Taylor series of $\left|\vec{R}-\vec{r}\right|^{-1}$ and definition of multipoles

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I. TAYLOR EXPANSION

The Taylor series any function $f(x)$ is written as

$$f(x+\delta x) = f(x) + \frac{\partial f(x)}{\partial x}\delta x + \frac{1}{2}\frac{\partial^2 f(x)}{\partial x^2}\delta x^2 + \cdots$$

with

$$\left.\frac{\partial(1+x)^n}{\partial x}\right|_{x=0} = n(1+x)^{n-1}\Big|_{x=0} = n,$$

and

$$\left.\frac{\partial^2(1+x)^n}{\partial x^2}\right|_{x=0} = \left.\frac{\partial n(1+x)^{n-1}}{\partial x}\right|_{x=0} = n(n-1)(1+x)^{n-2}\Big|_{x=0} = n(n-1),$$

we have

$$(1-x)^n \approx 1 - nx + \frac{n(n-1)}{2}x^2 + O(x^3).$$

Then the Taylor series of $\left|\vec{R}-\vec{r}\right|^{-1}$ can be written as

$$\begin{aligned}
\left|\vec{R}-\vec{r}\right|^{-1} &= \left[(\vec{R}-\vec{r})^2\right]^{-1/2} \\
&= \frac{1}{\left|\vec{R}\right|}\left[1-\left(\frac{2\vec{R}\cdot\vec{r}}{R^2}-\frac{r^2}{R^2}\right)\right]^{-1/2} \\
&\approx \frac{1}{\left|\vec{R}\right|}\left[1+\frac{1}{2}\left(\frac{2\vec{R}\cdot\vec{r}}{R^2}-\frac{r^2}{R^2}\right)+\frac{3}{8}\left(\frac{2\vec{R}\cdot\vec{r}}{R^2}-\frac{r^2}{R^2}\right)^2\right] \\
&= \frac{1}{\left|\vec{R}\right|}\left[1+\frac{\vec{R}\cdot\vec{r}}{R^2}-\frac{r^2}{2R^2}+\frac{3\left(\vec{R}\cdot\vec{r}\right)\left(\vec{R}\cdot\vec{r}\right)}{2R^4}-\frac{3r^2\vec{R}\cdot\vec{r}}{4R^4}+\frac{3r^4}{8R^4}\right],
\end{aligned}$$

Therefore the electrostatic potential on a grid $\vec{R}$ outside a sphere D generated by a group of charge $\{q_i\}$ within the sphere D is

$$\begin{aligned}
\phi(\vec{R}) &= \sum_i \frac{q_i}{\left|\vec{R}-\vec{r}_i\right|} \\
&\approx \sum_i \frac{q_i}{\left|\vec{R}\right|} + \sum_i \frac{\vec{R}\cdot\vec{r}_i q_i}{R^3} + \sum_i \frac{3\left(\vec{R}\cdot\vec{r}_i\right)\left(\vec{R}\cdot\vec{r}_i\right) - r_i^2 R^2}{2R^5} q_i.
\end{aligned}$$

Define

$$q_{tot} = \sum_i q_i,$$

$$\vec{\mu} = \sum_i \vec{r}_i q_i,$$

and

$$Q_{\alpha,\beta} = \frac{1}{2} \sum_i \left(3 r_{i\alpha} r_{i\beta} - r_i^2 \delta_{\alpha\beta}\right) q_i,$$

which is in accordance with A. J. Stone (*The Theory of Intermolecular Forces*, 2nd edition, Oxford University Press (April 5, 2013)). We have

$$\begin{aligned}
\phi(\vec{R}) &= \frac{q_{tot}}{\left|\vec{R}\right|} + \frac{\vec{R} \cdot \vec{\mu}}{R^3} + \sum_{\alpha\beta} \frac{Q_{\alpha\beta} R_\alpha R_\beta}{R^5} \\
&= \frac{q_{tot}}{\left|\vec{R}\right|} + \frac{\vec{R} \cdot \vec{\mu}}{R^3} + \sum_{\alpha\beta} \frac{Q_{\alpha\beta} \left(3 R_\alpha R_\beta - R^2 \delta_{\alpha\beta}\right)}{3R^5}.
\end{aligned}$$

The last equality holds because quadrupole is traceless, i.e.

$$\sum_\alpha Q_{\alpha\alpha} = \frac{1}{2} \sum_i \sum_\alpha \left(3 r_{i\alpha}^2 - r_i^2\right) q_i = 0.$$

Therefore

$$\sum_{\alpha\beta} Q_{\alpha\beta} R^2 \delta_{\alpha\beta} = R^2 \sum_\alpha Q_{\alpha\alpha} = 0.$$

Different softwares (papers) give different definitions of quadrupole, hence different formulae for the potential generated by quadrupoles. So be vigilant!

The electric field generated by multipoles can be calculated by

$$\begin{aligned}
F_\alpha &= -\frac{q_{tot} \cdot R_\alpha}{R^3} + \sum_\beta \frac{\mu_\beta}{R^3} \left[\frac{3 R_\alpha R_\beta}{R^2} - \delta_{\alpha\beta}\right] \\
&\quad + \sum_\beta \sum_\gamma Q_{\beta\gamma} \frac{5 R_\alpha R_\beta R_\gamma - R^2 \left(R_\alpha \delta_{\beta\gamma} + R_\beta \delta_{\alpha\gamma} + R_\gamma \delta_{\alpha\beta}\right)}{R^7}
\end{aligned}$$

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[1] http://en.wikipedia.org/wiki/Multipole_expansion.

[2] Yu, H. B.; van Gunsteren, W. F. *Comput. Phys. Commun.* **2005**, *172, 69-85.*

[3] *The Theory of Intermolecular Forces*, 2nd edition, Oxford University Press (April 5, 2013)