Notes on spectroscopy

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I. MULTIPOLE EXPANSIONS

This section is adapted from Chap. 2 of Barron's *Molecular Light Scattering and Optical Activity.*[1]

A collection of point charges has multipole moments. The n-th order multipole moment is defined as

$$\xi^{(n)}_{\alpha\beta\ldots\nu} = \frac{(-1)^n}{n!} \sum_i e_i r_i^{2n+1} \nabla_{i\alpha}\nabla_{i\beta}\ldots\nabla_{i\nu}\left(\frac{1}{r_i}\right), \quad (1)$$

The zeroth moment is the net charge:

$$q = \sum_i e_i. \quad (2)$$

The first moment is the dipole moment vector:

$$\boldsymbol{\mu} = \sum_i e_i \mathbf{r}_i. \quad (3)$$

The dipole moment is origin dependent if the system is not charge neutral: moving the origin $\mathbf{O}$ to $\mathbf{O}+\mathbf{a}$ changes the dipole moment to

$$\boldsymbol{\mu}' = \sum_i e_i(\mathbf{r}_i - \mathbf{a}) = \boldsymbol{\mu} - q\mathbf{a}. \quad (4)$$

The second moment is the quadrupole moment tensor:

$$\Theta = \frac{1}{2}\sum_i e_i\left(3\mathbf{r}_i\mathbf{r}_i - r_i^2\mathbf{I}\right), \quad (5)$$

where $\mathbf{r}_i\mathbf{r}_i$ is the outer product, and r_i^2 is the dot product $\mathbf{r}_i \cdot \mathbf{r}_i$. In Cartesian tensor notation, the quadrupole moment tensor is

$$\Theta_{\alpha\beta} = \frac{1}{2}\sum_i e_i\left(3r_{i\alpha}r_{i\beta} - r_i^2\delta_{\alpha\beta}\right). \quad (6)$$

The $\Theta_{\alpha\beta}$ tensor is a symmetric rank-2 tensor, with zero trace, hence has 5 independent components. Likewise, the quadrupole moment tensor is origin dependent if the net charge and dipole moment are nonzero.

An electric field is generated by a charge distribution $\rho(\mathbf{r})$:

$$\rho(\mathbf{r}) = \sum_i e_i \delta(\mathbf{r} - \mathbf{r}_i). \quad (7)$$

The corresponding potential can be found by solving the Poisson equation for static sources:

$$\nabla^2\phi = -\frac{\rho}{\epsilon\epsilon_0}, \quad (8)$$

whose solution is

$$\phi(\mathbf{R}) = \frac{1}{4\pi\epsilon\epsilon_0}\int\frac{\rho(\mathbf{r})\mathrm{d}V}{|\mathbf{R}-\mathbf{r}|}. \quad (9)$$

So in this case, the potential becomes

$$\phi(\mathbf{R}) = \frac{1}{4\pi\epsilon\epsilon_0}\sum_i\frac{e_i}{|\mathbf{R}-\mathbf{r}_i|}. \quad (10)$$

Assuming $|\mathbf{R}| \gg |\mathbf{r}_i|$, we can write down the following Taylor series:

$$\begin{aligned}\frac{1}{|\mathbf{R}-\mathbf{r}_i|} &= (R_\alpha R_\alpha - 2R_\alpha r_{i\alpha} + r_{i\alpha}r_{i\alpha})^{-1/2} \quad (11)\\ &= \frac{1}{R} + \frac{R_\alpha r_{i\alpha}}{R^3} + \frac{1}{2}\left(\frac{3R_\alpha r_{i\alpha}r_{i\beta}R_\beta}{R^5} - \frac{r_i^2}{R^3}\right) + \ldots.\end{aligned}$$

[1] L. D. Barron, *Molecular Light Scattering and Optical Activity*, 2nd ed. (Cambridge University Press, 2004).

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