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ON THE OPERATOR EQUIVALENTS

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A closed polynomial formula for the qth component of the diagonal operator equivalent of order k is derived in terms of angular momentum operators. The interest in various fields of molecular and solid state physics of using such a formula in connection with symmetry adapted operator equivalents is outlined.

The operator equivalents method was introduced by Stevens [1] for calculating matrix elements of Cartesian polynomials acting within a manifold $\varepsilon(\tau j) = \{ | \tau j m > ; m \}$ of given angular momentum j. The method consists in replacing u (= x, y, z) by the angular momentum operator J_u modulo the necessary symmetrizations. It has been of invaluable help in the interpretation of magnetic resonance (EPR or ENDOR) and optical data for transition-metal and rare-earth ions [2, 3]. The operator equivalents are still useful in the theory of magnetism [3, 4]. They may be used also in conjonction with density matrix techniques applied to interatomic collisions [5], relaxation for impurities in solids [6], and possibly polarization tensors for nuclear reactions.

There are now numerous tables [2, 3] of (diagonal) operator equivalents in either the tesseral Harmonics (i.e., Stevens') form $O_k^q(J)$ or the spherical Harmonics (i.e., Buckmaster's) form $T_{kq}(J)$. Recently, a closed-form expression [7] and a method based on a recursive relation [8] have been proposed for obtaining $T_{kq}(J)$. The latter two ways of deriving $T_{kq}(J)$ lead to specific expressions generally far from being closely related to the ones appearing in the existing tables. Furthermore, the expression obtained by Caola [7] turns out to be defined in the quotient field of the enveloping algebra of SU_2, a fact that prevents the expression to be easily manipulated and that may give rise to some difficulty when studying transformation properties of $T_{kq}(J)$.

It is one of the aims of this letter to report a formula for

$$u^k_q(J) = \left[2^k (2k)! \ (2j-k)! \ / (2j+k+1)! \right]^{1/2} T_{kq}(J) / k!$$

defined in the enveloping algebra of SU_2, as it should be, and which presents the (further) advantage of being a generalization of the particular expressions tabulated in the literature. The normalization chosen here makes that $u^k_q(J)$ identifies with the qth component of the Racah unit tensor u^k as far as matrix elements are concerned.

In the case $q \geqslant 0$, the formula reads

$$u^k_q(J) = \left[\frac{(k-q)!}{(k+q)! \ (2j-k)! \ (2j+k+1)!} \right]^{1/2} (-)^{k+q} J_+^q \left[(-)^q \frac{(2j-q)! \, (k+q)!}{q! \, (k-q)!} \right.$$

$$\left. + (1-\delta_{kq}) \sum_{z=q+1}^{k} (-)^z \frac{(2j-z)! \ (k+z)!}{z! (k-z)! (z-q)!} \prod_{t=1}^{z-q} (j+J_z+q-z+t) \right], \quad q \geqslant 0. \quad (1)$$

The formula for $q < 0$ may be derived from (1) with the help of the Hermitian conjugation property $u^k_{-q}(J) = (-)^q u^k_q(J)^\dagger$. Alternatively, $u^k_{q<0}(J)$ may be obtained by changing q, J_+, and J_z into $-q$, $-J_-$, and $-J_z$, respectively, in the r h s of (1) and by multiplying the expression so-obtained by $(-)^{k+q}$. In other words

$$u^k_q(J) = \left[\frac{(k+q)!}{(k-q)! \ (2j-k)! \ (2j+k+1)!} \right]^{1/2} (-)^q J_-^{-q} \left[(-)^q \frac{(2j+q)! \ (k-q)!}{(-q)! \ (k+q)!} \right.$$

$$\left. + (1-\delta_{k,-q}) \sum_{z=-q+1}^{k} (-)^z \frac{(2j-z)! \ (k+z)!}{z! \ (k-z)! \ (z+q)!} \prod_{t=1}^{z+q} (j-J_z-q-z+t) \right], \quad q \leqslant 0. \quad (2)$$

Equations (1-2) provide a formula for $T_{kq}(J)$ which may be worked out very easily. [Compare (1-2) to the other means of obtaining $T_{kq}(J)$.] As a special case, (1-2) lead to $T_{kk}(J) = (-)^k \sqrt{1/2^k} \ J_+^k$ and $T_{k-k}(J) = \sqrt{1/2^k} \ J_-^k$, a well-known result. As a more elaborated example, let us seek $T_{74}(J)$. From (1), we get

$$T_{74}(J) = 7!\left[\frac{(2j+8)!}{2^7\ 14!\ (2j-7)!}\right]^{1/2}\left[\frac{3!}{11!\ (2j-7)!\ (2j+8)!}\right]^{1/2}(-J_+^4)$$

$$\left[\frac{(2j-4)!\ 11!}{4!\ 3!} - \frac{(2j-5)!\ 12!}{5!\ 2!\ 1!}(j+J_z) + \frac{(2j-6)!\ 13!}{6!\ 1!\ 2!}(j+J_z-1)(j+J_z) - \frac{(2j-7)!\ 14!}{7!\ 0!\ 3!}(j+J_z-2)(j+J_z-1)(j+J_z)\right]$$

which can be rearranged to give

$$T_{74}(J) = \frac{1}{4}\sqrt{\frac{7}{26}}\ J_+^4\,(13J_z^3 + 78J_z^2 + 179J_z - 3J_zJ^2 - 6J^2 + 150),$$

in agreement with [3].

We prefer here discussing around various areas of applicability of (1-2) rather than detailing the proof. [The detailed proof of (1-2) is available from the authors.] Let us just mention that in order to verify (1), it is sufficient to prove that the matrix elements, on $\varepsilon(\tau j)$, of $u_q^k(J)$ as given by (1) yield an expression that can be converted to the (little-known) formula of Majumdar [9] for $\langle jkmq \mid jm+q\rangle / \sqrt{2j+1}$. Note that the same kind of proof is applicable equally well to the off-diagonal operator equivalent $t_{kq\alpha}(J, K)$ [10] recently investigated by many people [11]. Nevertheless, the proof is considerably more complicated and more technical in the off-diagonal case. The obtained formulas involve the 10 generators of the Schwinger algebra (i.e., 3 spherical angular momentum operators J, 3 hyperbolic angular momentum operators K, and 4 combinations of the 6 preceding ones) and will be the subject of a pending publication.

We now go to some general considerations concerning the $u_q^k(J)$'s and related quantities. In the physical applications, the operator equivalents of interest are most of the time symmetry adapted linear combinations of the $u_q^k(J)$'s rather than the $u_q^k(J)$'s themselves. Let

$$u_\mu^k(J) = \sum_q u_q^k(J) \langle kq \mid k\mu\rangle$$

be the μ th symmetry adapted (diagonal) operator equivalent of order k. Here μ stands for a collective label comprizing irreducible representations classes and branching multiplicity indices for a chain $G_1 \supset G_2 \supset \ldots$ of (point) subgroups of O_3. The $(2k+1) \times (2k+1)$ matrix of elements $\langle kq \mid k\mu \rangle$ allows to pass from the $O_3 \supset O_2$ scheme to the $O_3 \supset G_1 \supset G_2 \supset \ldots$ scheme. The diagonal operator equivalents adapted to the chain $G_1 \supset G_2 \supset \ldots$ play an important role in Wigner-Racah calculus. First, we have the Lie product :

$$\left[u^{k_1}_{\mu_1}(J),\ u^{k_2}_{\mu_2}(J) \right] = \sum_{k_3 \mu_3} (-)^{2j-k_3} \left[1 - (-)^{k_1+k_2+k_3} \right] (2k_3+1) \begin{Bmatrix} k_3 & k_1 & k_2 \\ j & j & j \end{Bmatrix} f\begin{pmatrix} k_3 & k_1 & k_2 \\ \mu_3 & \mu_1 & \mu_2 \end{pmatrix} u^{k_3}_{\mu_3}(J),$$

where f is a coupling coefficient for the chain $O_3 \supset G_1 \supset G_2 \supset \ldots$ [12]. Consequently, the $u^k_\mu(J)$'s with $k \leq 2j$ may be used for generating the Lie algebra of some subgroup of $GL(2j+1)$, a result of considerable importance in nuclear, atomic, and molecular physics. Second, the (Hilbert-Schmidt) scalar product :

$$\mathrm{tr}_{\varepsilon(\iota j)}\ u^k_\mu(J)^\dagger\ u^{k'}_{\mu'}(J) = \delta_{kk'}\ \delta_{\mu\mu'} / (2k+1)$$

shows that $\{ u^k_\mu(J)\ ;\ k\mu \}_{k \leq 2j}$ is a set of mutually orthogonal operators on the space $\varepsilon(\iota j)$. As a consequence, the $u^k_\mu(J)$'s with $k \leq 2j$ may be used for constructing a symmetry adapted Hamiltonian acting on $\varepsilon(\iota j)$; the orthogonality property of the $u^k_\mu(J)$'s ensures mutual independence of the corresponding (fitted) parameters. Along that vein, it has been shown how the symmetry adapted operator equivalents render easier the construction, the study of the transformation properties, and the diagonalization of a generalized spin Hamiltonian [13].

Among the various diagonal operator equivalents adapted to the chain $G_1 \supset G_2 \supset \ldots$, the equivalents $u^k_{\ldots\Gamma_o\ldots}(J)$ invariant with respect to $G_i \equiv H$ appear to be of central importance for the state labelling problem [14-16]. [Here Γ_o stands for the identity representation class of H.] In many cases, $u^k_{\ldots\Gamma_o\ldots}(J)$ is pseudo-invariant with respect to the supergroup $G_{i-1} \equiv G$ of H. By a G pseudo-invariant operator equivalent of order k associated with the irreducible representations class

Γ of G, we mean an H invariant $u^k_{\ldots\Gamma\Gamma_o\ldots}(J)$ satisfying

$$P_R \, u^k_{\ldots\Gamma\Gamma_o\ldots}(J) \, P_R^{-1} = \chi^\Gamma(R) \, u^k_{\ldots\Gamma\Gamma_o\ldots}(J) \quad \forall R \in G ,$$

where χ^Γ denotes the irreducible character relative to Γ. Then, $u^k_{\ldots\Gamma\Gamma_o\ldots}(J)$ may be used as a state labelling operator. The labelling operators enter into the theory of level splitting applied either to the electronic spectroscopy of partly filled shell ions in molecules and solids [16] or to the vibration-rotation spectroscopy of symmetric-top molecules [17, 18]. In particular, the mathematical spectra of the cubical invariant $u^4_{A_1}(J)$ of order 4 has been recently discussed in connection with high-resolution spectroscopy of tetrahedral XY_4 and octahedral XY_6 molecules [17]. The levels of $u^4_{A_1}(J)$ exhibit a clustering phenomenon in the limit of high j values. A similar clustering phenomenon and unexpected symmetries have been pointed out by the present authors for the levels, corresponding to a not necessarily high value of j, of various cubical, tetragonal, and orthorhombic invariants. In a forthcoming paper [18], the (exact) symmetries of the spectra of such H invariants shall be explained through a generalized Wigner theorem valid for G pseudo-invariant operators. In addition, the qualitative structure of the clusters shall be clarified on the basis of the induced representations technique. Finally, simple perturbation calculations shall be achieved to predict semi-quantitatively the cluster positions.

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