Ewald Sum 中无穷边界项补遗

授课教师：胡中汉 *zhonghanhu@sdu.edu.cn*
整理：赵艺浩 *zhaoyihao@protonmail.com*

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在电中性条件下无穷边界项最终可化简为：

$$E^{IB} = \lim_{\mathbf{k}\to 0} -\frac{1}{4V}\sum_i\sum_j q_i q_j \frac{4\pi}{k^2}(\mathbf{k}\cdot\mathbf{r}_{ij})^2$$

整理：

$$\begin{aligned}
E^{IB} &= \lim_{\mathbf{k}\to 0} -\frac{1}{4V}\sum_i\sum_j q_i q_j (\mathbf{k}\cdot\mathbf{r}_{ij})^2 \frac{4\pi}{k^2} \\
&= \lim_{\mathbf{k}\to 0} -[(\frac{1}{4V}\sum_i\sum_j q_i q_j)^{\frac{1}{2}}\mathbf{r}_{ij}\cdot\mathbf{k}]^2 \frac{4\pi}{k^2} \\
&= \lim_{\mathbf{k}\to 0} -(\mu\cdot\mathbf{k})^2 \frac{4\pi}{k^2} \\
&= \lim_{\mathbf{k}\to 0} u(\mu,\mathbf{k})
\end{aligned}$$

其中：

$$\mu = (\frac{1}{4V}\sum_i\sum_j q_i q_j)^{\frac{1}{2}}\mathbf{r}_{ij}$$

$$u(\mu,\mathbf{k}) = -(\mu\cdot\mathbf{k})^2\frac{4\pi}{k^2}$$

由讲义附录知：

$$\begin{aligned}
\frac{4\pi}{k^2} &= \int_{-\infty}^{\infty} d\mathbf{r}\cdot\frac{1}{r}e^{-i\mathbf{k}\cdot\mathbf{r}} \\
\frac{1}{r} &= \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty} d\mathbf{k}\cdot\frac{4\pi}{k^2}e^{i\mathbf{k}\cdot\mathbf{r}}
\end{aligned}$$

易知：

$$\begin{aligned}\mu\cdot\nabla\frac{1}{r} =&\mu\cdot\nabla\frac{1}{(2\pi)^3}\int_{-\infty}^{\infty}d\mathbf{k}\cdot\frac{4\pi}{k^2}e^{i\mathbf{k}\cdot\mathbf{r}}\\ =&i\mathbf{k}\cdot\mu\frac{1}{(2\pi)^3}\int_{-\infty}^{\infty}d\mathbf{k}\cdot\frac{4\pi}{k^2}e^{i\mathbf{k}\cdot\mathbf{r}}\\ \mu\cdot\nabla[\mu\cdot\nabla\frac{1}{r}] =&(i\mathbf{k}\cdot\mu)^2\frac{1}{(2\pi)^3}\int_{-\infty}^{\infty}d\mathbf{k}\cdot\frac{4\pi}{k^2}e^{i\mathbf{k}\cdot\mathbf{r}}\\ =&\frac{1}{(2\pi)^3}\int_{-\infty}^{\infty}d\mathbf{k}\cdot[-(\mathbf{k}\cdot\mu)^2\frac{4\pi}{k^2}]e^{i\mathbf{k}\cdot\mathbf{r}}\\ =&\mathscr{F}^{-1}[-(\mathbf{k}\cdot\mu)^2\frac{4\pi}{k^2}]\end{aligned}$$

故：

$$-(\mathbf{k}\cdot\mu)^2\frac{4\pi}{k^2}=\mathscr{F}[\mu\cdot\nabla(\mu\cdot\nabla\frac{1}{r})]$$

则：

$$\begin{aligned}E^{IB} =&\lim_{\mathbf{k}\to 0}[-(\mu\cdot\mathbf{k})^2\frac{4\pi}{k^2}]\\ =&\lim_{\mathbf{k}\to 0}\mathscr{F}[\mu\cdot\nabla(\mu\cdot\nabla\frac{1}{r})]\\ =&\lim_{\mathbf{k}\to 0}\int_{-\infty}^{\infty}d\mathbf{r}\cdot[\mu\cdot\nabla(\mu\cdot\nabla\frac{1}{r})]e^{-i\mathbf{k}\cdot\mathbf{r}}\\ =&\int_{-\infty}^{\infty}d\mathbf{r}\cdot[\mu\cdot\nabla(\mu\cdot\nabla\frac{1}{r})]\\ =&\lim_{\Omega\to\infty}\int_{\Omega}d\mathbf{r}\cdot[\mu\cdot\nabla(\mu\cdot\nabla\frac{1}{r})]\end{aligned}$$

其中

$$\begin{aligned}\nabla[\mu(\mu\cdot\nabla\frac{1}{r})] =&(\mu\cdot\nabla\frac{1}{r})\nabla\cdot\mu+\mu\cdot\nabla(\mu\cdot\nabla\frac{1}{r})\\ =&\mu\cdot\nabla(\mu\cdot\nabla\frac{1}{r})\end{aligned}$$

并高斯定理：

$$\int_{\Omega}d\mathbf{r}\nabla\cdot\mathbf{A}=\oint_{\partial\Omega}dS\mathbf{n}\cdot\mathbf{A}$$

则：

$$E^{IB}=\lim_{\Omega\to\infty}\oint_{\partial\Omega}dS\mathbf{n}\cdot\mu(\mu\cdot\nabla\frac{1}{r})$$

当保持球体的形状使得体积趋于无穷时：

$$
\begin{aligned}
dS =& R^2 \sin\theta d\theta d\varphi \\
\mathbf{n} =& \frac{\mathbf{R}}{R} \\
E^{IB} =& \lim_{R\to 0} R^2 \int_0^{\pi} d\theta \sin\theta \int_{-\pi}^{\pi} d\varphi \frac{\mathbf{R}}{R} \cdot \mu(\mu \cdot \nabla \frac{1}{R})
\end{aligned}
$$

$$
\begin{aligned}
\nabla \frac{1}{R} =& \mathbf{e_x} \frac{\partial}{\partial x} \frac{1}{\sqrt{x^2+y^2+z^2}} + \mathbf{e_y} \frac{\partial}{\partial y} \frac{1}{\sqrt{x^2+y^2+z^2}} + \mathbf{e_z} \frac{\partial}{\partial z} \frac{1}{\sqrt{x^2+y^2+z^2}} \\
=& -\mathbf{e_x} \frac{x}{R^3} - \mathbf{e_y} \frac{y}{R^3} - \mathbf{e_z} \frac{z}{R^3} \\
=& -\frac{\mathbf{R}}{R^3}
\end{aligned}
$$

$$
\begin{aligned}
E^{IB} =& \lim_{R\to 0} R^2 \int_0^{\pi} d\theta \sin\theta \int_{-\pi}^{\pi} d\varphi \frac{\mathbf{R}\cdot\mu}{R} (-\frac{\mathbf{R}\cdot\mu}{R^3}) \\
=& -\lim_{R\to 0} \int_0^{\pi} d\theta \sin\theta \int_{-\pi}^{\pi} d\varphi \frac{(\mathbf{R}\cdot\mu)^2}{R^2} \\
=& -\lim_{R\to 0} \int_0^{\pi} d\theta \sin\theta \int_{-\pi}^{\pi} d\varphi \frac{R^2\mu^2\cos^2\theta}{R^2} \\
=& -\int_0^{\pi} d\theta \sin\theta \int_{-\pi}^{\pi} d\varphi \cos^2\theta \\
=& -\frac{4\pi}{3}\mu^2
\end{aligned}
$$

代 μ:

$$
\begin{aligned}
E^{IB} =& -\frac{4\pi}{3}[(\frac{1}{4V}\sum_i \sum_j q_i q_j)^{\frac{1}{2}} \mathbf{r}_{ij}]^2 \\
=& \frac{2\pi}{3V}(\sum_i q_i r_i)^2 \\
=& \frac{2\pi}{3V}(M_x^2 + M_y^2 + M_z^2)
\end{aligned}
$$

当保持立方体的形状使得体积趋于无穷时：置坐标原点于体心处，立方体边长为 2L。对于 $x = L$ 面：

$$
\begin{aligned}
\mathbf{n} =& \mathbf{e}_x \\
E^{IB}_{x=L} =& \lim_{\Omega\to\infty} \oint_{\partial\Omega} dS\mathbf{n}\cdot\mu(\mu\cdot\nabla\frac{1}{r}) \\
=& \lim_{L\to\infty}\int_{-L}^{L} dy \int_{-L}^{L} dz \mathbf{e}_x \mu[\mu\cdot(\nabla\frac{1}{r})_{x=L}]
\end{aligned}
$$

$$
\begin{aligned}
\nabla\frac{1}{r} =& \mathbf{e_x}\frac{\partial}{\partial x}\frac{1}{\sqrt{x^2+y^2+z^2}} + \mathbf{e_y}\frac{\partial}{\partial y}\frac{1}{\sqrt{x^2+y^2+z^2}} + \mathbf{e_z}\frac{\partial}{\partial z}\frac{1}{\sqrt{x^2+y^2+z^2}} \\
=& -\mathbf{e_x}\frac{x}{(x^2+y^2+z^2)^{\frac{3}{2}}} - \mathbf{e_y}\frac{y}{(x^2+y^2+z^2)^{\frac{3}{2}}} - \mathbf{e_z}\frac{z}{(x^2+y^2+z^2)^{\frac{3}{2}}}
\end{aligned}
$$

由 $\mathbf{e}_x\cdot\mathbf{e}_y = 0$、$\mathbf{e}_x\cdot\mathbf{e}_z = 0$：

$$
\begin{aligned}
E^{IB}_{x=L} =& \lim_{L\to\infty}\int_{-L}^{L} dy \int_{-L}^{L} dz \mathbf{e}_x \mu[\mu\cdot(\nabla\frac{1}{r})_{x=L}] \\
=& \lim_{L\to\infty}\int_{-L}^{L} dy \int_{-L}^{L} dz \frac{-\mu_x^2 L}{(L^2+y^2+z^2)^{\frac{3}{2}}} \\
=& -\lim_{L\to\infty} 4\mu_x^2 L \int_{0}^{L} dy \int_{0}^{L} dz \frac{1}{(L^2+y^2+z^2)^{\frac{3}{2}}} \\
=& -\lim_{L\to\infty} 4\mu_x^2 L \int_{0}^{L} dy [\frac{z}{(L^2+y^2)\sqrt{L^2+y^2+z^2}}\Bigg|_{z=0}^{z=L}] \\
=& -\lim_{L\to\infty} 4\mu_x^2 L \int_{0}^{L} dy \frac{L}{(L^2+y^2)\sqrt{2L^2+y^2}} \\
=& -\lim_{L\to\infty} 4\mu_x^2 L^2 \int_{0}^{L} dy \frac{1}{(L^2+y^2)\sqrt{2L^2+y^2}}
\end{aligned}
$$

令 $\sqrt{y^2+2L^2} = t - y$，则：

$$
\begin{aligned}
t &= \sqrt{y^2+2L^2} - y & \qquad y &= \frac{t}{2} - \frac{L^2}{t} \\
y^2 &= \frac{t^2}{4} + \frac{L^4}{t^2} - L^2 & \qquad dy &= (\frac{1}{2} + \frac{L^2}{t^2})dt \\
\sqrt{2L^2+y^2} &= \frac{t}{2} + \frac{L^2}{t} & \qquad (L^2+y^2) &= \frac{t^2}{4} + \frac{L^4}{t^2}
\end{aligned}
$$

$$
\begin{aligned}
E^{IB}_{x=L} &= -\lim_{L\to\infty} 4\mu_x^2 L^2 \int_{\sqrt{2}L}^{(1+\sqrt(3)L} dt \frac{\frac{1}{2}+\frac{L^2}{t^2}}{(\frac{t^2}{4}+\frac{L^4}{t^2})(\frac{t}{2}+\frac{L^2}{t})} \\
&= -\lim_{L\to\infty} 4\mu_x^2 L^2 \int_{\sqrt{2}L}^{(1+\sqrt(3)L} dt \frac{\frac{1}{t}(\frac{t}{2}+\frac{L^2}{t})}{(\frac{t^2}{4}+\frac{L^4}{t^2})(\frac{t}{2}+\frac{L^2}{t})} \\
&= -\lim_{L\to\infty} 4\mu_x^2 L^2 \int_{\sqrt{2}L}^{(1+\sqrt(3)L} dt \frac{\frac{t}{t^2}}{\frac{t^2}{4}+\frac{L^4}{t^2}} \\
&= -\lim_{L\to\infty} 4\mu_x^2 L^2 \int_{\sqrt{2}L}^{(1+\sqrt(3)L} dt^2 \frac{1}{2} \frac{1}{\frac{t^4}{4}+L^4} \\
&= -\lim_{L\to\infty} 2\mu_x^2 L^2 \int_{2L^2}^{(4+2\sqrt{3})L^2} dT \frac{1}{\frac{T^2}{4}+L^4} \\
&= -\lim_{L\to\infty} 4\mu_x^2 L^2 \int_{L^2}^{(2+\sqrt{3})L^2} dX \frac{1}{X^2+(L^2)^2} \\
&= -\lim_{L\to\infty} 4\mu_x^2 L^2 [\frac{1}{L^2}\arctan\frac{X}{L^2}\Big|_{X=L^2}^{X=(2+\sqrt{3})L^2}] \\
&= -4\mu_x^2[\frac{5\pi}{12}-\frac{\pi}{4}] \\
&= -\frac{2\pi}{3}\mu_x^2
\end{aligned}
$$

$x=-L$ 面与 $x=L$ 面等同，且有三对等同面，因此：

$$
\begin{aligned}
E^{IB} &= -\frac{4\pi}{3}\mu_x^2 - \frac{4\pi}{3}\mu_y^2 - \frac{4\pi}{3}\mu_z^2 \\
&= -\frac{4\pi}{3}\mu^2
\end{aligned}
$$