Implications of non-feasible transformations among icosahedral \( h \) orbitals

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The symmetric group \( S_6 \) that permutes the six five-fold axes of an icosahedron is introduced to go beyond the simple rotations that constitute the icosahedral group \( I \). Owing to the correspondence \( h \leftrightarrow d \), the calculation of the Coulomb energies for the icosahedral configurations \( h^N \) based on the sequence \( O(5) \supset S_6 \supset S_5 \supset I \) can be brought to bear on Racah’s classic theory for the atomic d shell based on \( SO(5) \supset SO_L(3) \supset I \). Among the elements of \( S_6 \) is the kalesidoscope operator \( K \) that rotates the weight space of \( SO(5) \) by \( \frac{2}{3} \). Its use explains some puzzling degeneracies in d\(^2\) involving the spectroscopic terms \(^2\)P, \(^4\)F, \(^4\)G and \(^2\)H.

One of the most enduring mysteries in the theoretical analysis of the atomic d shell was noticed over 60 years ago by Condon and Shortley \[1\]. They remarked that the spectroscopic terms \(^2\)P, \(^4\)F, \(^4\)G and \(^2\)H for SO(3) scalars \( e_i \) of Racah, he found that there were five two-electron icosahedral scalars, three of which coincide with Racah’s operators. In spite of the existence now of five operators of various strengths \( H^e \) (called molecular invariants by Oliva), it turns out that, for any choice of \( H^e \), one of the two \(^2T_1\) levels always coincides with a \(^2T_2\) level. The eigenfunction of that \(^2T_1\) level is a mixture of states that, in the atomic picture, correspond to \(^2\)P and \(^2\)H, and which therefore appear to be connected to Eqs.\[4\] and \[3\] above. Oliva speculated that an additional symmetry operation transforming \(^2\)H into \(^2\)P and vice versa should exist. It is this kind of possibility that we wish to explore in the present Letter.

Because of the correspondence \( h \leftrightarrow d \), any problem for \( h^N \) can be recast for \( d^N \). The advantage of using d electrons lies in being able to call upon the familiar theory for SO(3). Each of the two new Coulomb operators, for example, can be expressed in terms of the components of a spherical tensor \( T^{(6)} \) (this having the lowest nonzero rank that can provide an icosahedral scalar \[4\]). We write

\[
e^{(6)} = \frac{\sqrt{5}}{5} T_0^{(6)} + \frac{\sqrt{15}}{5} \left( T_5^{(6)} - T_{-5}^{(6)} \right)
\]

in which

\[
T^{(6)} = \sum_{i \neq j} \left\{ a(u_i^{(2)} v_j^{(4)})^{(6)} + b(v_i^{(4)} v_j^{(4)})^{(6)} \right\},
\]

where the reduced matrix element \( (d||v^{(k)}||d) \) for electron \( i \) or \( j \) is arbitrarily set at \( \sqrt{2k+1} \). The two operators \( e^{(6)}_2 \) and \( e^{(6)}_3 \) are defined by taking \((a, b) = (4, -2\sqrt{5})\) and \((10, 2\sqrt{5})\) respectively, and correspond to the irreducible representations \( (22) \) and \( (40) \) of SO(5). Such operators represent the effect of second-order in perturbation theory of a d-shell atom placed in an electric field of icosahedral symmetry, there being no first-order effect because an electric potential of rank 6 cannot split a d state.

If, on the other hand, we work with molecular \( h \) orbitals, the two operators \( e^{(6)}_2 \) and \( e^{(6)}_3 \) (together with \( e_0, e_1 \) and \( e_2 \)) represent the first-order Coulomb interaction between the pairs \((i, j)\) of electrons. To have an image of an \( h \) orbital, we follow Plakhutin \[7\], who constructed icosahedral \( g \) orbitals by superposing atomic s
orbitals on the 20 vertices of a dodecahedron. For \( h \) orbitals, we can reduce the basis to six pairs \( \frac{1}{\sqrt{2}}(\Psi_n + \Psi_{13-n}) \) of identical atomic s orbitals \( \Psi \) on opposite ends \((n \text{ and } 13-n)\) of the 6 five-fold axes of an icosahedron. This is shown in Fig. [1]. There is only one complication: the 6 pairs can be combined to produce the icosahedral scalar \( \sum_n \Psi_n \). The five remaining combinations have to be orthogonalized to this scalar to produce an \( h \) state.

The details of how this is done are not important because our interest lies in the permutations of the 6 axes among themselves. These operations comprise the symmetric group \( S_6 \). Among these operations are those that describe rotations of the icosahedron as a whole, so \( S_6 \supset I \). But there are many operations that twist the icosahedron out of shape and are non-feasible. The scalar \( \sum \Psi_n \) is untouched; that is, it belongs to the IR \([6]\) of \( S_6 \), in the notation of Littlewood [3]. However, the components of the \( h \) state undergo transformations that span the IRs \((10)^-\) of \( O(5) \) and \([51]\) of its subgroup \( S_5 \) [2]. Branching rules for some of the IRs of \( O(5) \) occurring in \( h^N \) are set out in Table [I].

The fact that \( I \) is isomorphic to the alternating group \( A_5 \) [10], a subgroup of \( S_5 \) and thus of \( S_6 \) too, allows us to include it in the sequence

\[
O(5) \supset S_6 \supset S_5 \supset I,
\]

which can be considered an alternative to the more familiar scheme

\[
SO(5) \supset SO(3) \supset I.
\]

The IRs of \( S_5 \) contained in a particular IR \([\lambda]\) of \( S_6 \) can be found by interpreting \([\lambda]\) as a Young tableau and then removing from it a single cell in all possible ways that leave an acceptable shape, with the proviso that the automorphism of \( S_5 \) that produces the interchanges

\[
[51] \leftrightarrow [2^3], \ [41^2] \leftrightarrow [31^3], \ [3^2] \leftrightarrow [2^4^1]
\]

be carried out first, if \([\lambda]\) appears in \([3]. \) As an example of the alternative schemes \([3] \) and \([4] \), we express the linear combination

\[
p\{\frac{2}{5} -2\} + q\{\frac{1}{5} -1\} + r\{\frac{1}{5} +1\} + q\{-\frac{1}{5} -1\} + p\{-\frac{2}{5} -2\}
\]

of Slater determinants for the four states

\[
|d^2(20)^3D^H\rangle, \ |d^2(20)^1G^H\rangle,
\]

\[
|h^2(20)^+ [51][2^2]1^1^H\rangle, \ |h^2(20)^+ [42][32]1^2H\rangle
\]

by the respective specifications

\[
(p, q, r) = \begin{cases} \frac{1}{\sqrt{2}}(-2, -1, 2) , & \frac{1}{\sqrt{2}}(1, 4, 6) , \\ \frac{1}{\sqrt{2}}(-1, 1, 4) , & \frac{1}{2}(1, 1, 0) . \end{cases}
\]

In our analysis of \( g \) orbitals [1], we introduced the kaleidoscope operator \( \mathcal{K} \) which rotates the SO(4) weight space by \( \frac{\pi}{2} \) and which interchanges the \( T_1 \) and \( T_2 \) states. The SO(5) weight space is very similar to that for SO(4), and we define \( \mathcal{K} \) in the present case by its action on the components \( h^1_m \) of the orbital creation tensor \( h^1 \):

\[
\mathcal{K}h^1_m\mathcal{K}^{-1} = h^1_{\pm m}, \quad \mathcal{K}h^1_0\mathcal{K}^{-1} = -h^1_0 ,
\]

\[
\mathcal{K}h^1_{\pm 1}\mathcal{K}^{-1} = h^1_{\mp 1} , \quad \mathcal{K}h^1_{\pm 2}\mathcal{K}^{-1} = -h^1_{\mp 2} , \quad \mathcal{K}h^1_{\pm 3}\mathcal{K}^{-1} = h^1_{\mp 3} , \quad \mathcal{K}h^1_{\pm 4}\mathcal{K}^{-1} = -h^1_{\mp 4} , \quad \mathcal{K}h^1_{\pm 5}\mathcal{K}^{-1} = h^1_{\mp 5} .
\]

The five weights \((-2 \leq m \leq 2\) are again rotated by \( \frac{\pi}{2} \), as can be seen by inspecting the labels \( m \) of the root vectors [2]. The phases in Eq. (14) have been chosen, first, to preserve the anticommutation relations for fermions when each \( h^1_m \) is replaced by \( h^1_m (= (-1)^m h_{-m}) \); and, second, to give the usual phases for the time-reversal operator \( \mathcal{T} \) when we interpret it as \( \mathcal{K}^2 \). As in the \( g \)-orbital case, the \( \mathcal{K} \) transformation changes \( m \) to \( 3m \text{mod} 5 \), and, for many-electron states, \( M_L \) to \( 3M_L \text{mod} 5 \). It again interchanges the states \( T_1 \) and \( T_2 \), and we can now see that there must be as many \( T_1 \) as \( T_2 \) states for any \( h^N \), a result that is not obvious when the SO(3) basis is used. As for the states \([11]\), \( \mathcal{K} \) sends the first into itself and reverses the sign of the second; while the Russell-Saunders states \([10]\) merely become mixed.

The icosahedral scalars that appear in the Hamiltonian fall into four categories. They belong to \([6][5]A, [2^3][5]A, [3^2][1^5]A \) or \([1^6][1^5]A \). The first two are invariant under the \( \mathcal{K} \) transformation, while the last two change sign. The \( \mathcal{K} \) operation belongs to the class \((1^24) \) and \((14) \) of \( S_6 \) and \( S_5 \) (in the notation of Littlewood [8]), but it does not belong to \( I \). The characters of \( S_6 \) or \( S_5 \) indicate whether the \( A \) component (for which \( M_L \equiv 0 \text{mod} 5 \) ) is invariant or changes sign. We can now use \( S_6 \) and \( S_5 \) to recast the three Coulomb operators \( e_2, e_2^{(6)} \) and \( e_3^{(6)} \). The first two belong to the IR \((22)^+ \) of \( O(5) \), which, from Table [II] can be combined into operators belonging to \((2^3)[5]A \) and \((3^2)[1^5]A \). They are given by \( \frac{1}{7}(e_2 + 15^{(6)} e_2) \) and \( \frac{1}{4}(e_2 - 3e_2^{(6)}) \) respectively. The \( S_5 \) descriptions account for their non-vanishing matrix elements often taking complementary block forms. The exception is the \( T_{1,2} \) states; they belong to the self-conjugate IR \([31^2] \) of \( S_5 \), which allows both the scalar \([5] \) and the pseudo-scalar \([1^5] \) to be non-vanishing at the same time. The operator \( e_3^{(6)} \) belongs to \((40)^+[6][5] \), and is therefore diagonal in the \( S_6 \) basis. This operator \( e_3^{(6)} \), as well as \( e_0, e_1 \) and \( e_2 + \frac{15}{7}^{(6)} e_2 \), are all invariant under \( \mathcal{K} \); hence we would have three pairs of \( T_{1,2} \) degenerate levels if they were the only operators in the Hamiltonian. The presence of the remaining operator \( e_2 - 3e_2^{(6)} \) breaks this symmetry, but incompletely; leaving us a single \( T_{1,2} \) degeneracy as found by Oliva [1].

It sometimes happens that the \((S_6, S_5) \) classification of a state coincides with that provided by SO(3). In \( h^3 \), for example, the \( 4^P \) term can be labelled by \([31^3][31^2]T_1 \) (see the first column of Table [II]). An unexpected double
labelling occurs for $^2\text{F}$ and $^2\text{H}$ terms, whose $T_2$ components are $[321][31^2]$ and $[41^2][31^2]$ respectively. To prove this, we first combine the two equations (with $M_L = 0$ specified)

$$K|d^{2\text{F}}\rangle = -|d^{2\text{P}}\rangle, \quad K|d^{2\text{P}}\rangle = |d^{2\text{F}}\rangle$$

(15)

with the invariance of $(h^\dagger h)^{[51]}_0$ and the non-vanishing $[31]$ of the icosahedral Clebsch-Gordan coefficient $(T_10, H0/T_20)$ to show that

$$([41^2]T_1 + [51]H) | [41^2]T_2 \rangle = 0,$$

(16)

using the notation of Racah $[3]$ for the isoscalar factor. It remains to make the correspondence

$$h^{[51]} | h^2[41^2]T_1 \rangle \leftrightarrow d^\dagger | d^{2\text{P}}\rangle$$

(17)

and note that the only state on the left that can contain $^2T_2$ is $[321]$, since the only other possibility that $[51] \times [41^2]$ can give rise to is $[41^2]$ (see $[4]$, and this is excluded by $[3]$. On the right of $[17]$, however, no $^2\text{H}$ can be produced from angular momenta of 2 and 1; and so the missing term $[41^2]T_2$ is purely $^2\text{H}$, and $[321]T_2$ can only belong to the remaining source, namely $^2\text{F}$.

The $L$-purity of the $^2T_2$ states of $h^2$ leads to an explanation for Eqs. (4) and (6). The branching $[6]$ for the IR $(30)^4$ of O(5) yields the labels $[2]^4[5]A$ and $[16]^4[5]A$ for the two combinations $t_3 - 10t_6^1$ and $t_3 + 18t_6^1$ given in Table II. Now

$$\langle F[321] | t_3 + 18t_6^1 | H[41^2] \rangle = 0$$

(18)

because $[16]^4 \times [41^2]$ does not contain $[321]$. Also, $\langle F|t_3\rangle = 0$ for the $SO(3)$ scalar $t_3$. So both parts of the operator in $[6]$ yield zero, and so must the combination

$$C = \frac{9}{14}(t_3 - 10t_6^1) - \frac{5}{14}(t_3 + 18t_6^1),$$

(19)

which becomes $t_3$ under the $K$ transformation. Thus

$$0 = \langle [321][312^2T_1 | t_3 | [411][31^2T_1]\rangle = (\alpha^2\text{PT}_1 + \beta^2\text{HT}_1)) t_3 (\beta^2\text{PT}_1 - \alpha^2\text{HT}_1)$$

$$= \alpha^2 (\langle [3] | t_3 | ^2\text{P}\rangle - \langle [2] | t_3 | ^2\text{H}\rangle).$$

(20)

Neither $\alpha$ nor $\beta$ is zero (being in fact $\sqrt{2/7}$ and $\sqrt{5/7}$), so Eq. (2) is recovered. A similar analysis for the $G$ states coming from $^2\text{F}$ and $^2\text{G}$ yields Eq. (3).

The success of this analysis suggests that it could be repeated to obtain Eq. (5). However, the analog of Eq. (5) cannot come directly from $S_6$ because the required null matrix element, although appearing in Table I, is not a consequence of a selection rule for the IRs of $S_6$. However, $S_6$ immediately yields Eq. (6) for $c_6^4$, indicating that all we need to do is prove this equation for either of the two operators prefixed by $a$ and $b$ in Eq. (6). If we pick the second and separate both this operator and the two states $^2\text{F}$ and $^2\text{H}$ into spin-up and spin-down parts (distinguished by the symbols $A$ and $B$ [14]), we are ultimately led to calculate a matrix element of the form

$$\langle (P_A d_B) F | (A_B (1^4) B_1^4) | (P_A d_B) H \rangle.$$  

(21)

This is proportional to the vanishing 9-\(j\) symbol

$$\begin{pmatrix} 1 & 2 & 3 \\ 4 & 4 & 6 \\ 3 & 2 & 5 \end{pmatrix} = 0,$$

(22)

and so justifies our again following the procedure starting with the analog of Eq. (18).

What the above analysis shows is that insight into the properties of a free atom, which are based on $SO(3)$ symmetry, can be gained by using the intrinsic icosahedral symmetry of $SO(3)$ and, more significantly, the spatial distortions associated with the group $S_6$ that permutes the axes of the icosahedron. We are reluctant to assert that any aspect of the theory we have presented can be thought of as being caused by another part, since the theory forms an interlocking whole. Nevertheless, it is remarkable that some long-standing puzzles in the classical theory of atomic structure should receive explanations when $S_6$ is brought into play.

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FIG. 1. Atomic s orbitals on the vertices of an icosahedron.

TABLE I. Branching rules for some IRs $W$ of O(5) into IRs $[\lambda]$ of $S_6$. The signs attached to the IRs of SO(5) indicate the proper (+) or improper (−) nature of the rotations.

| $W$  | $[\lambda]$ | $W$  | $[\lambda]$ |
|------|-------------|------|-------------|
| (00)$^+$ | [6] | (00)$^-$ | [1$^6$] |
| (10)$^+$ | $[21]^4$ | (10)$^-$ | [51] |
| (11)$^+$ | $[41]^2$ | (11)$^-$ | $[31]^3$ |
| (20)$^+$ | $[42][51]$ | (20)$^-$ | $[21]^4[2^21^2]$ |
| (21)$^+$ | $[2^21^2][31]^3[321]$ | (21)$^-$ | $[321][41]^2[42]$ |
| (22)$^+$ | $[3^3][321][3^2][42]$ | (22)$^-$ | $[2^41^2][2^3][321][3^2]$ |
TABLE II. Some Coulomb matrix elements for the configuration $h^3$.

| Term     | IRs of mixtures scheme (6) | $(22)^+ [222] [5] A$ | $(22)^+ [33] [1^5] A$ | $(40)^+ [6] [5] A$ |
|-----------|---------------------------|----------------------|----------------------|----------------------|
| $^4F$     | $(11)^- [31]^3 [41]^4 G$  | $- \frac{3}{2}$      | 0                    | 0                    |
| $^4P$     | $(11)^- [31]^3 [31]^2 [1^5] T_1$ | 3                    | 3                    | 0                    |
| $^4F$     | $(11)^- [31]^3 [31]^2 [4^1] T_2$ | 3                    | -3                   | 0                    |
| $^2D$     | $(10)^- [51]^2 [2^1] [2^1]^2 H$ | $0 \quad 3\sqrt{6} \quad 0 \quad 0$ | $0 \quad 0 \quad \frac{6\sqrt{6}}{5} \quad \frac{18}{5}$ | 0                    |
| $^2D, G, H$ | $(21)^- [321] [2^1] [2^1]^2 H$ | $3\sqrt{6} \quad -\frac{3}{2} \quad 0 \quad 0$ | $0 \quad 0 \quad \frac{6\sqrt{6}}{5} \quad \frac{18}{5}$ | 5                    |
| $^2D, G, H$ | $(21)^- [321] [32]^2 H$ | $0 \quad 0 \quad -\frac{39}{2} \quad 3\sqrt{6}$ | $0 \quad 0 \quad \frac{6\sqrt{6}}{5} \quad \frac{18}{5}$ | 5                    |
| $^2D, G, H$ | $(21)^- [42] [32]^2 H$ | $0 \quad 0 \quad 3\sqrt{6} \quad -\frac{3}{2}$ | $0 \quad 0 \quad \frac{6\sqrt{6}}{5} \quad \frac{18}{5}$ | $-\frac{20}{3}$ |
| $^2F, G$  | $(21)^- [41]^2 [21]^3 G$ | $\frac{2}{3} \quad 0$ | $0 \quad \sqrt{15}$ | -2 |
| $^2F, G$  | $(21)^- [42] [41]^2 G$ | $0 \quad -\frac{1}{2}$ | $\sqrt{15} \quad 0$ | $-\frac{20}{3}$ |
| $^2P, H$  | $(21)^- [321] [32]^2 [2^1] T_1$ | $\frac{2}{3} \quad 0$ | $-3 \quad 0$ | 5 |
| $^2P, H$  | $(21)^- [41]^2 [31]^2 [2^1] T_1$ | $0 \quad -3$ | $0 \quad 0$ | -2 |
| $^2F$     | $(21)^- [321] [31]^2 [2^1] T_2$ | $\frac{2}{3} \quad 0$ | $3 \quad 0$ | 5 |
| $^2H$     | $(21)^- [41]^2 [31]^2 [2^1] T_2$ | $0 \quad -3$ | $0 \quad 0$ | -2 |

TABLE III. Some matrix elements for the operators $t_3$ and $t_4^{(6)}$ in $h^3$.

| IRs scheme (6) | $(30)^+ [222] [5] A$ | $(30)^+ [1^6] [1^5] A$ |
|----------------|----------------------|----------------------|
| $(21)^- [41]^2 [21]^3 G$ | $-2 \quad 0$ | $0 \quad 0$ |
| $(21)^- [42] [41]^2 G$ | $0 \quad -2$ | $0 \quad 0$ |
| $(21)^- [321] [31]^2 [2^1] T_1$ | $-\frac{3}{2} \quad 0$ | $3 \quad 0$ |
| $(21)^- [41]^2 [31]^2 [2^1] T_1$ | $0 \quad -\frac{1}{2}$ | $0 \quad 0$ |
| $(21)^- [321] [31]^2 [2^1] T_2$ | $-\frac{3}{2} \quad 0$ | $-3 \quad 0$ |
| $(21)^- [41]^2 [31]^2 [2^1] T_2$ | $0 \quad -\frac{1}{2}$ | $0 \quad 0$ |