Supplementary Information for "A Finite Field Method for Calculating Molecular Polarizability Tensors for Arbitrary Multipole Rank" by D.M. Elking et al.

# Inter-conversion Formulae Between $\hat{\zeta}^{(l)}_{l_x l_y l_z}(\mathbf{r})$ and $C_{lm}(\mathbf{r})$

Inter-conversion formulae (given in eqns. A.11- A.14 of the main text) between the traceless multipole operator $\hat{\zeta}^{(l)}_{l_x l_y l_z}(\mathbf{r})$ (eqn. 24) and the solid harmonic function $C_{lm}(\mathbf{r})$ (eqn. A.7) are derived in the following report. Eqns. A.11 – A.14 of the main text are summarized by

$$\hat{\zeta}^{(l)}_{l_x l_y l_z}(\mathbf{r}) = \sum_{n=0}^{l_x+l_y} b_n^{l_x,l_y,l} C_{l,2n-l_x-l_y}(\mathbf{r}) \qquad \text{(A.11)}$$

$$C_{lm}(\mathbf{r}) = \sum_{k=0}^{|m|} c_k^{lm} \hat{\zeta}^{(l)}_{|m|-k,k,l-|m|}(\mathbf{r}) \qquad \text{(A.12)}$$

where $b_n^{l_x,l_y,l}$ and $c_k^{l,m}$ are constants given by

$$b_n^{l_x,l_y,l} \equiv \frac{i^{l_y} A_{l,2n-l_x-l_y}}{2^{l_x+l_y} l!} \sum_{q=\max(0,n-l_x)}^{\min(l_y,n)} \binom{l_x}{n-q}\binom{l_y}{q}(-1)^{n+q} \qquad \text{(A.13)}$$

$$c_k^{lm} \equiv \begin{cases} \dfrac{l!(-1)^{m_+}}{A_{lm}}\dbinom{|m|}{k} i^k & m \geq 0 \\ \dfrac{l!(-1)^{k}}{A_{lm}}\dbinom{|m|}{k} i^k & m < 0 \end{cases} \qquad \text{(A.14)}$$

and $A_{lm} \equiv \sqrt{(l+m)!(l-m)!}$ (eqn. A.5). Background information is summarized in the next section, which is followed by a proof of eqns. A.11 and A.12.

## I) Background

1) Traceless Cartesian Multipole Operator

Recall the definition for the traceless Cartesian multipole operator given in eqn. 24

$$\hat{\zeta}^{(l)}_{l_x l_y l_z}(\mathbf{r}) \equiv \frac{(-1)^l}{l!} r^{2l+1} \partial_x^{l_x} \partial_y^{l_y} \partial_z^{l_z} \frac{1}{r} \tag{S1}$$

where $l \equiv l_x + l_y + l_z$.

2) Polynomial expression for $C_{lm}(\mathbf{r})$

Recall the polynomial expression for $C_{lm}(x, y, z)$ for $-l \le m \le l$ in eqn. A.7

$$C_{lm}(\mathbf{r}) = (-1)^{m_+} \frac{A_{lm}}{2^{|m|}} \sum_{k=0}^{\left[\frac{l-|m|}{2}\right]} \left(\frac{-1}{4}\right)^k \frac{z^{l-|m|-2k}(x+iy)^{m_+ +k}(x-iy)^{m_- +k}}{(l-|m|-2k)!(m_+ +k)!(m_- +k)!} \tag{S2}$$

where $m_\pm \equiv (|m| \pm m)/2$.

3) Expansion of $1/|\mathbf{r} - \mathbf{r}'|$

For $r < r'$, $1/|\mathbf{r} - \mathbf{r}'|$ can be expanded by[86]

$$\begin{aligned} \frac{1}{|\mathbf{r}-\mathbf{r}'|} &= \sum_{l=0}^{\infty}\sum_{m=-l}^{l} \frac{4\pi}{2l+1} Y_{lm}(\theta,\phi) Y^*_{lm}(\theta',\phi') \frac{r^l}{r'^{l+1}} \\ &= \sum_{l=0}^{\infty}\sum_{m=-l}^{l} C_{lm}(\mathbf{r}) I^*_{lm}(\mathbf{r}') \end{aligned} \tag{S3}$$

where $Y_{lm}(\theta,\phi)$ is a spherical harmonic (eqn. A.1), $C_{lm}(\mathbf{r}) \equiv r^l \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\theta,\phi)$ (eqn. A.3), and

$I_{lm}(\mathbf{r}') \equiv C_{lm}(\mathbf{r}')/r'^{2l+1}$ is an irregular solid harmonic function.

4) Derivative Transformations between $(x, y)$ and $(x_+, x_-)$

The complex variables $x_+$ and $x_-$ are defined in terms of $x$ and $y$ by

$$x_\pm \equiv x \pm iy \tag{S4}$$

Similarly, $x$ and $y$ can be expressed in terms of $x_+$ and $x_-$ by

$$x = \frac{1}{2}(x_+ + x_-) \qquad\qquad y = \frac{1}{2i}(x_+ - x_-) \tag{S5}$$

Derivatives with respect to $x$ and $y$ can be transformed to derivatives with respect to $x_+$ and $x_-$ by

$$\partial_\pm \equiv \frac{\partial}{\partial x_\pm} = \frac{\partial x}{\partial x_\pm}\frac{\partial}{\partial x} + \frac{\partial y}{\partial x_\pm}\frac{\partial}{\partial y} = \frac{1}{2}\left(\frac{\partial}{\partial x} \mp i\frac{\partial}{\partial y}\right) = \frac{1}{2}\left(\partial_x \mp i\partial_y\right) \tag{S6}$$

Similarly, derivatives with respect to $x_+$ and $x_-$ can be transformed to derivatives with respect to $x$ and $y$ by

$$\partial_x = \frac{\partial}{\partial x} = \frac{\partial x_+}{\partial x}\frac{\partial}{\partial x_+} + \frac{\partial x_-}{\partial x}\frac{\partial}{\partial x_-} = \frac{\partial}{\partial x_+} + \frac{\partial}{\partial x_-} = \partial_+ + \partial_- \tag{S7}$$

$$\partial_y = \frac{\partial}{\partial y} = \frac{\partial x_+}{\partial y}\frac{\partial}{\partial x_+} + \frac{\partial x_-}{\partial y}\frac{\partial}{\partial x_-} = i\left(\frac{\partial}{\partial x_+} - \frac{\partial}{\partial x_-}\right) = i\left(\partial_+ - \partial_-\right) \tag{S8}$$

4) Binomial Theorem

For an integer $m \geq 0$, the binomial theorem is given by

$$(a+b)^m = \sum_{k=0}^{m} \binom{m}{k} a^{m-k} b^k \tag{S9}$$

where $\binom{m}{k} \equiv \frac{m!}{k!(m-k)!}$

## II) Proof of Eqns. A.11 and A.12

**Theorem** 1: $$\partial_z^{l-|m|-2k}\partial_+^{m_++k}\partial_-^{m_-+k} C_{lm'}(\mathbf{r}) = \begin{cases} \frac{(-1)^{m_++k}}{2^{|m|+2k}} A_{lm} & m = m' \\ 0 & m \neq m' \end{cases} \tag{S10}$$

where $m_\pm \equiv (|m| \pm m)/2$, $A_{lm} \equiv \sqrt{(l+m)!(l-m)!}$ (eqn. A.5), and $k \leq (l - |m|)/2$.

Proof: From eqn. S2,

$$\partial_z^{l-|m|-2k}\partial_+^{m_++k}\partial_-^{m_-+k}C_{lm'}(\mathbf{r}) =$$

$$\left(-1\right)^{m_+'}\frac{A_{lm'}}{2^{|m'|}}\sum_{k'=0}^{\left[\frac{l-|m'|}{2}\right]}\left(\frac{-1}{4}\right)^{k'}\frac{\partial_z^{l-|m|-2k}\partial_+^{m_++k}\partial_-^{m_-+k}\left(z^{l-|m'|-2k'}(x+iy)^{m_+'+k'}(x-iy)^{m_-'+k'}\right)}{(l-|m'|-2k')!(m_+'+k')!(m_-'+k')!} \tag{S11}$$

The sum contains non-zero terms which satisfy

$$l-|m|-2k \le l-|m|'-2k' \quad \text{or} \quad |m|'+2k' \le |m|+2k \tag{S12}$$

$$m_+ + k \le m_+' + k' \tag{S13}$$

$$m_- + k \le m_-' + k' \tag{S14}$$

Note $|m| = m_+ + m_-$ and $m = m_+ - m_-$ (with similar expressions for $|m'|$ and $m'$. Adding eqns. S13 and S14 and comparing this result to eqn. S12 gives

$$|m|' + 2k' = |m| + 2k \tag{S15}$$

Substituting eqn. S15 into eqn. S13 gives

$$m_- + k \ge m_-' + k' \tag{S16}$$

Comparing eqn. S16 with eqn. S14 shows that

$$m_- + k = m_-' + k' \tag{S17}$$

Substituting eqn. S17 into eqn. S15 gives

$$m_+ + k = m_+' + k' \tag{S18}$$

From explicit consideration of both cases $m \ge 0$ and $m < 0$, it is clear from eqns. S17 and S18 that

$$m = m' \qquad\qquad k = k' \tag{S19}$$

Thus, the only non-zero terms in the sum of eqn. S11 are when $m = m'$ and $k = k'$ giving the desired result

$$\partial_z^{l-|m|-2k}\partial_+^{m_++k}\partial_-^{m_-+k}C_{lm'}(\mathbf{r}) = \begin{cases}\dfrac{\left(-1\right)^{k+m_+}A_{lm}}{2^{|m|+2k}} & m = m' \\ 0 & m \ne m'\end{cases} \tag{S20}$$

**Theorem** 2: $C_{lm}(\mathbf{r}) = r^{2l+1}\dfrac{2^{|m|+2k}}{A_{lm}}(-1)^{l+k+m_+}\partial_z^{l-|m|-2k}\partial_-^{m_++k}\partial_+^{m_-+k}\dfrac{1}{r}$ (S21)

where $k \le (l-|m|)/2$.

Proof: Recall eqn. S3, for $r < r'$

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \sum_{l'=0}^{\infty}\sum_{m'=-l'}^{l'} C_{l'm'}(\mathbf{r})I^*_{l'm'}(\mathbf{r}')$$

Now apply the derivative operator $\partial_z^{l-|m|-2k}\partial_+^{m_++k}\partial_-^{m_-+k}$ to both sides of eqn. S3

$$\partial_z^{l-|m|-2k}\partial_+^{m_++k}\partial_-^{m_-+k}\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \partial_z^{l-|m|-2k}\partial_+^{m_++k}\partial_-^{m_-+k}\sum_{l'=l}^{\infty}\sum_{m'=-l'}^{l'} C_{l'm'}(\mathbf{r})I^*_{l'm'}(\mathbf{r}') \tag{S22}$$

since $C_{l'm'}(\mathbf{r})$ is a homogenous polynomial of degree $l$, $\partial_z^{l-|m|-2k}\partial_+^{m_++k}\partial_-^{m_-+k}\, C_{l'm'}(\mathbf{r}) = 0$ for $l' < l$.

Applying Theorem 1 to eqn. S22 gives

$$\partial_z^{l-|m|-2k}\partial_+^{m_++k}\partial_-^{m_-+k}\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \frac{(-1)^{k+m_+}A_{lm}I^*_{lm}(\mathbf{r}')}{2^{|m|+2k}} + \partial_z^{l-|m|-2k}\partial_+^{m_++k}\partial_-^{m_-+k}\sum_{l'=l+1}^{\infty}\sum_{m'=-l'}^{l'} C_{l'm'}(\mathbf{r})I^*_{l'm'}(\mathbf{r}') \tag{S23}$$

Note that taking derivatives of $1/|\mathbf{r}-\mathbf{r}'|$ with respect to $\mathbf{r}'$ instead of $\mathbf{r}$ results in a factor of $(-1)^l$

$$\partial_z^{l-|m|-2k}\partial_+^{m_++k}\partial_-^{m_-+k}\frac{1}{|\mathbf{r}-\mathbf{r}'|} = (-1)^l\,\partial_{z'}^{l-|m|-2k}\partial_{+'}^{m_++k}\partial_{-'}^{m_-+k}\frac{1}{|\mathbf{r}-\mathbf{r}'|} \tag{S24}$$

Substituting eqn. S24 into eqn. S23 gives

$$\begin{aligned}(-1)^l\,\partial_{z'}^{l-|m|-2k}\partial_{+'}^{m_++k}\partial_{-'}^{m_-+k}\frac{1}{|\mathbf{r}-\mathbf{r}'|} &= \frac{(-1)^{k+m_+}A_{lm}I^*_{lm}(\mathbf{r}')}{2^{|m|+2k}} \\ &\quad + \partial_z^{l-|m|-2k}\partial_+^{m_++k}\partial_-^{m_-+k}\sum_{l'=l+1}^{\infty}\sum_{m'=-l'}^{l'} C_{l'm'}(\mathbf{r})I^*_{l'm'}(\mathbf{r}')\end{aligned} \tag{S25}$$

Now take the limit as $\mathbf{r} \to 0$ in eqn. S25 and note $I_{lm}(\mathbf{r}') \equiv C_{lm}(\mathbf{r}')/r'^{2l+1}$

$$(-1)^l\,\partial_{z'}^{l-|m|-2k}\partial_{+'}^{m_++k}\partial_{-'}^{m_-+k}\frac{1}{|\mathbf{r}'|} = \frac{(-1)^{k+m_+}A_{lm}}{2^{|m|+2k}}\frac{C^*_{lm}(\mathbf{r}')}{r'^{2l+1}} \tag{S26}$$

since $\partial_z^{l-|m|-2k}\partial_+^{m_++k}\partial_-^{m_-+k}\, C_{l'm'}(\mathbf{r})$ is a homogenous polynomial of degree $l' - l$ for $l' > l$ and vanishes as $\mathbf{r} \to 0$. Solving for $C_{lm}(\mathbf{r}')$ in eqn. S26 gives the desired result (after dropping the ′ symbol)

$$C_{lm}(\mathbf{r}) = r^{2l+1}\frac{2^{|m|+2k}}{A_{lm}}(-1)^{l+k+m_+}\partial_z^{l-|m|-2k}\partial_-^{m_++k}\partial_+^{m_-+k}\frac{1}{r} \tag{S27}$$

where $\partial_\pm^* = \partial_\mp$.

**Theorem** 3: Transformation from $\hat{\zeta}_{l_x l_y l_z}^{(l)}(\mathbf{r})$ to $C_{lm}(\mathbf{r})$:

$$C_{lm}(\mathbf{r}) = \sum_{k=0}^{|m|} c_k^{lm}\,\hat{\zeta}_{|m|-k,k,l-|m|}^{(l)}(\mathbf{r}) \tag{S28}$$

where $c_k^{lm}$ are constants given by

$$c_k^{lm} \equiv \begin{cases} \dfrac{l!(-1)^{m_+}}{A_{lm}}\dbinom{|m|}{k} i^k & m \ge 0 \\[2ex] \dfrac{l!(-1)^{k}}{A_{lm}}\dbinom{|m|}{k} i^k & m < 0 \end{cases}$$

Proof: Consider Theorem 2 with $k = 0$ and $m \ge 0$ ($m_+ = m$ and $m_- = 0$)

$$C_{lm}(\mathbf{r}) = \frac{(-1)^{l+m}2^m}{A_{lm}} r^{2l+1}\partial_z^{l-m}\partial_-^m\frac{1}{r} \tag{S29}$$

Insert the expression for $\partial_-$ from eqn. S6 into eqn. S29

$$C_{lm}(\mathbf{r}) = \frac{(-1)^{l+m}}{A_{lm}} r^{2l+1}\partial_z^{l-m}\left(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y}\right)^m\frac{1}{r} \tag{S30}$$

The binomial theorem (eqn. S9) is applied to eqn. S30 to give the desired result.

$$\begin{aligned} C_{lm}(\mathbf{r}) &= \frac{(-1)^{l+m}}{A_{lm}}\sum_{k=0}^{m}\binom{m}{k} i^k r^{2l+1}\partial_x^{m-k}\partial_y^k\partial_z^{l-m}\frac{1}{r} \\ &= \frac{l!(-1)^m}{A_{lm}}\sum_{k=0}^{m}\binom{m}{k} i^k\,\hat{\zeta}_{m-k,k,l-m}^{(l)}(\mathbf{r}) \end{aligned} \tag{S31}$$

where the definition for $\hat{\zeta}^{(l)}_{l_x l_y l_z}(\mathbf{r})$ (eqn. S1) with $l_x = m - k$, $l_y = k$, $l_z = l - m$ was used in the last step.

Thus, for $m \geq 0$

$$c_k^{lm} \equiv \frac{l!(-1)^{m_+}}{A_{lm}} \binom{|m|}{k} i^k \quad m \geq 0 \tag{S32}$$

For $m < 0$, $c_k^{lm}$ can be found by considering $C_{l-m}(\mathbf{r}) = (-1)^m C^*_{lm}(\mathbf{r})$ as

$$c_k^{lm} \equiv \frac{l!(-1)^{k}}{A_{lm}} \binom{|m|}{k} i^k \quad m < 0 \tag{S33}$$

**Theorem** 4: Transformation from $C_{lm}(\mathbf{r})$ to $\hat{\zeta}^{(l)}_{l_x l_y l_z}(\mathbf{r})$:

$$\hat{\zeta}^{(l)}_{l_x l_y l_z}(\mathbf{r}) = \sum_{n=0}^{l_x + l_y} b_n^{l_x, l_y, l} C_{l, 2n - l_x - l_y}(\mathbf{r}) \tag{S34}$$

where

$$b_n^{l_x, l_y, l} \equiv \frac{i^{l_y} A_{l, 2n - l_x - l_y}}{2^{l_x + l_y} l!} \sum_{q = \max(0, n - l_x)}^{\min(l_y, n)} \binom{l_x}{n-q} \binom{l_y}{q} (-1)^{n+q} \tag{S35}$$

Proof: Recall the definition for $\hat{\zeta}^{(l)}_{l_x l_y l_z}(\mathbf{r})$ in eqn. S1

$$\hat{\zeta}^{(l)}_{l_x l_y l_z}(\mathbf{r}) \equiv \frac{(-1)^l}{l!} r^{2l+1} \partial_x^{l_x} \partial_y^{l_y} \partial_z^{l_z} \frac{1}{r} \tag{S1}$$

and eqns. S7 and S8

$$\partial_x = \partial_+ + \partial_- \tag{S7}$$

$$\partial_y = i(\partial_+ - \partial_-) \tag{S8}$$

Inserting eqns. S7 and S8 into eqn. S1 and applying the binomial theorem (eqn. S9) gives

$$\hat{\zeta}^{(l)}_{l_x l_y l_z}(\mathbf{r}) = \frac{(-1)^l}{l!} i^{l_y} r^{2l+1} \left(\partial_+ + \partial_-\right)^{l_x} \left(\partial_+ - \partial_-\right)^{l_y} \partial_z^{l_z} \frac{1}{r}$$

$$\begin{aligned}\hat{\zeta}^{(l)}_{l_x l_y l_z}(\mathbf{r}) &= \frac{(-1)^l}{l!} i^{l_y} r^{2l+1} \sum_{p=0}^{l_x} \sum_{q=0}^{l_y} \binom{l_x}{p}\binom{l_y}{q} (-1)^q \partial_+^{l_x+l_y-p-q} \partial_-^{p+q} \partial_z^{l_z} \frac{1}{r} \\ &= \frac{(-1)^l}{l!} i^{l_y} r^{2l+1} \sum_{n=0}^{l_x+l_y} (-1)^n I_n^{l_x,l_y} \partial_+^{l_x+l_y-n} \partial_-^{n} \partial_z^{l_z} \frac{1}{r}\end{aligned} \qquad \text{(S36)}$$

where

$$I_n^{l_x,l_y} \equiv \sum_{q=\max(0,n-l_x)}^{\min(l_y,n)} \binom{l_x}{n-q}\binom{l_y}{q} (-1)^{n+q} \qquad \text{(S37)}$$

Recall Theorem 2,

$$r^{2l+1} \partial_+^{m_-+k} \partial_-^{m_++k} \partial_z^{l-|m|-2k} \frac{1}{r} = \frac{A_{lm}}{2^{|m|+2k}} \left(-1\right)^{l+k+m_+} C_{lm}(\mathbf{r}) \qquad \text{(S38)}$$

Now let $l_z \equiv l - |m| - 2k$ and $n \equiv m_+ + k$, then $m_- + k = m_- + n - m_+ = n - m$. And $|m| + 2k = m_- + m_+ + 2k = l - l_z = l_x + l_y = n + n - m$. So, $m = 2n - l_x - l_y$ and $m_- + k = n - m = l_x + l_y - n$. Eqn. S38 becomes

$$r^{2l+1} \partial_+^{l_x+l_y-n} \partial_-^{n} \partial_z^{l_z} \frac{1}{r} = \frac{(-1)^{l+n} A_{l,2n-l_x-l_y}}{2^{l_x+l_y}} C_{l,2n-l_x-l_y}(\mathbf{r}) \qquad \text{(S39)}$$

Inserting eqn. S39 into eqn. S36 gives the desired result

$$\begin{aligned}\hat{\zeta}^{(l)}_{l_x l_y l_z}(\mathbf{r}) &= \sum_{n=0}^{l_x+l_y} \frac{i^{l_y}}{l!} I_n^{l_x,l_y} \frac{A_{l,2n-l_x-l_y}}{2^{l_x+l_y}} C_{l,2n-l_x-l_y}(\mathbf{r}) \\ &= \sum_{n=0}^{l_x+l_y} b_n^{l_x,l_y,l} C_{l,2n-l_x-l_y}(\mathbf{r})\end{aligned} \qquad \text{(S40)}$$

where

$$\begin{aligned}b_n^{l_x,l_y,l} &\equiv \frac{i^{l_y}}{l!} \frac{A_{l,2n-l_x-l_y}}{2^{l_x+l_y}} I_n^{l_x,l_y} \\ &= \frac{i^{l_y} A_{l,2n-l_x-l_y}}{2^{l_x+l_y} l!} \sum_{q=\max(0,n-l_x)}^{\min(l_y,n)} \binom{l_x}{n-q}\binom{l_y}{q} (-1)^{n+q}\end{aligned} \qquad \text{(S41)}$$