TENSOR ELEMENTS OF THE MOLECULAR ELECTRIC MULTIPOLE MOMENTS FOR ALL POINT GROUP SYMMETRIES

S. KIELICH* and R. ZAWODNY
Institute of Physics, A. Mickiewicz University, Poznań, Grunwaldzka 6, Poland

Received 26 July 1971
Revised manuscript received 24 September 1971

Tables of non-zero tensor elements of the electric quadrupole, octupole and hexadecapole moments for all point groups are given, with examples of their application to numerical calculations of molecular fields and potential energies of multipolar interaction.

Whereas the literature [1] gives predominantly the number of independent tensor elements of multipole (dipole, quadrupole, octupole, hexadecapole, etc.) moments for 40 point groups, the non-zero elements of these multipoles have been published explicitly for certain cases only (i.e., for the axial [1,2], tetrahedral [3] and octahedral [4] symmetries). Since in recent years various methods have been developed for the numerical determination of quadrupole [1,2,5], octupole [3,6–8] and hexadecapole [4,9] moments of simple molecules, the necessity was felt of proposing in explicit form all the non-zero elements of multipole tensors for 51 point groups. This is the aim of this communication.

Quite generally, the 2^n-pole electric moment of an arbitrary charge distribution can be defined as the nth rank symmetric tensor [10,11]:

$$\mathbf{M}^{(n)} = \sum_i e_i r_i^n \mathbf{Y}^{(n)}(\boldsymbol{r}_i) , \tag{1}$$

where e_i is the ith electric charge of the molecule, and $\boldsymbol{r}_i$ its radius vector. The tensorial operator of nth rank

$$\mathbf{Y}^{(n)}(\boldsymbol{r}_i) = \{(-1)^n/n!\} r_i^{n+1} \boldsymbol{\nabla}^n (1/r_i) ,$$

is to be found in previous papers [6,11]; $\boldsymbol{\nabla}$ is the space differential operator.

The 2^n-pole moment tensor defined by (1) occurs in numerous problems of molecular physics, e.g., in the multipole potential energy of a system of charges in an external electrostatic field E [11]:

$$U(E) = -\sum_{n=0}^{\infty} \{2^n n!/(2n)!\} \mathbf{M}^{(n)} [n]\, \mathbf{E}^{(n)} , \tag{2}$$

where the symbol $[n]$ in Jansen's [10] notation denotes n-fold contraction of the product of the two nth rank tensors $\mathbf{M}^{(n)}$ and $\mathbf{E}^{(n)}$. Above, $\mathbf{E}^{(n)} = -\boldsymbol{\nabla}^n \varphi(\boldsymbol{r})$ is an external electric field of nth order, with $\varphi(\boldsymbol{r})$ the external potential at $\boldsymbol{r}$.

* Present address, University of Bordeaux I, 33-Talence, France.

Similarly to the multipolar expansion (2), one has for the potential energy of electrostatic interaction of two multipole molecules [6,10,11]:

$$U_{pq} = -\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} (-1)^m \{2^{n+m} n!m!/(2n)!(2m)!\} \mathbf{M}_p^{(n)} [n]^{(n)}\mathbf{T}_{pq}^{(m)} [m] \mathbf{M}_q^{(m)} , \tag{3}$$

where the tensor of rank $n+m$

$${}^{(n)}\mathbf{T}_{pq}^{(m)} = -\boldsymbol{\nabla}^{n+m}(1/r_{pq}) = (-r_{pq})^{-(n+m+1)}\mathbf{Y}^{(n+m)}(r_{pq}) ,$$

describes the (2^n-pole) – (2^m-pole) type interactions between molecules p and q, possessing electric multipoles $\mathbf{M}_p^{(n)}$ and $\mathbf{M}_q^{(m)}$ respectively.

With the general definition of the multipole tensor (1), we define the molecular electric field of degree n [6,10]:

$$\mathbf{F}_p^{(n)} = \sum_{m=1}^{\infty} (-1)^m \{2^m m!/(2m)!\} \, {}^{(n)}\mathbf{T}_{pq}^{(m)} [m] \mathbf{M}_q^{(m)} , \tag{4}$$

existing at the centre of molecule p due to the electric multipoles of molecule q.

Electric multipole tensors occur moreover in the higher-order inductional and dispersional energies discussed elsewhere [11,12].

Tables 1, 2 and 3 contain all the non-zero tensor elements of the quadrupole, octupole and hexadecapole moments for all point groups derived by group theory [13]. The number of independent elements of a polar tensor of arbitrary rank for group $G\{g_1, g_2, ..., g_N\}$ is given by the formula [13,14]:

$$I = (1/N) \sum_{g_i \in G} \chi^0(g_i) , \tag{5}$$

where

$$\chi^0(g_i) = (1/N_P) \sum_{p \in P} \chi(g_i^{l_1})\chi(g_i^{l_2}) \dots \chi(g_i^{l_\sigma}) \tag{6}$$

and $\chi(g_i)$ are characters of g_i, respectively, in tensor representation taking into account the permutational group of indices P, and in the reducible vector representation of G. The summation in (5) extends over all the elements of the group (numbering N), and in (6) over all N elements of the permutational group P. By l_i, we denote the lengths of the cycles into which the permutation of indices $p \in P$ (element of the permutational group P) decomposes. The linear combinations of tensor elements belonging to distinct irreducible representations of group G were determined by means of Wigner's projection operator [15]:

$$\hat{O} = (f_\alpha/N) \sum_{g_i \in G} \chi^\alpha(g_i)\hat{g}_i , \tag{7}$$

where f_α and $\chi^\alpha(g_i)$ denote respectively the dimension of the irreducible representation α of G and the character of the group element g_i in this representation. Eqs. (5) and (7) served for finding the transformational properties of the tensor of electric quadrupole $\Theta_{\alpha\beta}$, octupole $\Omega_{\alpha\beta\gamma}$, and hexadecapole $\Phi_{\alpha\beta\gamma\delta}$ moments which provided the basis for determining the relations between their non-zero elements. These relations are assembled in tables 1–3.

We denote by $M_{i_1 \dots i_n}^{(n)}$ the multipole moment tensor elements (1) in a given system of coordinate axes, and by $M_{\alpha_1 \dots \alpha_n}^{(n)}$ those in the coordinate system in which the molecular symmetry is investigated; the transformation from the one system to the other is now:

Table 1
Non-zero and independent tensor elements of the electric quadrupole moment $\Theta_{\alpha\beta}$ for all point groups. Each element is denoted by its subscripts x, y, z only. N is the number of non-zero tensor elements, I that of independent tensor elements. Elements shared by various point groups are assembled under a capital letter

Groups C_1 and C_i :	$N = 9,\ I = 5$ $A \equiv xx,\quad C \equiv xy = yx,\quad D \equiv xz = zx,$ $B \equiv yy,\quad E \equiv yz = zy,\quad F \equiv zz = -(xx + yy).$
Groups C_s, C_2, C_{2h} :	$N = 5,\ I = 3$ elements A, B, C and F.
Groups C_{2v}, D_2, D_{2h} :	$N = 3,\ I = 2$ elements A, B and F.
Groups C_4, S_4, C_{4h}, C_{4v}, D_{2d}, D_{4h}, D_4, C_3, S_6, C_{3v}, D_3, D_{3d}, C_{3h}, C_6, C_{6h}, D_{3h}, C_{6v}, D_6, D_{6h}, D_{4d}, C_5, C_{5v}, C_{5h}, D_5, D_{5h}, D_{5d}, D_{6d}, S_8, S_{10}, S_{12}, C_∞, $C_{\infty v}$, $C_{\infty h}$ and $D_{\infty h}$:	$N = 3,\ I = 1$ elements $A = B$ and F.

In point groups T, T_h, O, O_h, Y, Y_h, T_d, K and K_h all tensor elements vanish.

Table 2
Non-zero and independent tensor elements of the electric octupole moment $\Omega_{\alpha\beta\gamma}$ for all point groups

Group C_1 :	$N = 27,\ I = 7$	
	$G \equiv xyy = yyx = yxy,$	$K \equiv xxz = zxx = xzx,$
	$H \equiv xxy = yxx = xyx,$	$L \equiv yyz = zyy = yzy,$
	$J \equiv xyz = xzy = yxz = yzx = zxy = zyx,$	
	$M \equiv xzz = zzx = zxz,$	$P \equiv yzz = zzy = zyz,$
	$Q \equiv xxx = -(xyy + xzz),$	$R \equiv yyy = -(xxy + yzz),$
	$S \equiv zzz = -(xxz + yyz).$	
Group C_s :	$N = 14,\ I = 4$	elements G, H, M, P, Q and R.
Group C_2 :	$N = 13,\ I = 3$	elements J, K, L and S.
Group C_{2v} :	$N = 7,\ I = 2$	elements K, L and S.
Groups D_2, D_{2d}, T, T_d :	$N = 6,\ I = 1$	element J.
Groups C_4, C_{4v}, C_6, C_{6v}, $C_{\infty v}$, C_∞, C_5, C_{5v} :	$N = 7,\ I = 1$	elements $K = L$ and S.
Group S_4 :	$N = 12,\ I = 2$	elements $K = -L$ and J.
Group C_3 :	$N = 15,\ I = 3$	
	$V \equiv xxx = -xyy = -yxy = -yyx,$	
	$U \equiv yyy = -yxx = -xyx = -xxy,$	
	$K = L$ and S.	
Group C_{3v} :	$N = 11,\ I = 2$	elements $K = L$, U and S.
Group D_3 :	$N = 4,\ I = 1$	element V.
Group C_{3h} :	$N = 8,\ I = 2$	elements V and U.
Group D_{3h} :	$N = 4,\ I = 1$	element V.

In point groups C_i, C_{2h}, D_{2h}, C_{4h}, D_4, D_{4h}, S_6, D_{3d}, C_{6h}, D_6, D_{6h}, D_{4d}, C_{5h}, D_5, D_{5h}, D_{5d}, D_{6d}, S_8, S_{10}, S_{12}, T_h, O, O_h, $C_{\infty h}$, $D_{\infty h}$, Y, Y_h, K and K_h all tensor elements vanish.

$$M^{(n)}_{i_1 \ldots i_n} = c_{i_1\alpha_1} \cdots c_{i_n\alpha_n} M^{(n)}_{\alpha_1 \ldots \alpha_n} \tag{8}$$

with $c_{i_1\alpha_1}$ the direction cosine between axes i_1 and α_1 of the two systems.

Inserting the appropriate non-zero tensor elements of tables 1–3, in the right-hand term of (8), one obtains the multipole tensors for the various molecular symmetries. Thus, e.g., for the point group C_{2v} (molecules H_2O, $C_6H_5NO_2$, etc.), we obtain consecutively, for the dipole, quadrupole, octupole and hexadecapole moments:

$$M^{(1)}_i = \mu_z z_i\,,$$

$$M^{(2)}_{ij} = \tfrac{1}{2}(\Theta_{xx} - \Theta_{yy})(x_i x_j - y_i y_j) + \tfrac{1}{2}\Theta_{zz}(3z_i z_j - \delta_{ij})\,,$$

Table 3
Non-zero and independent tensor elements of the electric hexadecapole moment $\Phi_{\alpha\beta\gamma\delta}$ for all point groups

Groups C_1, C_i :	$N = 81$, $I = 9$	$A_1 \equiv xxyy = xyxy = xyyx = yyxx = yxyx = yxxy$, $B_1 \equiv xxzz = xzxz = xzzx = zzxx = zxzx = zxxz$, $D_1 \equiv yyzz = yzyz = yzzy = zzyy = zyzy = zyyz$, $E_1 \equiv xxxx = -(yyxx + zzxx)$, $F_1 \equiv yyyy = -(xxyy + zzyy)$, $G_1 \equiv zzzz = -(xxzz + yyzz)$, $H_1 \equiv yyyx = yyxy = yxyy = xyyy$, $J_1 \equiv zzyx = xzzy = xzyz = xyzz = yxzz = yzxz = yzzx = zxyz = zyxz = zyzx = zxzy = zzxy$, $K_1 \equiv yyzx = yyxz = yxyz = yxzy = yzyx = yzxy = xyyz = xyzy = xzyy = zyyx = zxyy = zyxy$, $L_1 \equiv zzzx = zzxz = zxzz = xzzz$, $M_1 \equiv xxyz = xyxz = xyzx = xxzy = xzxy = xzyx = yxxz = yxzx = yzxx = zxxy = zxyx = zyxx$, $P_1 \equiv zzzy = zzyz = zyzz = yzzz$, $Q_1 \equiv xxxy = xxyx = xyxx = yxxx = -(yyyx + zzyx)$, $R_1 \equiv xxxz = xxzx = xzxx = zxxx = -(zzzx + yyzx)$, $S_1 \equiv yyyz = yyzy = yzyy = zyyy = -(zzzy + xxyz)$.
Groups C_s, C_2, C_{2h} :	$N = 41$, $I = 5$	elements $A_1, B_1, D_1, E_1, F_1, G_1, H_1, J_1$ and Q_1.
Groups C_{2v}, D_2, D_{2h} :	$N = 21$, $I = 3$	elements A_1, B_1, D_1, E_1, F_1 and G_1.
Groups C_4, S_4, C_{4h} :	$N = 29$, $I = 3$	elements $A_1, B_1 = D_1, E_1 = F_1, G_1$ and Q_1 $(zzyx = 0)$.
Groups D_4, C_{4v}, D_{4h}, D_{2d} :	$N = 21$, $I = 2$	elements $A_1, B_1 = D_1, E_1 = F_1, G_1$.
Groups C_3, S_6 :	$N = 53$, $I = 3$	elements $A_1 = -\frac{1}{4}B_1 = -\frac{1}{4}D_1$, R_1 $(zzzx = 0)$, S_1 $(zzzy = 0)$, $U_1 \equiv xxxx = yyyy = 3xxyy = -\frac{3}{4}xxzz$, $zzzz = -2xxzz = 8xxyy$.
Groups D_3, C_{3v}, D_{3d} :	$N = 37$, $I = 2$	elements $A_1 = -\frac{1}{4}B_1 = -\frac{1}{4}D_1$, S_1 $(zzzy = 0)$ and U_1.
Groups C_6, C_{3h}, C_{6h}, D_6, C_{6v}, D_{3h}, D_{6h}, D_{4d}, C_5, C_{5v}, C_{5h}, D_5, D_{5h}, D_{5d}, D_{6d}, S_8, S_{10}, S_{12}, C_∞, $C_{\infty v}$, $C_{\infty h}$ and $D_{\infty h}$:	$N = 21$, $I = 1$	elements $A_1 = -\frac{1}{4}B_1 = -\frac{1}{4}D_1$, U_1.
Groups T, T_h, O, O_h, T_d :	$N = 21$, $I = 1$	elements $A_1 = B_1 = D_1$ and $xxxx = yyyy = zzzz = -2xxyy$.

In point groups Y, Y_h, K and K_h all tensor elements vanish.

$$M^{(3)}_{ijk} = \tfrac{1}{2}(\Omega_{xxz} - \Omega_{yyz}) \sum_3 (x_i x_j - y_i y_j) z_k + \tfrac{1}{2}\Omega_{zzz}(5 z_i z_j z_k - \sum_3 \delta_{ij} z_k) ,$$

$$M^{(4)}_{ijkl} = \tfrac{1}{2}(\Phi_{xxzz} - \Phi_{yyzz})[7 y_i y_j y_k y_l - 7 x_i x_j x_k x_l + \sum_6 (x_i x_j - y_i y_j)\delta_{kl}]$$
$$+ \tfrac{1}{8}(\Phi_{xxzz} + 8\Phi_{xxyy} + \Phi_{yyzz})[3 z_i z_j z_k z_l - 4 x_i x_j x_k x_l - 4 y_i y_j y_k y_l - \sum_6 z_i z_j \delta_{kl} + \sum_3 \delta_{ij}\delta_{kl}]$$
$$+ \tfrac{1}{8}\Phi_{zzzz}(35 z_i z_j z_k z_l - 5 \sum_6 z_i z_j \delta_{kl} + \sum_3 \delta_{ij}\delta_{kl}) , \quad (9)$$

where we have used the notation $x_i = c_{ix}$, $y_i = c_{iy}$, $z_i = c_{iz}$, with $\sum_3$ and $\sum_6$ being sums of the terms resulting from a given expression by all possible permutations of tensor indices.

On assuming z-axis symmetry in the tensors (9), we obtain the well-known expressions for groups C_∞ and $C_{\infty v}$ (axially symmetric molecules [1,16]).

Groups D_2 and D_{2d} possess no dipole moment; their octupole moment tensor is of the form:

$$M^{(3)}_{ijk} = \Omega_{xyz} \sum_6 x_i y_j z_k \,, \tag{10}$$

for group D_2, the quadrupole and hexadecapole moments are of the same form as in eqs. (9), whereas for group D_{2d} one has to put additionally $\Theta_{xx} = \Theta_{yy}$ and $\Phi_{xxzz} = \Phi_{yyzz}$, $\Phi_{xxxx} = \Phi_{yyyy}$. Eq. (10) is applicable to groups T and T_d also (which present neither dipoles nor octupoles) with, moreover, $\Phi_{zzzz} = -2\Phi_{xxzz}$ in (9), yielding [4]:

$$M^{(4)}_{ijkl} = \Phi_{xxzz} \{\sum_3 \delta_{ij}\delta_{kl} - 5(x_i x_j x_k x_l + y_i y_j y_k y_l + z_i z_j z_k z_l)\} \,. \tag{11}$$

Clearly, the hexadecapole moment (11) holds for groups O and O_h too, where lower multipoles are absent.

With the multipole tensors in the form (9), (10) or (11), it is easy to calculate the explicit expressions for the energies (2), (3) and the molecular field (4) as a function of Euler's angles, or polar in the case of the axial symmetry [1,16]. Calculations run similarly for the remaining point groups with which one has to deal in statistical-molecular problems extending beyond the simpler cases to molecules of the lower symmetries.

References

[1] L.L. Boyle, Intern. J. Quantum Chem. 3 (1969) 231;
A.D. Buckingham, in: Physical chemistry, Vol. 4, Molecular properties, ed. D. Henderson (Academic Press, New York, 1970) p. 349.
[2] D.E. Stogryn and A.P. Stogryn, Mol. Phys. 11 (1966) 371.
[3] S. Kielich, Acta Phys. Polon. 24 (1963) 389; 27 (1965) 457.
[4] S. Kielich, Acta Phys. Polon. 25 (1964) 39.
[5] W.H. Flygare and R.C. Benson, Mol. Phys. 20 (1971) 225.
[6] S. Kielich, Physica 31 (1965) 444; Mol. Phys. 9 (1965) 549.
[7] G. Birnbaum and A. Rosenberg, Phys. Letters 27A (1968) 272.
[8] S. Kielich, IEEE J. Quantum Electron. QE-4 (1968) 744.
[9] A. Rosenberg and G. Birnbaum, J. Chem. Phys. 52 (1970) 683;
J.R. Nelson Jr. and R.H. Cole, J. Chem. Phys. 54 (1971) 4033.
[10] L. Jansen, Phys. Rev. 110 (1958) 661.
[11] S. Kielich, Acta Phys. Polon. 28 (1965) 459.
[12] D.E. Stogryn, J. Chem. Phys. 50 (1969) 4967.
[13] S. Bhagavantam and D. Suryanarayana, Acta Cryst. 2 (1949) 21;
H.A. Jahn, Acta Cryst. 2 (1949) 30;
F.G. Fumi, Acta Cryst. 5 (1952) 44, 691; Nuovo Cimento 9 (1952) 739;
R.R. Birss, Rept. Progr. Phys. 26 (1963) 307.
[14] G.J. Lyubarskii, Group theory and its applications in physics (Moskva, 1958) ch. 8, section 41, in Russian.
[15] E.P. Wigner, Group theory (Academic Press, New York, 1959).
[16] S. Kielich, Acta Phys. Polon. 22 (1962) 65; 27 (1964) 395;
S. Kielich, J.R. Lalanne and F.B. Martin, J. Phys. (Paris) 32 (1971), to be published.