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CLASSIFICATION OF SYMMETRIC COORDINATES FOR POINT CLUSTERS. I. THE METHOD*

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A group-theoretical method for the classification and determination of sets of symmetric coordinates for a cluster of points, invariant in its equilibrium position under a point group, is proposed. This method relies on describing the configuration space for the cluster as a simple product of a "positional space" related to labels of members of the cluster, and a three-dimensional space of "free" vectors. An internal structure of the positional space and a reduction of the symmetry have been investigated.

1. Introduction

Determination of symmetric coordinates of clusters consisting of atoms or ions, whose equilibrium distribution possesses the symmetry of a point group G, is the starting point of many quantum-mechanical calculations in chemistry and solid state theory, since such coordinates are related to the normal modes, which determine the dynamics of a physical system in the harmonic approximation. Methods for the determination of these coordinates base themselves essentially on a standard group-theoretical projection procedure, realizing a decomposition of the mechanical representation into irreducible representations of the group G [1–3]. This procedure is usually treated as a "black box", transforming the set of cartesian coordinates of the nodes of a cluster into appropriate linear combinations symmetrised under the group G, without any deeper insight into the internal structure of the mechanical representation. On the other hand, such a structure is naturally imposed by an obvious statement that any operation of the group G leads to a transformation of displacements of nodes from their equilibrium positions, accompanied by a permutation of these nodes. Consequently, the carrier space of the mechanical representation can be treated as a simple product of a three-dimensional "free" vector space by a linear space

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associated with the distribution of equilibrium positions of the nodes of the cluster (see e.g. Lax [3], Chapter 5).

We proceed in this paper to give a group-theoretical analysis of an internal structure of the mechanical representation M for a point cluster symmetric under a point group G, and to propose a method for the classification and determination of symmetric coordinates. This method will be demonstrated in part II for cases of the nodes of a cube and a regular tetrahedron.

2. *A structure of the positional representation*

Let e_i^α, $\alpha = x, y, z$; $i = 1, 2, \ldots, N$ be a cartesian basis for the configuration space $\mathscr{M}$ for a cluster consisting of N points, and let G be the geometrical symmetry group for this cluster. The transformation of the basis e_i^α under $g \in G$ is given by

$$M(g)e_i^\alpha = \sum_{\alpha'} V_{\alpha'\alpha}(g)e_{p_i}^{\alpha'}, \tag{1}$$

where $V_{\alpha'\alpha}(g)$ are matrix elements of the vector representation V of the group G in a three--dimensional real cartesian basis e^α, and $p_i \equiv p_i(g)$ is the label of the position, occupied after the transformation g by a node from the position i. The set of operators $M(g)$ forms the mechanical representation M.

Putting

$$e_i^\alpha = |i\rangle e^\alpha, \tag{2}$$

we express the configuration space $\mathscr{M}$ as a simple product

$$\mathscr{M} = \Pi \otimes \mathscr{V}, \tag{3}$$

where the space Π and $\mathscr{V}$ is spanned over the basis $|i\rangle$ and e^α, respectively. The scalar products in Π, $\mathscr{V}$ are given respectively by

$$\langle i|i'\rangle = \delta_{ii'}, \qquad e^\alpha \cdot e^{\alpha'} = \delta_{\alpha\alpha'}. \tag{4}$$

The group G operates in the space $\mathscr{V}$ according to the vector representation V, whereas its action in the space Π is determined by the permutations

$$\sigma(g) = \begin{pmatrix} 1 & 2 & \ldots & N \\ p_1 & p_2 & \ldots & p_N \end{pmatrix}. \tag{5}$$

Introducing operators $P(g)$ defined by the relation

$$P(g)\,|i\rangle = |p_i\rangle, \tag{6}$$

we obtain a representation P of the group G in the space Π. The representation P in the space Π, referred hereafter to as the positional representation, is evidently isomorphic with the permutation representation (5). In this Chapter we give an analysis of a general structure of the positional representation.

The representation P is, in general, reducible. First of all, a set of N nodes constituting a cluster can be decomposed into transitive blocks ("simple clusters"), i.e. such subsets that for any pair (i, i') belonging to a block there exists such $g \in G$ that $p_i(g) = i'$. Correspondingly, the space Π decomposes into invariant subspaces Π_p, where p is the label of the simple cluster.

Let the cluster considered hereafter be simple. Let $G_i \subset G$ be the stability group for the i-th node, i.e. the set of all elements which leave the position of this node unchanged. It follows from simple geometrical considerations that for $N > 1$ the only accessible stability groups are group C_{nv} and (or) their subgroups embedded in G. There exists a one-to-one mapping between the nodes of the simple cluster, and the left cosets of the group G with respect to the stability group G_1, given by the decomposition

$$G = \bigcup_{i=1}^{N} g_i G_1. \tag{7}$$

The mapping given by Eq. (7) allows one to use the cosets $g_i G$ (or their representatives g_i) as labels of the nodes of the cluster. It follows that

$$N = |G|/|G_1|, \tag{8}$$

where $|G|$ is the order of the group G, i.e. that the number of nodes for a simple cluster has to be a divisor of the order of its symmetry group. When $N = |G|$, the cluster is termed to have a general position, and for $N < |G|$ — several special positions. It is also evident that the group $G(p)$ of the stability of the whole cluster, defined by

$$G(p) = \bigcap_{i=1}^{N} G_i, \tag{9}$$

is the maximal invariant subgroup of the group G, contained in subgroup G_i, and the set $\Sigma_p(G)$ of different permutations $\sigma(g)$, called the constituent set of G on a cluster p, is isomorphic with the quotient group $G/G(p)$. It follows that the positional representation P of the group G is a true representation of the constituent set $\Sigma_p(G)$.

It follows from Eq. (7) that the positional representation P is essentially a transitive permutation representation, i.e. a representation of the group G by permutations of its left cosets with respect to a subgroup G_1 (cf. Hall [4], § 5.3).

Let

$$P = \sum_{\Lambda} n(P, \Lambda)\Lambda \tag{10}$$

be the decomposition of P into irreducible representations Λ of the group G. We proceed to discuss two general features of this decomposition.

Firstly, the representation P can be extended to the group Σ_N of all permutations of N nodes of the cluster (by an ordinary extension of the definitions (5) and (6) to arbitrary permutations), and can be therefore decomposed as

$$P = \{N\} \oplus \{N-1, 1\}, \tag{11}$$

where $\{N\}$ and $\{N-1, 1\}$ denote the Young diagrams for appropriate irreducible representations of the group Σ_N. Eq. (11) follows immediately from a comparison of appropriate characters, since the character $\chi^P(\sigma)$ is given, according to Eqs. (5) and (6), by

$$\chi^P(\sigma) = \nu_1, \quad \sigma \in \Sigma_N, \tag{12}$$

whereas

$$\chi^{\{N\}}(\sigma) = 1; \quad \chi^{\{N-1,1\}}(\sigma) = \nu_1 - 1, \tag{13}$$

where ν_1 is the number of one-element cycles of the permutation σ (i.e. the number of nodes, which are invariant under σ). Under the restriction $\Sigma_N \to \Sigma(G)$, the representation $\{N\}$ becomes the unit representation A_1 of the group G, and $\{N-1, 1\}$ is, in general, reducible and requires further decomposition. It is worth noting that the latter decomposition does not involve any unit representation since

$$n(P, A_1) = \frac{1}{|G|} \sum_{g \in G} \nu_1 = \frac{1}{|G|} \sum_{i=1}^{N} |G_i| = \frac{1}{|G|} N |G_1| = 1, \tag{14}$$

so that $\{N\} = A_1$ is the only unit representation occurring in P.

Secondly, the positional representation P (or, more exactly, its member $\{N-1, 1\}$) encloses, in cases of three-dimensional clusters, the vector representation V of the group G, and in cases of plane (linear) clusters — the appropriate component of V, related to the plane (axis) of the cluster. In order to prove this statement, we express the equilibrium position for a cluster as

$$\boldsymbol{r}^0 = \sum_\alpha \varphi_\alpha \boldsymbol{e}^\alpha, \quad \varphi_\alpha \in \Pi. \tag{15}$$

Since $\boldsymbol{r}^0$ is, by definition, invariant under the group G, and the vectors $\boldsymbol{e}^\alpha$ span the vector representation V for this group, it follows that, in general, the elements φ_α also have to span the vector representation in the space Π. For exceptional cases when the cluster is placed in a plane (line), i.e. when $\boldsymbol{e}^\alpha$ span a two (one)-dimensional space, the elements φ_α have to span appropriate two (one)-dimensional space transforming under the group G like the plane (line) of the cluster. Moreover, when the point group G leaves an axis invariant (i.e. any of groups C_{nv} and their subgroups), then the positional representation of a plane cluster can also enclose that component of the vector representation, which is perpendicular to the plane of the cluster. This component coincides with $\{N\}$.

An irreducible basis for the space Π, related to the decomposition (10), can be written in a form

$$|pAt\lambda\rangle = \sum_{i=1}^{N} c^{pi}_{At\lambda} |i\rangle, \quad t = 1, 2, \ldots, n(P, A), \tag{16}$$

where p labels simple clusters, λ is a basis function for the representation A, and t — the repetition index distinguishing identical A's in P. For $A = A_1$ we have

$$c^i_{A_1 a_1} = N^{-1/2}, \tag{17}$$

since for a simple cluster the unit representation is associated with the symmetrical representation $\{N\}$ of the group Σ_N. The coefficients $c^i_{At\lambda}$ for the vector component of the positional representation can be easily determined from Eq. (15) assuming that the equilibrium position $\boldsymbol{r}^0$ of the cluster is known (cf. examples in Part II). The remaining coefficients of Eq. (16) should be determined by a projection procedure.

3. The classification scheme

According to formula (3), the mechanical representation M of the group G for a simple cluster p is a simple product

$$M = P \otimes V. \tag{18}$$

The decomposition of P into irreducible representations Λ is given by Eq. (10), and the corresponding decomposition for V can be formally written in a similar form

$$V = \sum_{\Delta} n(V, \Delta)\Delta, \tag{19}$$

(actually, we have $n(V, \Delta) \leqslant 1$ for $N > 1$). Irreducible representations enclosed in the mechanical representation are determined by the Clebsch–Gordan series

$$\Lambda \otimes \Delta = \sum_{\Gamma} c(\Lambda\Delta\Gamma)\Gamma. \tag{20}$$

The formulas (18), (10), (19), and (20) provide a complete group-theoretical classification scheme of symmetric coordinates for a given simple cluster.

The unit vectors for the symmetric coordinates can be expressed in this scheme as

$$|p, \Lambda t, \Delta d, \Gamma w\gamma\rangle = \sum_{\lambda\delta} \begin{bmatrix} \Lambda & \Delta & \Gamma & w \\ \lambda & \delta & \gamma & \end{bmatrix} |p\Lambda t\lambda\rangle\, |\Delta d\delta\rangle,$$

$$t = 1, 2, \ldots, n(P, \Lambda); \quad d = 1, 2, \ldots, n(V, \Delta); \quad w = 1, 2, \ldots, c(\Lambda\Delta\Gamma), \tag{21}$$

where the symbol in rectangular brackets is a Clebsch–Gordan coefficient associated with the series (20), the kets $|p\Lambda t\lambda\rangle$ are given by Eq. (16), and $|\Delta d\delta\rangle$'s — by a similar formula for the vector representation V. Determination of symmetric coordinates is thus reduced essentially to evaluation of the decomposition coefficients of Eq. (16), since the remaining coefficients are known in literature (e.g. Griffith [5]). The classification proposed in Eq. (21) is more complete than the ordinary one based only on Γ and γ, since it provides a sensible label for repeated representations (cf. Part II).

The position of nodes of the cluster after a deviation from their equilibrium position $\boldsymbol{r}^0$ (Eq. (15)) can be written in a form

$$\boldsymbol{r} = \boldsymbol{r}^0 + \sum b(p, \Lambda t, \Delta d, \Gamma w\gamma)\, |p, \Lambda t, \Delta d, \Gamma w\gamma\rangle, \tag{22}$$

where the sum runs over $p, \Lambda t, \Delta d, \Gamma w\gamma$, and the coefficients b are the symmetric coordinates.

Some symmetric coordinates associated with the vectors (21) allow for a general geometrical interpretation, independent of a particular cluster. The three symmetric coordinates related to $\Lambda = A_1$ correspond, by virtue of Eqs. (14), (17), and (22), to the three-dimensional translations of the whole cluster. Similarly, we can give an interpretation to coordinates $(\Lambda\Delta\Gamma)$ related to the vector constituent V of the positional representation P: since

$$V \otimes V = A_1 \oplus V' \oplus V^{(2)}, \tag{23}$$

where $V^{(2)}$ is the traceless part of the symmetric square of the vector representation, and V' is the pseudo-vector representation, it follows that for cases when V is irreducible in the group G (it occurs for those groups which have no distinguished n-fold axis for $n > 2$, i.e. for tetrahedral, octahedral, and icosahedral symmetry), the set $(\Lambda\Delta\Gamma) = (VVA_1)$ describes displacements preserving the shape of the cluster, sometimes called "the breathing mode", and the set (VVV') describes rotations of the whole cluster. The remaining sets are related to non-trivial displacements of the cluster. The breathing mode, as well as rotations of the whole cluster, can be obviously determined also for groups G with a distinguished axis; these coordinates are some linear combinations of the coordinates $(\Lambda\Delta\Gamma)$ resulting from the vector part of the positional representation.

4. A reduction of symmetry

Now we proceed to discuss the classification of symmetric coordinates symmetrised with respect to a chain of subgroups $G_c \to G$, which can be physically related to a perturbation causing a descent in symmetry from G_c to G. We consider three naturally arising reduction schemes.

(*i*) A formal reduction for the resultant representation Γ. The symmetrized basis for the mechanical representation is given here by the formula

$$|p_c, \Lambda_c t_c, \Delta_c d_c, \Gamma_c w_c, \Gamma v\gamma\rangle = \sum_{\gamma_c} a^{\Gamma_c\gamma_c}_{\Gamma v\gamma} |p_c, \Lambda_c t_c, \Delta_c d_c, \Gamma_c w_c \gamma_c\rangle,$$

$$v = 1, 2, \ldots, n(\Gamma_c, \Gamma), \tag{24}$$

where a is a standard decomposition coefficient for the restriction $\Gamma_c \to \Gamma$.

(*ii*) A formal reduction for the positional representation. Here, we reduce in the first step the positional representations Λ_c to Λ according to a formula

$$|p_c \Lambda_c t_c \Lambda \bar{v} \lambda\rangle = \sum_{\lambda_c} a^{\Lambda_c \lambda_c}_{\Lambda \bar{v} \lambda} |p_c \Lambda_c t_c \lambda_c\rangle, \tag{25}$$

repeat the same procedure for the components Δ_c, and in the next step form the desired basis $|p_c, \Lambda_c t_c \Lambda \bar{v}, \Delta_c d_c \Delta \tilde{v}, \Gamma w\gamma\rangle$ according to Eq. (21), with $|p\Lambda\lambda\rangle$ and $|\Delta d\delta\rangle$ substituted by $|p_c \Lambda_c t_c \Lambda \bar{v} \lambda\rangle$ and $|\Delta_c d_c \Delta \tilde{v} \delta\rangle$, respectively.

(*iii*) A geometric reduction. We can take into account the fact that a cluster p_c, which is simple with respect to the group G_c, ceases, in general, to be simple under a subgroup G. It can be decomposed into clusters p, each of them being simple with respect to G. Accordingly, the basis for the positional representation can be written as $|p_c p \Lambda t \lambda\rangle$. This basis can be expressed in terms of the basis (25) as

$$|p_c p \Lambda t \lambda\rangle = \sum_{\Lambda_c t_c \bar{v}} A^{\Lambda_c t_c \bar{v}}_{pt}(\Lambda, p_c)\, |p_c \Lambda_c t_c \Lambda \bar{v} \lambda\rangle, \tag{26}$$

where the coefficients $A_{pt}^{\Lambda_c t_c \bar{v}}(\Lambda, p_c)$ are independent of λ and form, for each (Λ, p_c) a unitary matrix with rows and columns labelled by $(\Lambda_c t_c \bar{v})$ and (pt) respectively. The basis for symmetric coordinates can in this case be written as

$$|p_c p, \Lambda t, \Delta_c d_c \Delta\tilde{v}, \Gamma w\gamma\rangle$$

$$= \sum_{\Lambda_c t_c \bar{v}, \lambda_c \lambda, \delta_c \delta} A_{pt}^{\Lambda_c t_c \bar{v}}(\Lambda, p_c) a_{\Lambda\bar{v}\lambda}^{\Lambda_c \lambda_c} a_{\Delta\tilde{v}\delta}^{\Delta_c \delta_c} \begin{bmatrix} \Lambda & \Delta & \Gamma & w \\ \lambda & \delta & \gamma & \end{bmatrix} |p_c \Lambda_c t_c \lambda_c\rangle\, |\Delta_c d_c \delta_c\rangle,$$

$$t = 1, 2, \ldots, n(P, \Lambda); \quad d_c = 1, 2, \ldots, n(V, \Delta_c);$$

$$\bar{v} = 1, 2, \ldots, n(\Delta_c, \Delta); \quad w = 1, 2, \ldots, c(\Lambda\Delta\Gamma), \tag{27}$$

where P stands for the positional representation for the cluster p, which is simple under the subgroup G.

The transformation between bases (*i*) and (*ii*) is given by

$$|p_c, \Lambda_c t_c, \Delta_c d_c, \Gamma_c w_c, \Gamma w\gamma\rangle = \sum_{\bar{v}\tilde{v}w} [\Lambda_c \Lambda\bar{v}, \Delta_c \Delta\tilde{v}, w_c|\Gamma_c w\Gamma v]\, |p_c \Lambda_c t_c \Lambda\bar{v}, \Delta_c d_c \Delta\tilde{v}, \Gamma w\gamma\rangle, \tag{28}$$

where $[\Lambda_c \Lambda\bar{v}, \Delta_c \Delta\tilde{v}, w_c|\Gamma_c w\Gamma v]$ is a standard reduction coefficient, defined in our work [6]. The basis (*iii*) can be expressed by the basis (*ii*) in terms of the appropriate matrix $A(\Lambda, p_c)$ defined by Eq. (26). It can be written shortly as $\langle(iii)|(ii)\rangle = A$.

5. *Final remarks and conclusions*

We have proposed in this paper a group-theoretical method for the classification and determination of symmetric coordinates for point clusters. The key observation exploited here is a possibility of expressing the mechanical representation M (cf. Eq. (1)) for a cluster as a product of the positional representation P, related to permutations of nodes of the cluster (Eqs. (2)–(6)), by the vector representation V (cf. Eq. (18)). We have discussed some general properties of the positional representation P and found that it contains exactly one unit representation of the symmetry group G of the cluster, and it moreover includes the vector representation V for this group (or its appropriate component for plane or linear clusters).

A general classification scheme for symmetric coordinates, and, at the same time, a receipt for their determination, is provided by Eq. (21). This scheme is more complete than that usually quoted in literature, based only on the resultant irreducible representation Γ, since the former allows one sometimes to label identical Γ's by different irreducible representations Λ related to the equilibrium position of the cluster. Calculations for the proposed scheme are appreciably simplified, since the use of standard Clebsch–Gordan coefficients allows one to reduce the projection procedure from a $3N$-dimensional configuration space $\mathscr{M}$ to N-dimensional positional space Π. Moreover, the above mentioned general properties of the positional representation allow one to restrict a necessary projection to an $N-4$-dimensional subspace.

We have also discussed (Section 4) some modifications of this classification scheme under a reduction of the symmetry of the cluster. We proposed three natural schemes for the corresponding chain of subgroups, and presented appropriate transformations between these schemes.

The general methods described here will be demonstrated in Part II for the case of nodes of a regular tetrahedron and a cube.

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