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Unified treatment for arbitrary-rank cartesian electric and magnetic multipole moment operators

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In this study, the theory of cartesian electric and magnetic multipole moments is extended in a unified way. The general analytical expressions for distinct components of arbitrary rank cartesian electric and magnetic multipole moment operators are derived as linear combination of corresponding spherical operators, which can be used as inter-conversion between cartesian and spherical electric and magnetic multipole moment tensors. The transformation properties, such as translation and rotation of cartesian electric and magnetic multipole moments are given in a very simple general form. The relationship between distinct and linearly independent components of cartesian multipole moment tensors in system of linear symmetry is also presented. The formulae obtained in this paper can be utilized to calculate the interaction energies between charge distributions.

KEY WORDS: cartesian multipole moment tensor, translation of multipole moment tensors, rotation of multipole moment tensors

1. Introduction

The determination of electric and magnetic multipole moments (multipole moments) has been pursued with considerable enthusiasm in the past decade in large part because of the central role which they play in intermolecular interactions [1], and also as an outcome of studies on nonlinear optical properties [2–4], collisional effects in IR and NMR spectroscopy [4, 5], intensity differantials in Rayleigh and Raman scattering [6], hyperfine interactions [7], and theoretical prediction of the geometries of van der Waals molecules [8–10].

Since the experimental values for the higher moments are comparatively rare, there have regrettably been few recent studies of this type; the vast majority of recent published works consist of theoretical studies, usually by *ab initio* methods at both self-consistent field (SCF) and correlated levels.

Electric and magnetic multipole moment operators may be defined in two different ways, either on the basis of spherical harmonics [11,12] or in terms of cartesian coordinates [1,13–16], and also the relationship between the two sets of multipoles have been derived [17,18].

The electrostatic potential outside a sphere surrounding a given charge distribution may be expressed in terms of spherical multipole moments. A spherical multipole moment of order l has only $(2l + 1)$ independent components. A cartesian multipole tensor of order l has 3^l components of which, in general $(l + 1)(l + 2)/2$ are distinct. This suggests that in the calculation of the outer potential and of the interaction between charge distributions, the formulation in terms of spherical moments is to be preferred. On the other hand, in both analytical and numerical calculations the cartesian moments are often more convenient. In the following, we will show that all the distinct components can be obtained in terms of $(2l+1)$ linear independent components. Analytical formula for linear independent components is obtained through the spherical moments and therefore, the expression obtained for cartesian multipole tensor components can be regarded as the interconversion between cartesian and spherical multipole moment tensors.

In spite of the fact that formulae for spherical electric and magnetic multipole moment operators have been derived in literature, to the best of our knowledge, hitherto no general analytical formulae have been reported for arbitrary rank cartesian electric and magnetic multipole moment operators.

This work differs from previous works in many cases as discussed in section 4. In addition, it should be mentioned that despite this work seems similar to recent work of Hoffmann [18], this work have many advantages over previous literature. That is, since complex spherical harmonics used in paper by Hoffmann with tedious algebra, we have derived all expressions for both complex and real spherical harmonics with very simple algebra. Moreover, the unified expressions presented here are valid for both electric and magnetic multipole moment operators.

The first two sections of this paper are devoted to the general cartesian expressions for the spherical electric and magnetic multipole moment operators. In section 3, we give the general analytical expression for distinct components of arbitrary rank cartesian multipole moment operators in terms of spherical multipole moment operators that can also be regarded as interconversion between cartesian and spherical electric and magnetic multipole moment tensors. Then translational and rotational properties of cartesian multipole moments are given in a relatively simple general form. Consequently, the symmetry relations for linear molecules given by McLean and Yoshimine [14] generalized to any order.

2. General Cartesian expressions for spherical electric and magnetic multipole moment operators

2.1. Spherical electric multipole moment operators

Spherical electric multipole moment operator is given by the relation [11]:

$$M_{lm}^{(e)}(\vec{r}) = \sqrt{\frac{4\pi}{2l+1}} r^l \, S_{lm}(\theta, \varphi) \,, \tag{1}$$

where $S_{lm}(\theta, \varphi)$ are complex or real spherical harmonics [19]. Recently, we have expressed cartesian expressions for spherical electric multipole moment operator through the binomial coefficients by the relations [20];

$$M_{lm}^{(e)}(\vec{r}) \equiv M_{lm}^{(e)}(x, y, z) = (-1)^{1/2(|m|-m)} \sum_k (-1)^k c_{lm}^k (x+iy)^{k+m} (x-y)^k (z)^{l-(2k+m)} \tag{2}$$

for complex spherical electric multipole moment operators, and

$$M_{lm}^{(e)}(\vec{r}) \equiv M_{lm}^{(e)}(x, y, z) = f_m(x, y) \sum_k C_{lm}^k z^{l-(2k+m)} (z^2 - r^2)^{k+\frac{m}{2}(1-\varepsilon_m)} \tag{3}$$

for real spherical electric multipole moment operators. In equations (2) and (3), k varies as $\frac{1}{2}(|m| - m) \leqslant k \leqslant \frac{1}{2}\left[(l-m) - \frac{1}{2}(1-(-1)^{l-m})\right]$ and expansion coefficient c_{lm}^k is given by

$$c_{lm}^k = \frac{1}{2^{2k+m}} \left[F_{l-k}(l+m) F_{k+m}(l-k) F_{2k}(l-m) F_k(2k)\right]^{1/2} \quad . \tag{4}$$

In equations (2) and (3)

$$f_m(x, y) = \sqrt{\frac{2}{(1+\delta_{m0})}} \sum_{s=1/2(1-\varepsilon_m)}^{\lambda}{}^{(2)} (-1)^{\frac{1}{2}\left[s-\frac{1}{2}(1-\varepsilon_m)\right]} F_s(\lambda) \, x^{\lambda-s} y^s, \tag{5}$$

in which, $\lambda = |m|$, $F_m(n) = n!/m!(n-m)!$ is the binomial coefficient, the symbol $\sum^{(2)}$ indicates that the summation is to be performed in steps of two. The symbol ε_m is defined as follows:

$$\varepsilon_m = \begin{cases} 1 & \text{for } m \geqslant 0, \\ -1 & \text{for } m < 0. \end{cases} \tag{6}$$

In [20], spherical electric multipole moment components, up to rank 6, are tabulated.

2.2. Spherical magnetic multipole moment operators

There are number of definition for spherical magnetic multipole moment operator in literature and the most commonly used one [13,21] is

$$M_{lm}^{(m)}(\vec{r}) = \frac{2}{l+1}\left(\nabla M_{lm}^{(e)}(\vec{r})\right)\hat{\mu}. \tag{7}$$

Analytical expression for spherical magnetic multipole moment operator is given by employing closed formulas for derivatives of spherical electric multipole moment operators by the relation as [22]:

$$\hat{M}_{lm}^{(m)}(\vec{r}) = \frac{2}{l+1}\sum_{i=-1}^{1}\left\{\sum_{m'=-(l-1)}^{(l-1)} a_{lm,m'}^{i}\hat{M}_{l-1,m'}^{(e)}(\vec{r})\right\}\hat{\mu}_i(\vec{r}), \tag{8}$$

where $\hat{M}_{lm}^{(e)}$ is spherical electric multipole moment operator, $\hat{\mu}_i$ is magnetic dipole moment operator, and

$$\begin{aligned} a_{lm,m'}^{1} = {}& \frac{\varepsilon_m}{2}(1-2\delta_{m0})\left[(l+m)(l+m-1)\right]^{1/2}\delta_{m',m-1} \\ & -\frac{\varepsilon_m}{2}\left[(l-m)(l-m-1)\right]^{1/2}\delta_{m',m+1}, \end{aligned} \tag{9}$$

$$\begin{aligned} a_{lm,m'}^{-1} = {}& \frac{i\varepsilon_m}{2}(1-2\delta_{m0})\left[(l+m)(l+m-1)\right]^{1/2}\delta_{m',m-1} \\ & +\frac{i\varepsilon_m}{2}\left[(l-m)(l-m-1)\right]^{1/2}\delta_{mm'}, \end{aligned} \tag{10}$$

$$a_{lm,m'}^{0} = \left[(l+m)(l-m)\right]^{1/2}\delta_{mm'}, \quad a_{0m,m'}^{i} = 0, \;\; a_{1m,0}^{i} = \delta_{im} \tag{11}$$

for complex spherical magnetic multipole moment operator, and

$$\begin{aligned} a_{lm,m'}^{1} = {}& \frac{\varepsilon_m}{2}\left[(1-\delta_{m0})(1+\delta_{m1})(l+m)(l+m-1)\right]^{1/2}\delta_{m',m-1} \\ & -\frac{\varepsilon_m}{2}\left[(1+\delta_{m0})\left(1-\delta_{m,-1}\right)(l-m)(l-m-1)\right]^{1/2}\delta_{m',m+1}, \end{aligned} \tag{12}$$

$$\begin{aligned} a_{lm,m'}^{-1} = {}& -\frac{\varepsilon_m}{2}\left[(1-\delta_{m0})(1-\delta_{m1})(l+m)(l+m-1)\right]^{1/2}\delta_{m',-m+1} \\ & -\frac{\varepsilon_m}{2}\left[(1+\delta_{m0})\left(1+\delta_{m,-1}\right)(l-m)(l-m-1)\right]^{1/2}\delta_{m',-m-1} \end{aligned} \tag{13}$$

for real spherical magnetic multipole moment operator. In equations (8)–(12), δ_{ij} is Kronecker delta function.

Substituting equation (3) in equation (8), one obtains cartesian expression for spherical magnetic multipole moment operator.

3. General analytical expression for cartesian electric and magnetic multipole moment operators

Following Buckingham [1], the lth order cartesian multipole moment operator is given by

$$Q_l = \frac{(-1)^l}{l\,!}\left|\vec{r}\right|^{2l+1}\nabla^l\left(\left|\vec{r}\right|^{-1}\right). \tag{14}$$

The cartesian multipole moment operators of order l are symmetrical because of the commutativity of the differentiation operators, and traceless in each pair of indices. Thus, only $(l+1)\,(l+2)/2$ of its 3^l components are distinct; the $l\,(l-1)/2$ constraints implicit in the tracelessness property of the tensor reduce this number of distinct components to $(2l+1)$.

In this study, we investigate the distinct components of cartesian multipole moment operators in two parts: $(2l+1)$ linearly independent components and $l\,(l-1)/2$ distinct components obtained via traceless properties of cartesian multipole moment tensors. We will show all the distinct components for l order cartesian tensor by the general notation Q^l_{ijk}, in which i, j, and k indicate, respectively, the number of x, y, and z, with $i+j+k=l$.

For linear independent components, we will use the notation Q^l_μ by expression

$$Q^l_\mu\,(x,y,z) = \sum_{m=\min(m_1,m_2)}^{\max(m_1,m_2)}{}^{(2)}\; a^l_{\mu m}\, M_{lm}\,(\vec{r}), \tag{15}$$

where $m_1=\mu$ and $m_2=\frac{\varepsilon_\mu}{2}\,[1-(-1)^\mu]-2\delta_{\varepsilon_\mu,-1}$. The ranges of indices are $0\leqslant j\leqslant 1$, $0\leqslant i,k\leqslant l$ with $i+j+k=l$ and $\mu=(-1)^j\,(i+j)$.

The inverse relation for equation (15) is

$$M_{lm}(\vec{r}) = \sum_{\mu=\min(\mu_1,\mu_2)}^{\max(\mu_1,\mu_2)}{}^{(2)}b^{\,l}_{\,m\mu}\;Q^{\,l}_{\,\mu}\,(x,y,z)\,\frac{\varepsilon_m}{2}\left[1-(-1)^m\right], \tag{16}$$

where $\mu_1=m$ and $\mu_2=\frac{\varepsilon_m}{2}\left[1-(-1)^m\right]-2\delta_{\varepsilon_m,-1}$.

In equations (15) and (16), Q^l_μ is cartesian multipole moment operators and M_{lm} is spherical multipole moment operators.

The coefficients $a^l_{\mu m}$ and $b^l_{m\mu}$ are given by

$$a^l_{\mu m} = \begin{cases} \dfrac{(-1)^{\frac{(\mu-m)}{2}}}{F_\mu(l)}\left(\frac{2}{1+\delta_{m0}}\right)^{\frac{1}{2}}\;C^{\frac{(\mu-m)}{2}}_{lm} & \text{for } \mu\geqslant 0,\;\; m\geqslant 0,\\ \frac{m}{\mu}a^l_{|\mu||m|} & \text{for } \mu<0,\;\; m<0 \end{cases} \tag{17}$$

and

$$b^l_{m\mu} = \begin{cases} \left[\left(\frac{m}{m-\mu}\right)\left(\sqrt{2}\right)^{\mu-m+(2-m)\delta_{\mu 0}}\right]^{(1-\delta_{\mu m})} \frac{1}{a^l_{mm}} & \text{for } m \geqslant 0,\ \ \mu \geqslant 0, \\ \frac{\mu}{m} b^l_{|m||\mu|} & \text{for } m < 0,\ \ \mu < 0. \end{cases} \tag{18}$$

If we require that the transformations (15) and (16) be unitary, then

$$a^l = \tilde{b}^l \tag{19}$$

must be satisfied. Here $\tilde{b}^l$ means the transpose of b^l.

We express other $l\,(l-1)/2$ distinct tensor components in terms of linearly independent components as

$$Q^l_{ijk} = -\left(1-\delta_{i0}\delta_{k0}\right)\left(Q^l_{\xi} + Q^l_{\xi-2\varepsilon_\xi}\right) - \frac{1}{2}\left[1+(-1)^{\,l}\right]\delta_{i0}\delta_{k0}\sum_{\mu=0}^{l}{}^{(2)}\, F_{\frac{\mu}{2}}\left(\frac{l}{2}\right) Q^l_{\mu}, \tag{20}$$

where $i,\ j$, and k is the number of $x,\ y$, and z, respectively, in multipole moment tensor indices with $i+j+k=l$. For distinct components, the ranges of indices i, j, k are $2 \leqslant j \leqslant l, 0 \leqslant i, k \leqslant l$ and ξ in the first summation term is $\xi = (-1)^j$ $(i+j)$. Some results of equations (15) and (16) are given in Appendix A.

4. Transformation properties of Cartesian multipole moment tensors

The simplest or principal axis components of molecular tensor properties refer to body-fixed axes. On the other hand, what are directly measured in experiments are usually space-fixed axis components. Thus, one must know how to transform these tensors from body-fixed to space-fixed axes, and conversely.

The transformation properties of the spherical multipole moments are simpler than cartesian cases, and to the best of our knowledge, there is no study on transformation properties of cartesian electric and magnetic multipole moment tensors. In this part, we will discuss separately translational and rotational properties of cartesian multipole moment tensors.

4.1. Translational transformations

In calculating expectation values of electric or magnetic multipole moments, center of mass is taken as coordinate axes that multipole moments are calculated. It is well known that except for the first nonzero multipole moment, the higher order multipole moments are origin dependent and must be translated to the center of mass.

Translation formulas for spherical multipole moments have been discussed by several investigators with increasing generality [11,17,23], but for cartesian electric multipole moments only by McLean and Yoshimine [14] with tedious algebra and very special formulas.

To consider the properties of cartesian multipole moments under translation of coordinate origin, let first examine the translation of spherical multipole moments:

In this study, we use the translation formula for spherical multipole moments

$$\langle M_{lm}(\vec{r}_a)\rangle = \sum_{l'=0}^{l} \sum_{m'=-l'}^{l'} \Omega^{*}_{lm,l'm'}\left(\vec{R}\right) \langle M_{l'm'}(\vec{r}_b)\rangle\,, \tag{21}$$

where $\Omega^{*}_{lm,l'm'}\left(\vec{R}\right)$ is the translation coefficients for spherical multipole moment operators [23]. There should be a little modification in equations (5) and (6) of Ref. [23] with

$$\Omega^{*}_{lm,l'm'}\left(\vec{R}\right) = \hat{M}_{l-l',\,m-m'}\left(\vec{R}\right) \Lambda_{lm,l'm'} \tag{22}$$

and

$$\Lambda_{\nu\sigma,\nu'\sigma'} = \left[F_{l'+m'}(l+m)\, F_{l'-m'}(l-m)\right]^{1/2}. \tag{23}$$

As can be seen from equation (20), the translated multipole moments include all the lower order moments where $\langle M_{lm}(\vec{r}_a)\rangle$ and $\langle M_{lm}(\vec{r}_b)\rangle$ denotes spherical multipole moments in old and new coordinate systems, respectively.

Since we have expressed cartesian multipole moment operators through the spherical multipole moment operators with equations (16) and (20), there is no need to translate cartesian multipole moment tensor components as done in the study of McLean and Yoshimine [14] with cumbersome algebra.

4.2. Rotational transformations

The rotation of spherical multipole moment operators are given by the relations [11]:

$$M_{lm}(\text{new}) = \sum_{m'} G^{*\,l}_{m'm}(\alpha,\beta,\gamma)\, M_{lm'}(\text{old}). \tag{24.a}$$

The inverse of equation (24.a) is

$$M_{lm}(\text{old}) = \sum_{m'} G^{l}_{m'm}(\alpha,\beta,\gamma)\, M_{lm'}(\text{new}). \tag{24.b}$$

Since we have expressed the cartesian multipole moment operators in terms of spherical operators, the rotation of cartesian multipole moment operators are given by

$$Q^l_{\mu'}\left(r'\right) = \sum_{\mu=-l}^{l} G^l_{\mu'\mu}\left(\alpha,\beta,\gamma\right)\, Q^l_{\mu}\left(r\right) \tag{25.a}$$

with the inverse relation

$$Q^l_{\mu}\left(r\right) = \sum_{\mu'=-l}^{l} \left[G'_{\mu\mu'}{}^{l}\left(\alpha,\beta,\gamma\right)\right]^{-1} Q_{\mu'}{}^{l}\left(r'\right). \tag{25.b}$$

In equations (24) and (25), $G^{\,l}_{m'm}\left(\alpha,\beta,\gamma\right)$ are rotation matrices, for complex [24] or real spherical harmonics [25]. It can be seen from equations (25) that the rotation of cartesian multipole moment operators are as of spherical multipole moment operators.

5. Distinct components of Cartesian multipole moment tensors of linear molecules

The molecular symmetry places a restriction on the number of distinct components for the cartesian multipole moment tensors. Therefore, it is necessary to determine (following the symmetry of the molecules) the distinct components in the molecular Oxyz system.

In this section, we give basic analytical expressions for distinct tensor components of linear ($D_{\infty h}$, $C_{\infty v}$) molecules.

For linear molecules, Oz-axis is chosen as the molecular axis joining the center of molecules. We define the distinct components, Q^l_{ijk} of cartesian multipole moment tensors for linear molecules by the relation

$$\left\langle Q^l_{ijk}\right\rangle = \eta^l_{ij}\ \left\langle M_{l0}\right\rangle, \tag{26}$$

where $Q^l_{00l} = Q^l_0 = M_{l0}$ and the coefficient η^l_{ij} is defined by

$$\eta^l_{ij} = \frac{1}{F_{i/2}\left(\frac{i+j}{2}\right)} a^l_{io}\, a^l_{jo}. \tag{27}$$

By analyzing the coefficient η^l_{ij}, the following symmetry properties are obtained:

$$\eta^l_{ij} = \eta^l_{ji}, \tag{28}$$

$$\left\langle Q^l_{ijk}\right\rangle = \left\langle Q^l_{jik}\right\rangle. \tag{29}$$

As can be seen from the equations (26)–(29), the following results are obtained:

(i) any tensor component with x or y odd suffixes is identically null;

(ii) any tensor component remains unchanged under permutation of the x and y suffices;

(iii) only one independent scalar quantity is required to determine the magnitude of any component, which can be thus calculated from the Q^{l}_{00l} component value [14,25].

Equation (26) verifies and generalizes the results derived by McLean and Yoshimine [14] and Isnard et. al. [26] to any order with the best agreement of the results of Cipriani and Silvi [27]. Some results of equation (26) are listed in Appendix B.

6. Results and discussions

In this study, first, we have given an analytical formula for distinct components of cartesian electric and magnetic multipole moment tensors. By the use of this formula, the higher order cartesian electric and magnetic multipole moment tensors can be easily constructed.

Second, the translation and rotational transformations of cartesian electric and magnetic multipole moment tensors are investigated first in literature. Consequently, the relationships between the distinct and linearly independent tensor components for linear molecules are given. Thus, without calculating all tensor components, the cartesian electric and magnetic multipole moment tensors can be easily calculated.

The expressions obtained here are in general form, applicable to cartesian electric and magnetic multipole moment tensors of all orders. The obtained general analytical expressions for cartesian multipole moment tensor components can be used for interconversion between spherical and cartesian multipole moment tensors, and these formulas are simpler than in the study of Stone [17, 28].

Calculations of cartesian multipole moments using the methods in this paper give greatly improved agreement with all previous reliable theoretical and experimental values for a number of molecules.

Our derivation of (15) and (20) show the direct connection between the cartesian and spherical tensor forms of the multipole moments. Finally, we note that the obtained general formulas can be useful in other physical applications of cartesian tensor algebra. The advantages in adopting the notation for cartesian tensors in this study are as follows:

(i) It is easily seen that the formulae in the literature [16–18,28] are complex in structure and not generalized to arbitrary rank and also not applied to big molecules. On the other hand, our unified formula is general and valid for arbitrary rank. Also our formula is applied to polyatomic molecules H_2O, NH_3, and CH_4 in our recent paper in *Commun. Theor. Phys.* (*Beijing–China*), 38 (2002) 489.

(ii) The formulae in literature are special such as for linear molecules, tetrahedral molecules, etc. On the other hand, our approachz is valid for molecules having arbitrary symmetry.

(iii) To the best of our knowledge, literature does not contain formula for cartesian magnetic multipole moment operators. On the other hand, our unified formula is valid for cartesian magnetic multipole moment operators also.

(iv) The method presented in this study proves to have not only formal, but also practical computational advantages over the formulations given in the prior literature and allows a more systematic study of higher order molecular interactions, and can be employed in calculations of electrostatic multipole interactions, energies, molecular electrostatic potentials, electric fields, etc.

(v) The translational and rotational transformation properties are investigated relatively in a simple way.

(vi) Cartesian multipole moments may be easily related to their irreducible components as for spherical form and full advantage is taken of the symmetry of the molecules under consideration.

(vii) The notation used in this study helps to avoid much of tedious algebra needed in usual cartesian form.

Appendix A: linear independent components of Cartesian multipole moments tensors: cartesian–spherical and spherical–cartesian tensor transformation up to rank 4

In this section, cartesian–spherical and spherical–cartesian multipole moment tensor transformations up to hexadecapole moment are presented by the use of equations (15) and (16).

1. Cartesian–Spherical transformation for

Dipole moment tensor

$$\begin{aligned}
Q_1^1 &= Q_x = M_{11},\\
Q_{-1}^1 &= Q_y = M_{1-1},\\
Q_0^1 &= Q_z = M_{10}.
\end{aligned}$$

Quadrupole moment tensor

$$
\begin{aligned}
Q^2_2 &= Q_{xx} = -\tfrac{1}{2}M_{20} + \tfrac{\sqrt{3}}{2}M_{22},\\
Q^2_{-2} &= Q_{xy} = \tfrac{\sqrt{3}}{2}M_{2-2},\\
Q^2_1 &= Q_{xz} = \tfrac{\sqrt{3}}{2}M_{21},\\
Q^2_{-1} &= Q_{yz} = \tfrac{\sqrt{3}}{2}M_{2-1},\\
Q^2_0 &= Q_{zz} = M_{20}.
\end{aligned}
$$

Octopole moment tensor

$$
\begin{aligned}
Q^3_3 &= Q_{xxx} = -\tfrac{\sqrt{6}}{4}M_{31} + \tfrac{\sqrt{10}}{4}M_{33},\\
Q^3_{-3} &= Q_{xxy} = \tfrac{\sqrt{10}}{4}M_{3-3} - \tfrac{\sqrt{6}}{12}M_{3-1},\\
Q^3_2 &= Q_{xxz} = -\tfrac{1}{2}M_{30} + \tfrac{\sqrt{15}}{6}M_{32},\\
Q^3_{-2} &= Q_{xyz} = -\tfrac{\sqrt{15}}{6}M_{3-2},\\
Q^3_1 &= Q_{xzz} = \tfrac{\sqrt{6}}{3}M_{31},\\
Q^3_{-1} &= Q_{yzz} = \tfrac{\sqrt{6}}{3}M_{3-1},\\
Q^3_0 &= Q_{zzz} = M_{30}.
\end{aligned}
$$

Hexadecapole moment tensor

$$
\begin{aligned}
Q^4_4 &= Q_{xxxx} = \tfrac{3}{8}M_{40} - \tfrac{\sqrt{5}}{4}M_{42} + \tfrac{\sqrt{35}}{8}M_{44},\\
Q^4_{-4} &= Q_{xxxy} = \tfrac{\sqrt{35}}{8}M_{4-4} - \tfrac{\sqrt{5}}{8}M_{4-2},\\
Q^4_3 &= Q_{xxxz} = -\tfrac{3\sqrt{10}}{16}M_{41} + \tfrac{\sqrt{70}}{16}M_{43},\\
Q^4_{-3} &= Q_{xxyz} = \tfrac{\sqrt{70}}{16}M_{4-3} - \tfrac{\sqrt{10}}{16}M_{4-1},\\
Q^4_2 &= Q_{xxzz} = -\tfrac{1}{2}M_{40} + \tfrac{\sqrt{5}}{4}M_{42},\\
Q^4_{-2} &= Q_{xyzz} = \tfrac{\sqrt{5}}{4}M_{4-2},\\
Q^4_1 &= Q_{xzzz} = \tfrac{\sqrt{10}}{4}M_{41},\\
Q^4_{-1} &= Q_{yzzz} = \tfrac{\sqrt{10}}{4}M_{4-1},\\
Q^4_0 &= Q_{zzzz} = M_{40}.
\end{aligned}
$$

2. *Spherical–cartesian transformation for Dipole moment tensor*

Dipole moment tensor

$$M_{11} = Q_x,$$
$$M_{1-1} = Q_y,$$
$$M_{10} = Q_z.$$

Quadrupole moment tensor

$$M_{22} = \frac{1}{\sqrt{3}} Q_{zz} + \frac{2}{\sqrt{3}} Q_{xx},$$
$$M_{2-2} = \frac{2}{\sqrt{3}} Q_{xy},$$
$$M_{21} = \frac{2}{\sqrt{3}} Q_{xz},$$
$$M_{2-1} = \frac{2}{\sqrt{3}} Q_{yz},$$
$$M_{20} = Q_{zz}.$$

Octopole moment tensor

$$M_{33} = \frac{3}{\sqrt{10}} Q_{xzz} + \frac{4}{\sqrt{10}} Q_{zzz},$$
$$M_{3-3} = \frac{4}{\sqrt{10}} Q_{xxy} + \frac{1}{\sqrt{10}} Q_{yzz},$$
$$M_{32} = \frac{3}{\sqrt{15}} Q_{zzz} + \frac{6}{\sqrt{15}} Q_{xxz},$$
$$M_{3-2} = \frac{6}{\sqrt{15}} Q_{xyz},$$
$$M_{31} = \frac{3}{\sqrt{6}} Q_{xzz},$$
$$M_{3-1} = \frac{3}{\sqrt{6}} Q_{yzz},$$
$$M_{30} = Q_{zzz}.$$

Hexadecapole moment tensor

$$M_{44} = \frac{1}{\sqrt{35}} Q_{zzzz} + \frac{8}{\sqrt{35}} Q^{+}_{xxzz} \frac{8}{\sqrt{35}} Q_{xxxx},$$
$$M_{4-4} = \frac{8}{\sqrt{35}} Q_{yzzz} + \frac{4}{\sqrt{35}} Q_{xyzz},$$
$$M_{43} = \frac{12}{\sqrt{70}} Q_{xzzz} + \frac{16}{\sqrt{70}} Q_{xxxz},$$
$$M_{4-3} = \frac{12}{\sqrt{70}} Q_{xxyz} + \frac{4}{\sqrt{70}} Q_{yzzz},$$
$$M_{42} = \frac{2}{\sqrt{5}} Q_{zzzz} + \frac{4}{\sqrt{5}} Q_{xxzz},$$
$$M_{4-2} = \frac{4}{\sqrt{5}} Q_{xyzz},$$
$$M_{41} = \frac{4}{\sqrt{10}} Q_{xzzz},$$
$$M_{4-1} = \frac{4}{\sqrt{10}} Q_{yzzz},$$
$$M_{40} = Q_{zzzz}.$$

7. Appendix B: distinct components of cartesian multipole moment tensors for linear molecules

By the use of equation (25), distinct components of cartesian multipole moment tensors, up to hexadecapole, for linear molecules are obtained as in the following:

For quadrupole moment tensor:

$$Q^2_{200} = Q_{xx} = \eta^2_{20}\, Q^2_{002} = -\tfrac{1}{2}\, Q_{zz},$$
$$Q^2_{020} = Q_{yy} = \eta^2_{02}\, Q^2_{002} = -\tfrac{1}{2}\, Q_{zz}.$$

For octopole moment tensor :

$$Q^2_{201} = \Omega_{xxz} = \eta^3_{20}\, Q^3_{003} = -\tfrac{1}{2}\, Q_{zzz},$$
$$Q^2_{021} = \Omega_{yyz} = \eta^3_{02}\, Q^3_{003} = -\tfrac{1}{2}\, Q_{zzz}.$$

For hexadecapole moment tensor:

$$Q^4_{400} = \Phi_{xxxx} = \eta^4_{40}\, Q^4_{004} = \tfrac{3}{8}\, Q_{zzzz},$$
$$Q^4_{220} = \Phi_{xxyy} = \eta^4_{22}\, Q^4_{004} = -\tfrac{1}{8}\, Q_{zzzz},$$
$$Q^4_{202} = \Phi_{xxzz} = \eta^4_{20}\, Q^4_{004} = -\tfrac{1}{2}\, Q_{zzzz},$$
$$Q^4_{040} = \Phi_{yyyy} = \eta^4_{04}\, Q^4_{004} = \tfrac{3}{8}\, Q_{zzzz},$$
$$Q^4_{022} = \Phi_{yyzz} = \eta^4_{02}\, Q^4_{004} = -\tfrac{1}{2}\, Q_{zzzz}.$$

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