}\tilde{\varphi}_2^{(2)} - \tilde{\varphi}_2^{(1)}\tilde{\varphi}_5^{(2)} - \sqrt{1/3}\tilde{\varphi}_2^{(1)}\tilde{\varphi}_4^{(2)})$
$\Phi_3^{(\alpha_z)}$	$(\tilde{\varphi}_1^{(1)}\tilde{\varphi}_1^{(2)} + \tilde{\varphi}_3^{(1)}\tilde{\varphi}_3^{(2)})$
$\Phi_4^{(\alpha_z)}$	$\sqrt{1/2}(\tilde{\varphi}_8^{(1)}\tilde{\varphi}_1^{(2)} - \tilde{\varphi}_6^{(1)}\tilde{\varphi}_3^{(2)} + \tilde{\varphi}_3^{(1)}\tilde{\varphi}_6^{(2)} - \tilde{\varphi}_1^{(1)}\tilde{\varphi}_8^{(2)})$
$\Phi_5^{(\alpha_z)}$	$\sqrt{9/8}(\tilde{\varphi}_5^{(1)}\tilde{\varphi}_5^{(2)} + \sqrt{1/3}\tilde{\varphi}_4^{(1)}\tilde{\varphi}_5^{(2)} + \sqrt{1/3}\tilde{\varphi}_5^{(1)}\tilde{\varphi}_4^{(2)} + 1/3\tilde{\varphi}_4^{(1)}\tilde{\varphi}_4^{(2)})$
$\Phi_6^{(\alpha_z)}$	$\sqrt{9/8}(\tilde{\varphi}_4^{(1)}\tilde{\varphi}_4^{(2)} - \sqrt{1/3}\tilde{\varphi}_4^{(1)}\tilde{\varphi}_5^{(2)} - \sqrt{1/3}\tilde{\varphi}_5^{(1)}\tilde{\varphi}_4^{(2)} + 1/3\tilde{\varphi}_5^{(1)}\tilde{\varphi}_5^{(2)})$
$\Phi_7^{(\alpha_z)}$	$\sqrt{2}\tilde{\varphi}_7^{(1)}\tilde{\varphi}_7^{(2)}$
$\Phi_8^{(\alpha_z)}$	$(\tilde{\varphi}_6^{(1)}\tilde{\varphi}_6^{(2)} + \tilde{\varphi}_8^{(1)}\tilde{\varphi}_8^{(2)})$

the effective Hamiltonian for molecular orientational degrees of freedom within a crystal as a *rigid rotor cluster expansion*. The fact that coefficients in the effective Hamiltonian expansion are associated with clusters of sites suggests a natural hierarchy for truncating a Hamiltonian expression fit to first-principles energy data, wherein basis functions associated with small and compact clusters take precedence over higher order basis functions associated with large clusters.

A fascinating and complicating feature of the rigid rotor cluster expansion, which makes it distinct among most other crystal Hamiltonian models, is that it requires careful consideration of symmetry of the oriented molecule at each site, as well as that of the entire crystal. A key component of the rigid rotor cluster expansion that facilitates these dual symmetry considerations is the utilization of unit quaternions to express molecular orientation. Unlike the typical 3×3 rotation matrix, which is commonly used to describe orientation, the unit quaternions describe orientation as a coordinate on the surface of the four-dimensional sphere, which comprises a smooth, simply connected manifold. This simplification allows

us to describe orientation in terms of four, rather than nine, parameters, and to construct a complete basis set of functions of orientation using the set of hyperspherical harmonic functions. Although other types of orientational basis sets can be constructed, such as the Wigner D matrices, which find use in quantum mechanical treatments of lone molecules[46], the quaternion harmonics provide a compact and relatively simple set of functions that are amenable to symmetry considerations arising from both the molecular point group and the crystal space group. The total crystal rotor group, G, comprises all such operations that combine a space-group operation of the crystal with point-group operations of each of the constituent molecules. Similar constructions for combining disparate symmetries are commonly used, such as in magnetic space groups and point groups, which compose spatial symmetries with the time-reversal symmetry $t \to -t$. However, the total rotor group is unusual in that, unlike time reversal, the molecular point-group operations that are subgroups of G act locally and independently of each other (unlike time-reversal, which is a global operator). As such, the total rotor group is a generalized semidirect product of the crystal space group, which is a normal subgroup of G, and the individual molecular point groups, which are not normal in G.

The rigid rotor cluster expansion introduced here can be viewed as a natural extension of common lattice based effective Hamiltonians, including the Ising model[47], the alloy cluster expansion[29], Potts models[48, 49], classical XY model,[50] and the classical Heisenberg model and its extensions such as the spin cluster expansion, developed by Drautz and Fähnle[3]. The site degrees of freedom of the Ising model, alloy cluster expansions and the Potts models are occupation variables that take discrete values. The site degrees of freedom of the XY model are unit vectors in a two-dimensional Cartesian space, while those of the Heisenberg model and spin cluster expansions are unit vectors in a three-dimensional space. Despite being motivated by interactions in magnetic spin systems, the Heisenberg model has also been used successfully to model interactions in crystals of oriented dimers[7]. In contrast, the rigid rotor cluster expansion, when expressed in terms of quaternion variables, is a Hamiltonian with site degrees of freedom in a four-dimensional space. An additional degree of freedom emerges for a chiral molecule within a crystal if both enantiomers are present. The Hamiltonian then has a dependence not only on a four-dimensional rotational degree of freedom, but also on an additional Ising-like occupation variable that indicates the particular enantiomer at a site.

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In general, all lattice-based Hamiltonians must obey the space-group symmetries of some reference crystal. A rigid rotor cluster expansion must additionally be invariant to the point-group symmetries of the molecules that occupy crystallographic sites of the host crystal. For both chiral and achiral molecules, we have shown that the rigid rotor cluster expansion can be made invariant to both the space-group symmetry of the crystal and the molecular point-group symmetries in two distinct steps. In the first step, a site basis set is constructed for each molecule and made symmetry-invariant with respect to the point group of the molecule. This symmetrization step ensures that orientations of the molecule that are indistinguishable due to its symmetry evaluate to the same energy. In the second step, crystal basis functions are constructed, using the cluster expansion formalism, as a tensor product of these site basis functions. These crystal basis functions are made symmetry-invariant with respect to the crystal space group. This second symmetrization step ensures that microstates of the crystal that are related by rigid-body transformations of the entire crystal evaluate to the same energy.

While the rigid rotor cluster expansion has been formulated assuming rigid molecules, real molecules may deform due to vibrational excitations. The orientation of a deformed molecule nevertheless remains a well-defined quantity in a least-squares sense, relative to an oriented ideal rigid rotor. The residual deformation of the molecule relative to its rigid reference molecule can be expressed as a $3 \times n$ displacement matrix $\mathbf{D}^{(\nu)}$. The molecular orientation, as described by a unit quaternion, and the displacement matrix, $\mathbf{D}^{(\nu)}$, can be varied independently, and thus correspond to distinct degrees of freedom. The formalism presented here can be generalized to construct crystal basis functions that depend on both molecular orientation and deformation. Special considerations must be taken into account, however, when determining symmetry relations for the deformable molecules. A brief overview of these considerations is given in App. D.

The site basis functions of the unit quaternions, in addition to being essential ingredients for a rigid rotor cluster expansion, can also serve as order parameters to measure the degree of orientational order. For example, the three second-order site basis functions $\tilde{\varphi}_1$, $\tilde{\varphi}_2$, and $\tilde{\varphi}_3$ derived for $CH_3NH_3PbX_3$ are able to describe alignment of the three-fold axis of the $CH_3NH_3^+$ cation along the $\pm x$, $\pm y$, and $\pm z$ axes, respectively. The crystal averages of these site basis functions form a three-dimensional vector that describes the average orientation of the three-fold axes of the $CH_3NH_3^+$ cations. The magnitude of this vector indicates the

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degree of order. Furthermore, the absence of any preferred orientation becomes evident when all three site basis functions average to zero. Higher-order site basis functions can be thought of as higher-order moments of the distribution of orientations.

The existence of these macroscopic order parameters of molecular orientation may have particular importance in the construction of coarse-grained Landau free-energy functionals. In a crystal with a single basis site in the primitive cell, the symmetry-allowed terms in the Landau free energy correspond to the site-cluster basis functions of the rigid rotor cluster expansion, which are tabulated in the supporting information[42]. Results from polynomial invariant theory assert that any polynomial invariant to the molecular point group can be rewritten as a polynomial of a finite generating set of low-order invariant monomials[51]. As such, we propose that this generating set of invariant polynomials, known formally as a Gröbner basis, is a suitable set of order parameters for constructing Landau free energies.

Finally, the crystal basis functions can be utilized as symmetry-invariant descriptors of the total orientational microstate. As an example, the nearest-neighbor basis functions Φ_1, Φ_2, and Φ_3 when averaged over the entire crystal are the three symmetry-allowed entries of the covariance of the axial orientation of nearest-neighbor molecules. Averaged over the entire crystal, these functions are able to distinguish between states of the crystal that would be indistinguishable based on measurements of the site basis functions alone. The framework presented here expresses scalar properties of a molecular crystal as a linear expansion of these crystal descriptors. However, these descriptors can also be used within one of the many non-linear machine learning approaches, such as regression trees[52] or artificial neural networks[53].

VI. CONCLUSION

We have introduced a general approach to construct Hamiltonians for crystals of rigid rotors. The approach starts with the construction of a complete set of site basis functions for each oriented rotor. Crystal basis functions are then generated as a tensor product comprising one site basis function from each site of the crystal. By analogy to the configurational cluster expansion formalism for alloys, the crystal basis functions can be associated with clusters of sites within the crystal.

A number of mathematical concepts have been introduced to make the construction of

a rigid rotor cluster expansion Hamiltonian tractable. First, a unit quaternion description of molecular orientation was utilized, thereby enabling construction of a complete set of site basis functions in terms of four-dimensional hyperspherical harmonics. Second, we derived symmetry equivalence relations that describe how both the point group of each rotor and the space group of the crystal both give rise to indistinguishable and equivalent orientational states, respectively. Finally, we have introduced a composite total group that is used to bring the full symmetry of the crystal of rigid rotors to bear on the Hamiltonian construction, including the proper treatment of improper space-group operations. These symmetry relations are used to enforce the symmetry invariance of the crystal basis set and, consequently, the resulting Hamiltonian expression.

As an example, we have constructed an explicit Hamiltonian for the orientational degrees of freedom of the methylammonium molecules of hybrid organic-inorganic perovskites such as $CH_3NH_3PbI_3$. Further exploration of rigid rotor cluster expansion Hamiltonians, with their four-dimensional site degrees of freedom, using Monte Carlo simulations should reveal intriguing phase transformation phenomena and help elucidate the complex thermodynamic properties of molecular crystals and hybrid organic-inorganic crystals.

Appendix A: Mathematical properties of quaternions

In addition to the expression given in Eq. (31) relating a unit quaternion to a corresponding orientation via an axis and rotation angle, a unit quaternion can also be specified by the

elements of a rotation matrix, $\mathbf{Q}$, directly as[54]

$$q_1 = \frac{1}{2}\sqrt{1 + Q_{11} + Q_{22} + Q_{33}} \tag{A1}$$

$$q_2 = \frac{Q_{32} - Q_{23}}{4q_1} \tag{A2}$$

$$q_3 = \frac{Q_{13} - Q_{31}}{4q_1} \tag{A3}$$

$$q_4 = \frac{Q_{21} - Q_{12}}{4q_1}. \tag{A4}$$

However, because this parameterization is ill-behaved for angles near $180°$, conversions are typically performed via matrix decompositions in practice.

The multiplication of two rotation matrices can also be expressed a as a multiplication of their corresponding quaternions according to the multiplication rule[55]

$$
\begin{aligned}
\vec{q}^{(3)} &= \vec{q}^{(2)}\vec{q}^{(1)} \\
&= \begin{pmatrix}
q_1^{(2)} & -q_2^{(2)} & -q_3^{(2)} & -q_4^{(2)} \\
q_2^{(2)} & q_1^{(2)} & q_4^{(2)} & -q_3^{(2)} \\
q_3^{(2)} & -q_4^{(2)} & q_1^{(2)} & q_2^{(2)} \\
q_4^{(2)} & q_3^{(2)} & -q_2^{(2)} & q_1^{(2)}
\end{pmatrix} \vec{q}^{(1)},
\end{aligned}
\tag{A5}
$$

or, equivalently

$$
\begin{aligned}
\vec{q}^{(3)} &= \vec{q}^{(2)}\vec{q}^{(1)} \\
&= \begin{pmatrix}
q_1^{(1)} & -q_2^{(1)} & -q_3^{(1)} & -q_4^{(1)} \\
q_2^{(1)} & q_1^{(1)} & -q_4^{(1)} & q_3^{(1)} \\
q_3^{(1)} & q_4^{(1)} & q_1^{(1)} & -q_2^{(1)} \\
q_4^{(1)} & -q_3^{(1)} & q_2^{(1)} & q_1^{(1)}
\end{pmatrix} \vec{q}^{(2)},
\end{aligned}
\tag{A6}
$$

and inversion via

$$\vec{q}^{-1} = (q_1, -q_2, -q_3, -q_4)^{\top}. \tag{A7}$$

These multiplication rules faithfully represent the algebra formed by rigid rotation matrices, such that $\vec{q}(\mathbf{Q}^{(2)})\,\vec{q}(\mathbf{Q}^{(1)}) = \vec{q}(\mathbf{Q}^{(2)}\mathbf{Q}^{(1)})$, and $\vec{q}(\mathbf{Q}^{-1}) = \vec{q}^{-1}(\mathbf{Q})$. We denote the left-hand and right-hand matrix representation of the quaternions as $\mathbf{M}^{(L)}(\vec{q})$ and $\mathbf{M}^{(R)}(\vec{q})$, respectively.

Thus, Eqs. (A5) and (A6) is expressed more succinctly as

$$\vec{q}^{(3)} = \mathbf{M}^{(L)}\big(\vec{q}^{(2)}\big)\ \vec{q}^{(1)} = \mathbf{M}^{(R)}\big(\vec{q}^{(1)}\big)\ \vec{q}^{(2)}. \tag{A8}$$

This relation underscores a powerful advantage of the quaternion representation of rigid rotations: both the 'pre-rotation' by $\vec{q}^{(1)}$ before $\vec{q}^{(2)}$, Eq. (A5), and the 'post-rotation' by $\vec{q}^{(2)}$ after $\vec{q}^{(1)}$, Eq. (A6), can be expressed via left multiplication of a quaternion by a 4×4 matrix.

Appendix B: Application of symmetry to unit quaternions

The unit quaternion representation of molecular orientation provides an efficient way to represent the effect of symmetry on molecular orientation. For simplicity, we denote the unit quaternion corresponding to a particular molecular orientation, $\mathbf{Q}^{(\nu)}$ as simply $\vec{q}^{(\nu)}$. Starting from Eq. (6) and Eq. (16), we find equivalent expressions for the action of both the molecular point group and the total rigid rotation crystal group on the quaternion $\vec{q}^{(\nu)}$. For a proper molecular point-group operation, we use Eq. (A8) to convert Eq. (6) as

$$\hat{p}_\circ\big[\vec{q}^{(\nu)}\big] = \mathbf{M}^{(R)}(\hat{p}_\circ)\,\vec{q}^{(\nu)}. \tag{B1}$$

As described in Sec. II C, operations in the total rigid rotor crystal group transform molecular orientations via a combination of pre-rotation (i.e., a rotation operation before application of $\mathbf{Q}^{(\nu)}$) and post-rotation (i.e., a rotation operation applied after application of $\mathbf{Q}^{(\nu)}$). The quaternion representation is particularly amenable to such transformations. As an example, the operation described by the totally proper operation $\hat{g}_\circ$, which acts on $\mathbf{Q}^{(\nu)}$ via post-rotation by space-group operation $\hat{s}_\circ$ and pre-rotation by molecular point-group operation $\hat{p}_\circ^{(\nu)}$, is expressed as the single quaternion transformation

$$\hat{g}_\circ\big[\vec{q}^{(\nu)}\big] = \mathbf{M}^{(L)}(\hat{s}_\circ)\,\mathbf{M}^{(R)}\big(\hat{p}_\circ^{(\eta)}\big)\,\vec{q}^{(\eta)}. \tag{B2}$$

As Eq. (B2) demonstrates, an important and powerful advantage of using the quaternion parameterization of rotation is that the combined space-group and point-group symmetries of the total group can be represented unambiguously by left-multiplication of the quaternion

by a matrix.

Appendix C: Group theoretical properties of site clusters

Despite lacking the translational symmetry of the infinite crystal, an individual cluster α is invariant to a subgroup of the crystal space group, called the cluster point group,. The cluster point group and the crystal translation group, $\mathcal{T}$, are both subgroups of the crystal space group and have only the identity operation in common. The subgroups $P^{(\alpha)}$ and $\mathcal{T}$ enable a convenient partition of the space group into qualitatively distinct sets. We do this by defining cluster cosets, . To do this, we first define the cluster coset $\mathcal{C}^{\alpha \to \alpha'}$, which contains all space-group operations that map cluster α onto an equivalent cluster α' having a different orientation. Any space-group operation can then be uniquely expressed as the composition product $\hat{s} = \hat{\tau} \circ \hat{f}^{(\alpha \to \alpha')} \circ \hat{c}$, where $\hat{\tau}$ is a lattice translation operation, and $\hat{c}$ is a cluster point-group operation that leave α invariant (to within a permutation of sites). The operator $\hat{f}^{(\alpha \to \alpha')}$ is a preselected representative operation in $\mathcal{C}^{\alpha \to \alpha'}$ that we have selected as the canonical operation that maps from α to α'. This decomposition is particularly convenient because the number of operations $\hat{c}$ and $\hat{f}^{(\alpha \to \alpha')}$ are both finite and of manageable size, while the total space group, which we have up to this point, is an infinite group.

This group partition allows us to simplify the application of the Reynold's operator of the space group to a quantity associated with a particular cluster $\alpha\left(\vec{b}\right)$. Doing this for Eq. (41), we arrive at

$$
\begin{aligned}
\tilde{\Phi}_{\vec{b}}^{(sym)} = & \frac{1}{|\mathcal{T}|} \sum_{\hat{\tau} \in \mathcal{T}} \frac{1}{|\omega|} \sum_{\alpha' \in \omega} \frac{1}{\left|P^{\left(\alpha(\vec{b})\right)}\right|} \sum_{\hat{c} \in P^{\left(\alpha(\vec{b})\right)}} \\
& \hat{\tau} \circ \hat{f}^{\left(\alpha(\vec{b}) \to \alpha'\right)} \circ \hat{c} \left[\prod_{\nu \in \alpha(\vec{b})} \tilde{\varphi}_{b_\nu}\left(\vec{q}^{(\nu)}\right) \right],
\end{aligned}
\tag{C1}
$$

or, equivalently,

$$
\tilde{\Phi}_{\vec{b}}^{(sym)} = \hat{\mathcal{R}}^{(\mathcal{T})} \circ \hat{\mathcal{R}}^{(\omega)} \circ \hat{\mathcal{R}}^{\left(\alpha(\vec{b})\right)} \left[\prod_{\nu \in \alpha(\vec{b})} \tilde{\varphi}_{b_\nu}\left(\vec{q}^{(\nu)}\right) \right].
\tag{C2}
$$

In Eq. (C2) we have used the notation $\hat{\mathcal{R}}^{(\omega)}$ to denote the average over equivalent clusters

in the orbit ω even though the operations $\hat{f}^{(\alpha(\vec{b})\to\alpha')}$ do not necessarily form a group and thus $\hat{\mathcal{R}}^{(\omega)}$ does not constitute a Reynolds operator in a formal sense.

Because the cluster point group $P^{(\alpha(\vec{b}))}$ leaves $\alpha\left(\vec{b}\right)$ invariant, the rightmost Reynolds operator $\hat{\mathcal{R}}^{(\alpha(\vec{b}))}$ acts to enforce the symmetry invariance of $\tilde{\Phi}_{\vec{b}}$ with respect to the point-group symmetry of the cluster $\alpha\left(\vec{b}\right)$. The sum over ω, then accumulates $P^{(\alpha')}$-invariant functions over the equivalent cluster orientations, α', while the sum over the lattice translation group, $\mathcal{T}$, accumulates equivalent functions evaluated at other translational variants of cluster $\alpha\left(\vec{b}\right)$.

Appendix D: Extension to deformable molecules

For a deformable molecule, we can decompose the matrix of total molecular coordinates, $\mathbf{R}^{(\nu)}$, as

$$\mathbf{R}^{(\nu)} = \chi^{(\nu)}\mathbf{Q}^{(\nu)}\left(\mathbf{m} + \mathbf{D}^{(\nu)}\right) + \left(\vec{r}^{(\nu)}\right)\mathbf{1}^{(1\times n)}, \tag{D1}$$

where $\mathbf{D}^{(\nu)}$ is a $3 \times n$ matrix describing the displacement of atom of the molecule relative to its position in the ideal reference molecule, $\mathbf{m}$. Knowing only $\mathbf{R}^{(\nu)}$, the decomposition specified by Eq. (D1) can be performed uniquely by finding the orthogonal matrix $\mathbf{U}$ that solves the constrained minimization problem

$$\underset{\mathbf{Q}^{(\nu)}}{\arg\min}\sum_{i=1}^{n}||\vec{r}^{(\lambda,\mu_i)} - \vec{r}^{(\nu)} - \vec{d}^{(\nu)} - \mathbf{U}\,\vec{m}^{\,(\mu,i)}||^2, \tag{D2}$$

$$\mathbf{U}^{\top}\mathbf{U} = \mathbf{I}^{(3\times3)} \tag{D3}$$

where $\mathbf{I}$ is the 3×3 identity matrix. Equation (D3) constrains $\mathbf{U}$ to be an orthogonal matrix (i.e., identity, rotation, or rotoinversion). Equations (D2) and (D3) specify a special case of the orthogonal Procrustes problem and can be solved via the Kabsch algorithm[56]. Once $\mathbf{U}$ is found, we set $\mathbf{Q}^{(\nu)} = \det(\mathbf{U})\mathbf{U}$ and $\chi^{(\nu)} = \det(\mathbf{U})$, thus requiring that $\mathbf{Q}^{(\nu)}$ describes a proper rotation. The only remaining unknown value in Eq. (D1) is the molecular displacement matrix $\mathbf{D}^{(\nu)}$, which can be solved for explicitly.

Although the optimization problem in Eq. (D2) has a unique solution, it does assume that the molecular deformation is sufficiently small that atoms within the molecule do not exchange positions. If atoms are able to exchange positions, or if the original correspondence

between sites of the deformed and reference molecules are not known, then a combinatorial optimization must be performed over the set of all symmetrically distinct permutations of the sites of the reference molecule. The permutation that permits the best solution of Eq. (D2) is the one that should be used to define the orientation of the molecule.

Having shown that the molecular orientation $\mathbf{Q}^{(\nu)}$ and deformation $\mathbf{D}^{(\nu)}$ are uniquely defined and independent, the extension of our formalism to a deformable molecule is relatively straightforward. Care must be taken, however, in considering the molecular point-group symmetries on the combined orientation and deformation state of the molecule. A proper molecular point-group operation, $\hat{p}_\circ$, as before, permutes the sites of the deformed and oriented molecule according to $\mathbf{R}'^{(\nu)} = \mathbf{R}'^{(\nu)}\mathbf{W}(\hat{p}_\circ)^\top$. The action of $\hat{p}_\circ$ on $\mathbf{Q}^{(\nu)}$ and $\mathbf{D}^{(\nu)}$ is then

$$\begin{aligned}
\mathbf{R}'^{(\nu)}\mathbf{W}(\hat{p}_\circ)^\top &= \mathbf{Q}^{(\nu)}\left(\mathbf{m} + \mathbf{D}^{(\nu)}\right)\mathbf{W}(\hat{p}_\circ)^\top \\
&= \mathbf{Q}^{(\nu)}\,\mathbf{S}(\hat{p}_\circ)\left(\mathbf{m} + \mathbf{S}(\hat{p}_\circ)^\top\mathbf{D}^{(\nu)}\,\mathbf{W}(\hat{p}_\circ)^\top\right),
\end{aligned} \tag{D4}$$

and thus

$$\hat{p}_\circ\left[\mathbf{D}^{(\nu)}\right] = \mathbf{S}(\hat{p}_\circ)^\top\mathbf{D}^{(\nu)}\,\mathbf{W}(\hat{p}_\circ)^\top, \tag{D5}$$

where we have assumed, for clarity, that the molecule is centered at the origin.

We arrived at Eq. (D4) by utilizing the fundamental definition of point-group symmetry from Eq. (3). The molecular displacement matrix $\mathbf{D}^{(\nu)}$ is defined in the reference orientation of the molecule. Thus, applying a point-group operation of the molecule results in both a permutation and rotation of the displacement matrix, as indicated in Eq. (D5). By transforming both the displacement matrix and the the orientation of the deformed molecule simultaneously, we arrive at a state of the molecule that is indistinguishable from its initial state, even though both the orientational and deformational variables have changed.

By comparison, space-group operations have *no* orientational effect on the displacement matrix $\mathbf{D}^{(\nu)}$, because the displacement matrix is always expressed in the reference coordinate frame of the molecule. Space-group operations do affect a permutation of displacement matrices about the sites of the crystal, so that an arbitrary space group acts on the displacement matrix as

$$\mathbf{D}'^{(\nu)} = \hat{s}\left[\mathbf{D}^{(\nu)}\right] = \mathbf{D}^{(\eta)}, \tag{D6}$$

where, as before, $\eta = \hat{s}^{-1}[\nu]$. One final consideration arises when the deformation of an achiral molecule is acted upon by a total rotor group operation $\hat{g}_\circ$, comprising an improper space-group operation $\hat{s}_\star$ acting with improper point-group operations $\{\hat{p}_\star^{(\nu)}\}$. In this scenario, in addition to the molecular orientation transforming according to Eq. (24), the molecular displacement matrix transforms as

$$\mathbf{D}'^{(\nu)} = \hat{g}\left[\mathbf{D}^{(\nu)}\right] = \mathbf{S}(\hat{p}_\star^{(\eta)})^\top \, \mathbf{D}^{(\eta)} \, \mathbf{W}(\hat{p}_\star^{(\eta)})^\top, \tag{D7}$$

As such, the deformational contribution to the Hamiltonian is automatically invariant to rigid rotations of the crystal, as in [8]. A similar analysis can be performed to obtain symmetry relations for any additional internal degrees of freedom that the molecule may posses (e.g., discrete electronic states or species substitution of atoms within the molecule).

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