The definition of the $A_2^{(2)+}$ State Multipoles

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I. GENERALITIES

Following Orr-Ewing and Zare,[1] we define the $A_2^{(2)+}(J)$ state multipole as

$$A_2^{(2)+}(J) = 2^{-1/2}\left[\mathcal{A}_2^{(2)}(J) + \mathcal{A}_{-2}^{(2)}(J)\right], \tag{1}$$

where [Eq. (39) of Ref. 1]

$$\mathcal{A}_q^{(k)}(J) = \frac{(-1)^q c(k)}{\langle JM|\,\mathbf{J}^2\,|JM\rangle^{k/2}} \frac{(J \parallel \mathbf{J}^{(k)} \parallel J)}{\sqrt{2k+1}} \rho_{-q}^{(k)}(J)$$

In addition, the spherical tensor components of the density matrix are defined as [Eq. (21) of Ref. [1]

$$\rho_q^{(k)}(J) = \sum_{M,M'} (-1)^{J-M'} (2k+1)^{1/2} \begin{pmatrix} J & k & J \\ -M & -q & M' \end{pmatrix} \rho_{M'M}$$

In a collision experiment, the transition out of intial rotational level J'' into final rotational level J at scattering angle θ is fully described by the M-resolved (complex) scattering amplitudes $f_{J''M''\to JM}(\theta)$. (We will suppress the scattering angle unless explicitly needed). In terms of these, the $\{M, M'\}^{th}$ element of the density matrix for final rotational level J at scattering angle θ is

$$\rho_{M'M} = \sum_{M''} f^*_{J''M''\to JM'} f_{J''M''\to JM} \bigg/ \sum_{M'',M'} |f_{J''M''\to JM'}|^2 \tag{2}$$

The denominator is chosen so that

$$\mathrm{Tr}\,(\rho_{M'M}) = \sum_M \rho_{MM} = 1$$

We assume that the scattering amplitude is dimensionless, so that the degeneracy-averaged $J'' \to J$ differential cross section (the sum over all final projection states and average over all initial projection states of the $J''M'' \to JM'$ differential cross section) is

$$\frac{d\sigma(J'' \to J)}{d\Omega} = \frac{1}{(2J''+1)k_{J''}^2} \sum_{M'',M'} |f_{J''M'' \to JM'}|^2 \tag{3}$$

where $k_{J''}$ is the initial wavevector. We also note, as one might anticipate, that the density matrix is Hermitian

$$\rho^*_{M'M} = \rho_{MM'} \tag{4}$$

Note, again, that the rotational density matrix state multipoles of the scattered molecules are functions of the scattering angle.

In the particular case where $k = 2$ and $q = \pm 2$ we have

$$\begin{aligned}
\mathcal{A}_2^{(2)}(J) &= \frac{(-1)^2 c(2)}{\langle JM | \mathbf{J}^2 | JM \rangle^{2/2}} \frac{(J \parallel \mathbf{J}^{(2)} \parallel J)}{\sqrt{5}} \rho_{-2}^{(2)}(J) \\
&= \left[\frac{(2J-1)(2J+1)(2J+3)}{5J(J+1)} \right]^{1/2} \rho_{-2}^{(2)}(J) \\
&= (-1)^J \left[\frac{(2J-1)(2J+1)(2J+3)}{J(J+1)} \right]^{1/2} \sum_{MM'} (-1)^{-M'} \begin{pmatrix} J & 2 & J \\ -M & 2 & M' \end{pmatrix} \rho_{M'M}
\end{aligned} \tag{5}$$

Thus, from Eq. (1) and using

$$\langle JM | \mathbf{J}^2 | JM \rangle = J(J+1) \,,$$

and (see p. 231 of Ref. [2])

$$(J \parallel \mathbf{J}^{(2)} \parallel J) = \left[\frac{J(J+1)(2J-1)(2J+1)(2J+3)}{6} \right]^{1/2}$$

we have

$$\begin{aligned}
A_2^{(2)+}(J) &= (-1)^J \left[\frac{(2J-1)(2J+1)(2J+3)}{2J(J+1)} \right]^{1/2} \\
&\times \sum_{MM'} (-1)^{-M'} \left[\begin{pmatrix} J & 2 & J \\ -M & 2 & M' \end{pmatrix} + \begin{pmatrix} J & 2 & J \\ -M & -2 & M' \end{pmatrix} \right] \rho_{M'M}
\end{aligned} \tag{6}$$

In fact, the triangular relation contained in the $3j$ symbols restricts M' to a single value

($M' = M + 2$ or $M' = M - 2$), so that the double sums can be replaced by

$$A_2^{(2)+}(J) = (-1)^J \left[\frac{(2J-1)(2J+1)(2J+3)}{2J(J+1)}\right]^{1/2} \left[\sum_{M=-J+2}^{J} (-1)^{-M} \begin{pmatrix} J & 2 & J \\ -M & 2 & M-2 \end{pmatrix} \rho_{M,M-2} \right.$$
$$\left. + \sum_{M=-J}^{J-2} (-1)^{-M} \begin{pmatrix} J & 2 & J \\ -M & -2 & M+2 \end{pmatrix} \rho_{M,M+2} \right]$$

We can define $M' = M - 2$ in the first summation, then replace M' by M, and use the known symmetries of the $3j$ symbols to get

$$\sum_{M=-J+2}^{J} (-1)^{-M} \begin{pmatrix} J & 2 & J \\ -M & 2 & M-2 \end{pmatrix} \rho_{M,M-2} = \sum_{M'=-J}^{J-2} (-1)^{-M'-2} \begin{pmatrix} J & 2 & J \\ -M'-2 & 2 & M' \end{pmatrix} \rho_{M'+2,M'}$$
$$= \sum_{M=-J}^{J-2} (-1)^{-M} \begin{pmatrix} J & 2 & J \\ -M-2 & 2 & M \end{pmatrix} \rho_{M+2,M}$$
$$= \sum_{M=-J}^{J-2} (-1)^{-M} \begin{pmatrix} J & 2 & J \\ -M & -2 & M+2 \end{pmatrix} \rho_{M+2,M}$$

We use this result, and the hermiticity of the density matrix [Eq. (4)], to simplify Eq. (6) to

$$A_2^{(2)+}(J) = (-1)^J \left[\frac{(2J-1)(2J+1)(2J+3)}{2J(J+1)}\right]^{1/2}$$
$$\times \sum_{M=-J}^{J-2} (-1)^{-M} \begin{pmatrix} J & 2 & J \\ -M & -2 & M+2 \end{pmatrix} (\rho_{M+2,M} + \rho_{M,M+2})$$
$$= (-1)^J \left[\frac{2(2J-1)(2J+1)(2J+3)}{J(J+1)}\right]^{1/2}$$
$$\times \sum_{M=-J}^{J-2} (-1)^{-M} \begin{pmatrix} J & 2 & J \\ -M & -2 & M+2 \end{pmatrix} \mathcal{R}(\rho_{M+2,M}) \qquad (7)$$

where $\mathcal{R}$ designates the real part of a complex number. From Eq. (2) one can show that

$$\mathcal{R}(\rho_{M+2,M}) = \textstyle\sum_{M''} \left[\mathcal{R}(f_{J''M''\to JM})\,\mathcal{R}(f_{J''M''\to JM+2}) + \mathcal{I}(f_{J''M''\to JM})\,\mathcal{I}(f_{J''M''\to JM+2})\right]$$
$$/ \textstyle\sum_{M'',M} |f_{J''M''\to JM}|^2$$
$$= \textstyle\sum_{M''} \left[\mathcal{R}(f_{J''M''\to JM})\,\mathcal{R}(f_{J''M''\to JM+2}) + \mathcal{I}(f_{J''M''\to JM})\,\mathcal{I}(f_{J''M''\to JM+2})\right]$$
$$/ \textstyle\sum_{M'',M} \left[\mathcal{R}(f_{J''M''\to JM})\,\mathcal{R}(f_{J''M''\to JM}) + \mathcal{I}(f_{J''M''\to JM})\,\mathcal{I}(f_{J''M''\to JM})\right] \qquad (8)$$

[1] A. J. Orr-Ewing and R. N. Zare, Annu. Rev. Phys. Chem. **45**, 315–66 (1994).

[2] R. N. Zare, *Angular Momentum: Understanding Spatial Aspects in Chemistry and Physics* (Wiley, New York, 1988).