Supplementary Information for "Atomic Forces for Geometry-Dependent Point Multipole and Gaussian Multipole Models" by D.M. Elking et al.

Additional Mathematical Derivations

Introduction

In this section of the Supplementary Information, additional mathematical details and derivations are provided. In section S1, a short discussion on the Cartesian rotation matrix derivative $\mathbf{A}^{\Omega} \equiv (\partial\mathbf{R}/\partial\Omega)\mathbf{R}^{-1}$ matrix is given. The results for atomic gradients of Cartesian rotation matrices $(\partial\mathbf{R}/\partial\mathbf{r}_{a',q})\mathbf{R}^{-1}$ are derived in sections S2-S5. In sections S6, S7, and S8 the general expression for $\partial D^{l}_{m'm}/\partial\Omega$ is applied to the cases when Ω is an infinitesimal rotation, an Euler angle, and a quaternion, respectively. Lastly, the results $\boldsymbol{\tau}_a = \boldsymbol{\alpha}\times\mathbf{F}^{orient}_{a\rightarrow \mathrm{N1}} + \boldsymbol{\beta}\times\mathbf{F}^{orient}_{a\rightarrow \mathrm{N2}}$ and $\sum_{a'}\mathbf{r}_{a'}\times\partial\eta/\partial\mathbf{r}_{a'} = 0$, which are used in the main text, are derived in sections S9 and S10, respectively.

S1) Note on Cartesian Rotation Matrix Derivatives $\mathbf{A}^{\Omega} \equiv (\partial\mathbf{R}/\partial\Omega)\mathbf{R}^{-1}$

For many cases of Ω, the matrix $\mathbf{A}^{\Omega} \equiv (\partial\mathbf{R}/\partial\Omega)\mathbf{R}^{-1}$ is antisymmetric, i.e. $\mathbf{A}^{\Omega}_{ij} = -\mathbf{A}^{\Omega}_{ji}$. For example, if Ω is an Euler angle or a rotation about a coordinate axis, $\mathbf{A}^{\Omega}$ is antisymmetric. If $\mathbf{R}(\Omega)$ is an orthogonal rotation matrix for all of values of Ω, then the following relation holds

$$\mathbf{R}(\Omega)\mathbf{R}^{T}(\Omega) = \mathbf{I}, \qquad \text{(S1.1)}$$

where $\mathbf{I}$ is the constant identity matrix, and $\mathbf{R}^{-1} = \mathbf{R}^{T}$ for real orthogonal Cartesian rotation matrices. After taking the derivative with respect to Ω of both sides of eqn. S1.1, the following result is obtained

$$\frac{\partial\mathbf{R}}{\partial\Omega}\mathbf{R}^{T} + \left(\frac{\partial\mathbf{R}}{\partial\Omega}\mathbf{R}^{T}\right)^{T} = 0, \qquad \text{(S1.2)}$$

which shows that $\mathbf{A}^{\Omega} \equiv (\partial\mathbf{R}/\partial\Omega)\mathbf{R}^{-1}$ is antisymmetric. For the cases when Ω is an Euler angle or a rotation about a coordinate axis, $\mathbf{A}^{\Omega}$ is antisymmetric. Since an antisymmetric matrix $\mathbf{A}$ has the general form

$$\mathbf{A} \equiv \begin{pmatrix} 0 & -a_3 & a_2 \\ a_3 & 0 & -a_1 \\ -a_2 & a_1 & 0 \end{pmatrix}, \qquad \text{(S1.3)}$$

the infinitesimal rotation matrices $\mathbf{M}_i$ defined in eqn. 28 of the main text forms a basis for $\mathbf{A}$, i.e.

$$\mathbf{A} = \sum_{i=1}^{3} a_i \mathbf{M}_i \ . \qquad \text{(S1.4)}$$

A similar argument applies to $\bar{\mathbf{A}}^{\Omega} \equiv \mathbf{R}^{-1}(\partial\mathbf{R}/\partial\Omega) = \mathbf{R}^{-1}\mathbf{A}^{\Omega}\mathbf{R}$.

If $\mathbf{R}(\Omega)$ is a rotation matrix for only a limited subspace of the values for Ω, then eqn. S1.1 holds for the values in which $\mathbf{R}(\Omega)$ is a rotation matrix, i.e. $\mathbf{R}(\Omega)\mathbf{R}^{T}(\Omega) = \mathbf{I}(\Omega)$. In this case, $\mathbf{I}(\Omega)$ is the identity matrix only for the values in which $\mathbf{R}(\Omega)$ is a rotation matrix. Eqn. S1.2 is no longer valid, since $\partial\mathbf{I}/\partial\Omega$ is not necessarily zero. An example is quaternions (q_0, q_1, q_2, q_3), which satisfy an equation of constraint, $\sum_{\mu=0}^{3} q_{\mu}^{2} = 1$. In section S8, it is shown that $(\partial\mathbf{R}/\partial q_{\mu})\mathbf{R}^{-1}$ is not antisymmetric.

S2) Preliminary note on Cartesian vectors

The expressions for $(\partial\mathbf{R}/\partial\mathbf{r}_{a',q})\mathbf{R}^{-1}$ are derived using Cartesian vector analysis. In order to provide a more economical derivation of $(\partial\mathbf{R}/\partial\mathbf{r}_{a',q})\mathbf{R}^{-1}$, the Kronecker-delta δ_{ij} and Levi-Cita ε_{ijk} symbols[70] are used to express Cartesian vectors in component form. The δ_{ij} and ε_{ijk} symbols allow efficient evaluation and manipulations of vector equations and identities. These conventions are outlined below.

Suppose **a** and **b** are two arbitrary three dimensional vectors given by

$$\mathbf{a} \equiv (a_1, a_2, a_3) \equiv a_1\hat{x}_1 + a_2\hat{x}_2 + a_3\hat{x}_3 \qquad \text{(S2.1)}$$

$$\mathbf{b} \equiv (b_1, b_2, b_3) \equiv b_1\hat{x}_1 + b_2\hat{x}_2 + b_3\hat{x}_3 \ . \qquad \text{(S2.2)}$$

where $\hat{x}_p$ is the global or fixed coordinate basis for three dimensional space defined by $\hat{x}_1 \equiv (1,0,0)$, $\hat{x}_2 \equiv (0,1,0)$, and $\hat{x}_3 \equiv (0,0,1)$. The conventions used in this work can be summarized by the following rules:

1) Repeated indexes are summed over. For example, $a_i b_i \equiv \sum_{i=1}^{3} a_i b_i$.

2) The Kronecker-Delta symbol is defined by $\delta_{pq} \equiv \begin{cases} 1 \text{ if } p = q \\ 0 \text{ if } p \neq q \end{cases}$

3) The antisymmetric Levi-Cita symbol ε_{ijk} is defined by $\varepsilon_{123} = \varepsilon_{312} = \varepsilon_{231} = 1$, $\varepsilon_{321} = \varepsilon_{132} = \varepsilon_{213} = -1$, and $\varepsilon_{ijk} = 0$ if any index is repeated, e.g. $\varepsilon_{112} = 0$

4) The magnitude of a vector **a** is given by $a \equiv |\mathbf{a}| = \sqrt{a_1^{\ 2} + a_2^{\ 2} + a_3^{\ 2}}$

A scalar or dot product between two vectors $\mathbf{a} \equiv a_i\hat{x}_i$ and $\mathbf{b} \equiv b_i\hat{x}_i$ can be represented by

$$\mathbf{a} \cdot \mathbf{b} = a_i b_i , \qquad \text{(S2.3)}$$

and a vector or cross product between two vectors **a** and **b** can be represented by

$$\mathbf{a}\times\mathbf{b} = a_i b_j \varepsilon_{ijk}\hat{x}_k \,. \qquad \text{(S2.4)}$$

In particular, the k^{th} component of $\mathbf{a}\times\mathbf{b}$ is given by

$$(\mathbf{a}\times\mathbf{b})_k = a_i b_j \varepsilon_{ijk} \,. \qquad \text{(S2.5)}$$

The following important result can be readily verified

$$\varepsilon_{ijt}\varepsilon_{pqt} = \delta_{ip}\delta_{jq} - \delta_{iq}\delta_{jp} \,. \qquad \text{(S2.6)}$$

Note the $\hat{x}_i$ basis is orthonormal and right-handed, i.e.

$$\hat{x}_i \cdot \hat{x}_j = \delta_{ij} \qquad \text{(S2.7)}$$

$$\hat{x}_i \times \hat{x}_j = \varepsilon_{ijk}\hat{x}_k \qquad \text{(S2.8)}$$

Eqn. S2.7 is a short hand way of expressing $\hat{x}_1 \cdot \hat{x}_1 = 1$, $\hat{x}_1 \cdot \hat{x}_2 = 0$, .., while eqn. S2.8 is short for $\hat{x}_1 \times \hat{x}_2 = \hat{x}_3$, $\hat{x}_2 \times \hat{x}_3 = \hat{x}_1$, and $\hat{x}_3 \times \hat{x}_1 = \hat{x}_2$.

S3) Derivation of the local basis vector gradients

The local frame basis vectors $\hat{x}_i'$ for the type of local frame defined in Figure 1 of the main text are defined in terms of the bond vectors $\boldsymbol{\alpha} \equiv \mathbf{r}_{N1} - \mathbf{r}_a$ and $\boldsymbol{\beta} = \mathbf{r}_{N2} - \mathbf{r}_a$ by

$$\hat{x}_1' \equiv \frac{\boldsymbol{\alpha}}{\alpha} \qquad \hat{x}_2' \equiv \frac{\boldsymbol{\gamma}}{\gamma} \qquad \boldsymbol{\gamma} \equiv \boldsymbol{\beta} - \frac{\boldsymbol{\alpha}\cdot\boldsymbol{\beta}}{\alpha^2}\boldsymbol{\alpha} \qquad \hat{x}_3' \equiv \hat{x}_1' \times \hat{x}_2' \,. \qquad \text{(S3.1)}$$

It will be convenient to express the basis vectors in component form by

$$\hat{x}_{1,p}' \equiv \frac{\alpha_p}{\alpha} \qquad \hat{x}_{2,p}' \equiv \frac{\gamma_p}{\gamma} \qquad \gamma_p \equiv \beta_p - \frac{\beta_s \alpha_s}{\alpha^2}\alpha_p \qquad \hat{x}_{3,p}' \equiv \hat{x}_{1,s}'\hat{x}_{2,t}'\varepsilon_{stp} \qquad \text{(S3.2)}$$

The local basis vectors are orthonormal and right handed, i.e. $\hat{x}_i' \cdot \hat{x}_j' = \delta_{ij}$ and $\hat{x}_i' \times \hat{x}_j' = \varepsilon_{ijk}\hat{x}_k'$.

The Cartesian rotation matrix $\mathbf{R}$ from local to global frames is constructed by the column vectors of $\hat{x}_i'$ by

$$\mathbf{R} = \begin{pmatrix} \hat{x}_1' & \hat{x}_2' & \hat{x}_3' \\ \downarrow & \downarrow & \downarrow \\ & & \end{pmatrix}. \qquad \text{(S3.3)}$$

or in component from, $\mathbf{R}_{pi} = \hat{x}_{i,p}'$. The result for $(\partial\mathbf{R}_a/\partial\mathbf{r}_{a',q})\mathbf{R}_a^{-1}$ ($a' = a$, N1, N2; q = 1, 2, 3 for x, y, z) are found by first deriving expressions for $(\partial\mathbf{R}/\partial\alpha_q)\mathbf{R}^{-1}$ and $(\partial\mathbf{R}/\partial\beta_q)\mathbf{R}^{-1}$. The corresponding results for $(\partial\mathbf{R}/\partial\mathbf{r}_{a',q})\mathbf{R}^{-1}$ can be found from $(\partial\mathbf{R}/\partial\alpha_q)\mathbf{R}^{-1}$ and $(\partial\mathbf{R}/\partial\beta_q)\mathbf{R}^{-1}$ by a simple chain rule argument.

$$\frac{\partial \mathbf{R}}{\partial \mathbf{r}_{N1,q}}\mathbf{R}^{-1} = \frac{\partial \mathbf{R}}{\partial \alpha_q}\mathbf{R}^{-1}$$
$$\frac{\partial \mathbf{R}}{\partial \mathbf{r}_{N2,q}}\mathbf{R}^{-1} = \frac{\partial \mathbf{R}}{\partial \beta_q}\mathbf{R}^{-1} \qquad \text{(S3.4)}$$
$$\frac{\partial \mathbf{R}}{\partial \mathbf{r}_{a,q}}\mathbf{R}^{-1} = -\left(\frac{\partial \mathbf{R}}{\partial \alpha_q}\mathbf{R}^{-1} + \frac{\partial \mathbf{R}}{\partial \beta_q}\mathbf{R}^{-1}\right)$$

Since the Cartesian rotation matrix $\mathbf{R}$ is constructed from the *relative* atomic positions $\boldsymbol{\alpha} \equiv \mathbf{r}_{N1} - \mathbf{r}_1$ and $\boldsymbol{\beta} = \mathbf{r}_{N2} - \mathbf{r}_1$, $\mathbf{R}$ is translationally invariant, i.e. $(\partial\mathbf{R}/\partial\mathbf{r}_{N1,q})\mathbf{R}^{-1} + (\partial\mathbf{R}/\partial\mathbf{r}_{N2,q})\mathbf{R}^{-1} + (\partial\mathbf{R}/\partial\mathbf{r}_{a,q})\mathbf{R}^{-1} = 0$.

The general strategy for calculating $(\partial\mathbf{R}/\partial\alpha_q)\mathbf{R}^{-1}$ and $(\partial\mathbf{R}/\partial\beta_q)\mathbf{R}^{-1}$ is described as follows. Derivatives of $\hat{x}_{i,p}' = \mathbf{R}_{pi}$ with respect to α_q and β_q are found by differentiating eqn. S3.2. The derivatives $\partial\hat{x}_{i,p}'/\partial\alpha_q$ and $\partial\hat{x}_{i,p}'/\partial\beta_q$ are then converted back to the local basis vectors $\hat{x}_{i,p}'$ by

$$\alpha_p = \alpha\,\hat{x}_{1,p}'$$
$$\beta_p = \gamma\,\hat{x}_{2,p}' + \frac{\boldsymbol{\beta}\cdot\boldsymbol{\alpha}}{\alpha}\hat{x}_{1,p}' \qquad \text{(S3.5)}$$

The results for $\partial\hat{x}_{i,p}'/\partial\alpha_q = \partial\mathbf{R}_{pi}/\partial\alpha_q$ and $\partial\hat{x}_{i,p}'/\partial\beta_q = \partial\mathbf{R}_{pi}/\partial\beta_q$ are right multiplied by $\mathbf{R}_{ir}^{-1} = \mathbf{R}_{ri} = \hat{x}_{i,r}'$ and summed in section S4. The orthonormal property $\hat{x}_p'\cdot\hat{x}_q' = \delta_{pq}$ is used to derive compact expressions for $(\partial\mathbf{R}_{pi}/\partial\alpha_q)\mathbf{R}_{ri}$ and $(\partial\mathbf{R}_{pi}/\partial\beta_q)\mathbf{R}_{ri}$, which are then converted back into bond vectors $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$. Lastly, the antisymmetric matrices $(\partial\mathbf{R}/\partial\alpha_q)\mathbf{R}^{-1}$ and $(\partial\mathbf{R}/\partial\beta_q)\mathbf{R}^{-1}$ are expressed in the infinitesimal rotation matrix $\mathbf{M}_p$ basis in section S5. This last result is used to demonstrate the relationship between orientation force and torque.

A) Derivatives of $\hat{x}_{1,p}' = \mathbf{R}_{p1}$

The derivative of $\hat{x}_{1,p}'$ with respect to α_q is given by differentiating $\hat{x}_{1,p}'$ in eqn. S3.2

$$\frac{\partial}{\partial\alpha_q}\hat{x}_{1,p}' = \frac{\delta_{pq}}{\alpha} - \frac{\alpha_p\alpha_q}{\alpha^3} = \frac{1}{\alpha}\left(\delta_{pq} - \hat{x}_{1,p}'\hat{x}_{1,q}'\right) \qquad \text{(S3.6)}$$

while the derivative $\hat{x}_{1,p}'$ with respect to β_q is zero,

$$\frac{\partial}{\partial\beta_q}\hat{x}_{1,p}' = 0 \qquad \text{(S3.7)}$$

B) Derivatives of $\hat{x}_{2,p}' = \mathbf{R}_{p2}$

The derivatives of $\hat{x}_{2,p}'$ with respect to α_q or β_q can be derived through a chain rule argument using γ_r as an intermediate. For example,

$$\frac{\partial}{\partial \alpha_q}\hat{x}_{2,p}' = \frac{\partial \hat{x}_{2,p}'}{\partial \gamma_r}\frac{\partial \gamma_r}{\partial \alpha_q} \tag{S3.8}$$

The result for $\partial \hat{x}_{2,p}'/\partial \gamma_r$ has a form identical to eqn. S3.6

$$\frac{\partial \hat{x}_{2,p}'}{\partial \gamma_r} = \frac{1}{\gamma}\left(\delta_{pr} - \hat{x}_{2,p}'\hat{x}_{2,r}'\right) \tag{S3.9}$$

$\partial \gamma_r/\partial \alpha_q$ is given by

$$\begin{aligned}\frac{\partial}{\partial \alpha_q}\gamma_r &= \frac{\partial}{\partial \alpha_q}\left(\beta_r - \frac{(\beta_s\alpha_s)\alpha_r}{\alpha^2}\right) = -\beta_s\frac{\partial}{\partial \alpha_q}\left(\frac{\alpha_s\alpha_r}{\alpha^2}\right)\\ &= -\beta_s\left(\frac{\delta_{qs}\alpha_r + \alpha_s\delta_{qr}}{\alpha^2} - \frac{2\alpha_s\alpha_r\alpha_q}{\alpha^4}\right)\\ &= \frac{\boldsymbol{\beta}\cdot\boldsymbol{\alpha}}{\alpha^2}(\hat{x}_{1,q}'\hat{x}_{1,r}' - \delta_{qr}) - \frac{\gamma}{\alpha}\hat{x}_{2,q}'\hat{x}_{1,r}'\end{aligned} \tag{S3.10}$$

Similarly $\partial \gamma_r/\partial \beta_q$ is given by

$$\begin{aligned}\frac{\partial}{\partial \beta_q}\gamma_r &= \frac{\partial}{\partial \beta_q}\left(\beta_r - \frac{(\beta_s\alpha_s)\alpha_r}{\alpha^2}\right) = \delta_{qr} - \frac{\alpha_q\alpha_r}{\alpha^2}\\ &= \delta_{qr} - \hat{x}_{1,q}'\hat{x}_{1,r}'\end{aligned} \tag{S3.11}$$

Recall the local frame basis is constructed to be orthonormal, i.e. $\hat{x}_{1,p}'\hat{x}_{1,p}' = \hat{x}_{2,p}'\hat{x}_{2,p}' = 1$, and $\hat{x}_{1,p}'\hat{x}_{2,p}' = 0$. After inserting eqns. S3.9 and S3.10 into eqn. S3.8, the desired result for $\partial \hat{x}_{2,p}'/\partial \alpha_q$ becomes

$$\begin{aligned}\frac{\partial}{\partial \alpha_q}\hat{x}_{2,p}' &= \frac{1}{\gamma}\left(\delta_{pr} - \hat{x}_{2,p}'\hat{x}_{2,r}'\right)\left(\frac{\boldsymbol{\beta}\cdot\boldsymbol{\alpha}}{\alpha^2}(\hat{x}_{1,q}'\hat{x}_{1,r}' - \delta_{qr}) - \frac{\gamma}{\alpha}\hat{x}_{2,q}'\hat{x}_{1,r}'\right)\\ &= \frac{\boldsymbol{\beta}\cdot\boldsymbol{\alpha}}{\gamma\alpha^2}(\hat{x}_{1,p}'\hat{x}_{1,q}' + \hat{x}_{2,p}'\hat{x}_{2,q}' - \delta_{pq}) - \frac{1}{\alpha}\hat{x}_{1,p}'\hat{x}_{2,q}'\\ &= -\frac{\boldsymbol{\beta}\cdot\boldsymbol{\alpha}}{\gamma\alpha^2}\hat{x}_{3,p}'\hat{x}_{3,q}' - \frac{1}{\alpha}\hat{x}_{1,p}'\hat{x}_{2,q}'\end{aligned} \tag{S3.12}$$

The last line follows from

$$\hat{x}_{1,p}'\hat{x}_{1,q}' + \hat{x}_{2,p}'\hat{x}_{2,q}' + \hat{x}_{3,p}'\hat{x}_{3,q}' = \mathbf{R}_{pi}\mathbf{R}_{qi} = \mathbf{R}_{pi}\mathbf{R}_{iq}^{-1} = \delta_{pq}\,. \tag{S3.13}$$

Similarly, $\partial \hat{x}_{2,p}'/\partial \beta_q$ is given by combining eqns. S3.9 and S3.11

$$\frac{\partial}{\partial \beta_q}\hat{x}_{2,p}' = \frac{1}{\gamma}\left(\delta_{pr} - \hat{x}_{2,p}'\hat{x}_{2,r}'\right)\left(\delta_{qr} - \hat{x}_{1,q}'\hat{x}_{1,r}'\right)$$
$$= \frac{1}{\gamma}\left(\delta_{pq} - \hat{x}_{1,p}'\hat{x}_{1,q}' - \hat{x}_{2,p}'\hat{x}_{2,q}'\right) \quad \text{(S3.14)}$$
$$= \frac{1}{\gamma}\hat{x}_{3,p}'\hat{x}_{3,q}'$$

C) Derivatives of $\hat{x}_{3,p}' = \mathbf{R}_{p3}$

The expressions for $\partial\hat{x}_{1,p}'/\partial\alpha_q$ and $\partial\hat{x}_{2,p}'/\partial\alpha_q$ are used to find $\partial\hat{x}_{3,p}'/\partial\alpha_q$ by differentiating eqn. S3.2

$$\frac{\partial\hat{x}_{3,p}'}{\partial\alpha_q} = \frac{\partial}{\partial\alpha_q}\left(\hat{x}_{1,s}'\hat{x}_{2,t}'\varepsilon_{stp}\right)$$
$$= \frac{\partial\hat{x}_{1,s}'}{\partial\alpha_q}\hat{x}_{2,t}'\varepsilon_{stp} + \hat{x}_{1,s}'\frac{\partial\hat{x}_{2,t}'}{\partial\alpha_q}\varepsilon_{stp} \quad \text{(S3.15)}$$

After inserting eqns. S3.6 and S3.12 into eqn. S3.15, $\partial\hat{x}_{3,p}'/\partial\alpha_q$ becomes

$$\frac{\partial\hat{x}_{3,p}'}{\partial\alpha_q} = \frac{\partial\hat{x}_{1,s}'}{\partial\alpha_q}\hat{x}_{2,t}'\varepsilon_{stp} + \hat{x}_{1,s}'\frac{\partial\hat{x}_{2,t}'}{\partial\alpha_q}\varepsilon_{stp}$$
$$= \frac{1}{\alpha}\left(\delta_{sq} - \hat{x}_{1,s}'\hat{x}_{1,q}'\right)\hat{x}_{2,t}'\varepsilon_{stp} +$$
$$\hat{x}_{1,s}'\left(-\frac{\boldsymbol{\beta}\cdot\boldsymbol{\alpha}}{\gamma\alpha^2}\hat{x}_{3,t}'\hat{x}_{3,q}' - \frac{1}{\alpha}\hat{x}_{1,t}'\hat{x}_{2,q}'\right)\varepsilon_{stp} \quad \text{(S3.16)}$$
$$= \frac{1}{\alpha}\left(\varepsilon_{pqt}\hat{x}_{2,t}' - \hat{x}_{3,p}'\hat{x}_{1,q}'\right) + \frac{\boldsymbol{\beta}\cdot\boldsymbol{\alpha}}{\gamma\alpha^2}\hat{x}_{2,p}'\hat{x}_{3,q}'$$

where $\hat{x}_1'\times\hat{x}_2' = \hat{x}_3'$, $\hat{x}_3'\times\hat{x}_1' = \hat{x}_2'$, $\hat{x}_2'\times\hat{x}_3' = \hat{x}_1'$ has been used. Eqn. S3.16 can be simplified by first recalling the result $\varepsilon_{ijt}\varepsilon_{pqt} = \delta_{ip}\delta_{jq} - \delta_{iq}\delta_{jp}$ from eqn. S2.6 and noting

$$\hat{x}_{3,p}'\hat{x}_{1,q}' - \hat{x}_{1,p}'\hat{x}_{3,q}' = \hat{x}_{3,i}'\hat{x}_{1,j}'(\delta_{ip}\delta_{jq} - \delta_{iq}\delta_{jp})$$
$$= \hat{x}_{3,i}'\hat{x}_{1,j}'\varepsilon_{ijt}\varepsilon_{pqt} = (\hat{x}_3'\times\hat{x}_1')_t\,\varepsilon_{pqt} \quad \text{(S3.17)}$$
$$= \hat{x}_{2,t}'\varepsilon_{pqt}$$

Inserting eqns. S3.17 into S3.16, $\partial\hat{x}_{3,p}'/\partial\alpha_q$ becomes

$$\frac{\partial\hat{x}_{3,p}'}{\partial\alpha_q} = -\frac{1}{\alpha}\hat{x}_{1,p}'\hat{x}_{3,q}' + \frac{\boldsymbol{\beta}\cdot\boldsymbol{\alpha}}{\gamma\alpha^2}\hat{x}_{2,p}'\hat{x}_{3,q}'. \quad \text{(S3.18)}$$

Similarly, the result for $\partial\hat{x}_{3,p}'/\partial\beta_q$ can be found by combining eqns. S3.7 and S3.14,

$$
\begin{aligned}
\frac{\partial \hat{x}_{3,p}'}{\partial \beta_q} &= \frac{\partial \hat{x}_{1,s}'}{\partial \beta_q}\hat{x}_{2,t}'\varepsilon_{stp} + \hat{x}_{1,s}'\frac{\partial \hat{x}_{2,t}'}{\partial \beta_q}\varepsilon_{stp} \\
&= \hat{x}_{1,s}'\frac{1}{\gamma}\hat{x}_{3,t}'\hat{x}_{3,q}'\varepsilon_{stp} \quad . \\
&= -\frac{1}{\gamma}\hat{x}_{2,p}'\hat{x}_{3,q}'
\end{aligned}
\tag{S3.19}
$$

S4) Derivation of (∂R/$\partial\boldsymbol{\alpha_q}$)R^{-1} and ($\partial$R/$\partial\boldsymbol{\beta_q}$)R^{-1}

In this section, the $\mathbf{A}_{pr}^{\alpha_q}$ and $\mathbf{A}_{pr}^{\beta_q}$ matrices given by

$$
\mathbf{A}_{pr}^{\alpha_q} \equiv \frac{\partial \mathbf{R}_{pi}}{\partial \alpha_q}\mathbf{R}_{ir}^{-1} = \frac{\partial \hat{x}_{i,p}'}{\partial \alpha_q}\hat{x}_{i,r}' \tag{S4.1}
$$

$$
\mathbf{A}_{pr}^{\beta_q} \equiv \frac{\partial \mathbf{R}_{pi}}{\partial \beta_q}\mathbf{R}_{ir}^{-1} = \frac{\partial \hat{x}_{i,p}'}{\partial \beta_q}\hat{x}_{i,r}' \tag{S4.2}
$$

will be derived. $\mathbf{A}_{pr}^{\alpha_q}$ can be found by inserting eqns. S3.6, S3.12, and S3.18 into S4.1

$$
\begin{aligned}
\mathbf{A}_{pr}^{\alpha_q} &= \frac{\partial \hat{x}_{1,p}'}{\partial \alpha_q}\hat{x}_{1,r}' + \frac{\partial \hat{x}_{2,p}'}{\partial \alpha_q}\hat{x}_{2,r}' + \frac{\partial \hat{x}_{3,p}'}{\partial \alpha_q}\hat{x}_{3,r}' \\
&= \frac{1}{\alpha}\left(\delta_{pq} - \hat{x}_{1,p}'\hat{x}_{1,q}'\right)\hat{x}_{1,r}' - \left(\frac{\boldsymbol{\beta}\cdot\boldsymbol{\alpha}}{\gamma\alpha^2}\hat{x}_{3,p}'\hat{x}_{3,q}' + \frac{1}{\alpha}\hat{x}_{1,p}'\hat{x}_{2,q}'\right)\hat{x}_{2,r}' \\
&\quad + \left(-\frac{1}{\alpha}\hat{x}_{1,p}'\hat{x}_{3,q}' + \frac{\boldsymbol{\beta}\cdot\boldsymbol{\alpha}}{\gamma\alpha^2}\hat{x}_{2,p}'\hat{x}_{3,q}'\right)\hat{x}_{3,r}' \\
&= \frac{1}{\alpha}\left\{\delta_{pq}\hat{x}_{1,r}' - \hat{x}_{1,p}'\left(\hat{x}_{1,q}'\hat{x}_{1,r}' + \hat{x}_{2,q}'\hat{x}_{2,r}' + \hat{x}_{3,q}'\hat{x}_{3,r}'\right)\right\} \\
&\quad + \frac{\boldsymbol{\beta}\cdot\boldsymbol{\alpha}}{\gamma\alpha^2}\hat{x}_{3,q}'\left(\hat{x}_{2,p}'\hat{x}_{3,r}' - \hat{x}_{3,p}'\hat{x}_{2,r}'\right)
\end{aligned}
\tag{S4.3}
$$

Recall eqn. S3.17 after a cyclic change of indexes

$$
\hat{x}_{2,p}'\hat{x}_{3,r}' - \hat{x}_{3,p}'\hat{x}_{2,r}' = \hat{x}_{1,t}'\varepsilon_{prt} . \tag{S4.4}
$$

After substituting eqns. S3.13 and S4.4 into eqn. S4.3, $\mathbf{A}_{pr}^{\alpha_q}$ becomes

$$
\mathbf{A}_{pr}^{\alpha_q} = \frac{1}{\alpha}\left(\delta_{pq}\hat{x}_{1,r}' - \hat{x}_{1,p}'\delta_{qr}\right) + \frac{\boldsymbol{\beta}\cdot\boldsymbol{\alpha}}{\gamma\alpha^2}\hat{x}_{3,q}'\hat{x}_{1,t}'\varepsilon_{prt} \tag{S4.5}
$$

The antisymmetry property between the *p* and *r* indexes in the first term of eqn. S4.5 can be expressed by noting that

$$\begin{aligned}\delta_{pq}\hat{x}_{1,r}'-\hat{x}_{1,p}'\delta_{qr} &= \hat{x}_{1,s}'\left(\delta_{pq}\delta_{rs}-\delta_{ps}\delta_{rq}\right)\\ &= \hat{x}_{1,s}'\varepsilon_{qst}\varepsilon_{prt}\\ &= (\hat{x}_q\times\hat{x}_1')_t\varepsilon_{prt}\end{aligned} \tag{S4.6}$$

where $\hat{x}_{q,p}=\delta_{pq}$ is a global frame basis vector. Inserting this result into S4.5 gives

$$\mathbf{A}_{pr}^{\alpha_q}=\left(\frac{1}{\alpha}(\hat{x}_q\times\hat{x}_1')_t+\frac{\boldsymbol{\beta}\cdot\boldsymbol{\alpha}}{\gamma\alpha^2}\hat{x}_{3,q}'\hat{x}_{1,t}'\right)\varepsilon_{prt} \tag{S4.7}$$

It is evident from eqn. S4.7 that $\mathbf{A}_{pr}^{\alpha_q}$ is antisymmetric with respect to *p* and *r* from the antisymmetric Levi-Cita symbol ε_{prt}, i.e. $\mathbf{A}_{rp}^{\alpha_q}=-\mathbf{A}_{pr}^{\alpha_q}$. $\mathbf{A}_{pr}^{\alpha_q}$ can be expressed back in terms of the $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ vectors by recalling the definitions of $\hat{x}_i'$ in eqn. S3.2 and expressing this result as

$$\begin{aligned}\hat{x}_{1,p}' &= \frac{\alpha_p}{\alpha}\\ \hat{x}_{2,p}' &= \frac{1}{\gamma}\left(\beta_p-\frac{\boldsymbol{\alpha}\cdot\boldsymbol{\beta}}{\alpha^2}\alpha_p\right)\\ \hat{x}_{3,p}' &= \frac{1}{\alpha\gamma}(\boldsymbol{\alpha}\times\boldsymbol{\beta})_p\end{aligned} \tag{S4.8}$$

Substituting eqn. S4.8 into eqn. S4.7 results in

$$\mathbf{A}_{pr}^{\alpha_q}=\left(\frac{1}{\alpha^2}(\hat{x}_q\times\boldsymbol{\alpha})_t+\frac{\boldsymbol{\beta}\cdot\boldsymbol{\alpha}}{\gamma^2\alpha^4}(\boldsymbol{\alpha}\times\boldsymbol{\beta})_q\alpha_t\right)\varepsilon_{prt} \tag{S4.9}$$

Finally, γ^2 can be expressed in terms of $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ by

$$\gamma^2=\beta^2-\frac{(\boldsymbol{\beta}\cdot\boldsymbol{\alpha})^2}{\alpha^2} \tag{S4.10}$$

Inserting this result into eqn. S4.9 gives

$$\mathbf{A}_{pr}^{\alpha_q}=\left(\frac{1}{\alpha^2}(\hat{x}_q\times\boldsymbol{\alpha})_t+\frac{\boldsymbol{\alpha}\cdot\boldsymbol{\beta}}{\alpha^2[\alpha^2\beta^2-(\boldsymbol{\alpha}\cdot\boldsymbol{\beta})^2]}(\boldsymbol{\alpha}\times\boldsymbol{\beta})_q\alpha_t\right)\varepsilon_{prt} \tag{S4.11}$$

The result for $\mathbf{A}_{pr}^{\beta_q}$ can be found by inserting eqns. S3.7, S3.14, and S3.19 into eqn. S4.2 to give

$$\mathbf{A}_{pr}^{\beta_q}=\frac{1}{\gamma}\hat{x}_{3,q}'\left(\hat{x}_{3,p}'\hat{x}_{2,r}'-\hat{x}_{2,p}'\hat{x}_{3,r}'\right) \tag{S4.12}$$

Now apply eqn. S4.4 to eqn. S4.12 to get

$$\mathbf{A}_{pr}^{\beta_q}=-\frac{1}{\gamma}\hat{x}_{3,q}'\hat{x}_{1,t}'\varepsilon_{prt} \tag{S4.13}$$

$\mathbf{A}_{pr}^{\beta_q}$ can be expressed in terms of the vectors $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ by inserting eqns. S4.8 and S4.10 into eqn. S4.13

$$\mathbf{A}_{pr}^{\beta_q} = -\frac{(\boldsymbol{\alpha}\times\boldsymbol{\beta})_q \alpha_t \varepsilon_{prt}}{\alpha^2\beta^2 - (\boldsymbol{\alpha}\cdot\boldsymbol{\beta})^2} \tag{S4.14}$$

S5) Expression of $\mathbf{A}_{pr}^{\alpha_q}$ and $\mathbf{A}_{pr}^{\beta_q}$ in terms of infinitesimal rotation matrices

Recall the definitions for the infinitesimal rotation matrices from eqn. 28 of the main text

$$\mathbf{M}_1 \equiv \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix},\ \mathbf{M}_2 \equiv \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix},\ \mathbf{M}_3 \equiv \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{S5.1}$$

The matrix elements of $\mathbf{M}_t$ (t = 1,2,3) can be conveniently expressed in terms of the Levi-Cita antisymmetric symbol by

$$\mathbf{M}_{t,pr} = -\varepsilon_{prt} \tag{S5.2}$$

Therefore, the antisymmetric rotation derivative matrix $\mathbf{A}_{pr}^{\alpha_q}$ in eqn. S4.11 can be expressed in terms of $\mathbf{M}_t$ by

$$\mathbf{A}_{pr}^{\alpha_q} = -\left(\frac{1}{\alpha^2}(\hat{x}_q\times\boldsymbol{\alpha})_t + \frac{\boldsymbol{\alpha}\cdot\boldsymbol{\beta}}{\alpha^2[\alpha^2\beta^2 - (\boldsymbol{\alpha}\cdot\boldsymbol{\beta})^2]}(\boldsymbol{\alpha}\times\boldsymbol{\beta})_q\alpha_t\right)\mathbf{M}_{t,pr} \tag{S5.3}$$

or in matrix form

$$\mathbf{A}^{\alpha_q} = \sum_t X_t^{\alpha_q}\mathbf{M}_t \tag{S5.4}$$

where

$$X_t^{\alpha_q} \equiv -\left(\frac{1}{\alpha^2}(\hat{x}_q\times\boldsymbol{\alpha})_t + \frac{\boldsymbol{\alpha}\cdot\boldsymbol{\beta}}{\alpha^2[\alpha^2\beta^2 - (\boldsymbol{\alpha}\cdot\boldsymbol{\beta})^2]}(\boldsymbol{\alpha}\times\boldsymbol{\beta})_q\alpha_t\right) \tag{S5.5}$$

Similarly $\mathbf{A}^{\beta_q}$ can be expressed in terms of $\mathbf{M}_t$ by

$$\mathbf{A}^{\beta_q} = \sum_t X_t^{\beta_q}\mathbf{M}_t \tag{S5.6}$$

where

$$X_t^{\beta_q} \equiv \frac{(\boldsymbol{\alpha}\times\boldsymbol{\beta})_q\alpha_t}{\alpha^2\beta^2 - (\boldsymbol{\alpha}\cdot\boldsymbol{\beta})^2} \tag{S5.7}$$

Thus, the final Cartesian derivative matrixes with respect to atomic position $(\partial\mathbf{R}_a/\partial\mathbf{r}_{a',q})\mathbf{R}_a^{-1}$ (a' = a, N1, N2; q = 1, 2, 3 for x, y, z) are given by inserting eqns. S5.4 and S5.6 into eqn. S3.4

$$\boxed{\begin{aligned}&\frac{\partial \mathbf{R}}{\partial \mathbf{r}_{\mathrm{N1},q}}\mathbf{R}^{-1} = \mathbf{A}^{\alpha_q} = \sum\nolimits_t X_t^{\mathrm{N1},q}\mathbf{M}_t \\ &\frac{\partial \mathbf{R}}{\partial \mathbf{r}_{\mathrm{N2},q}}\mathbf{R}^{-1} = \mathbf{A}^{\beta_q} = \sum\nolimits_t X_t^{\mathrm{N2},q}\mathbf{M}_t \\ &\frac{\partial \mathbf{R}}{\partial \mathbf{r}_{a,q}}\mathbf{R}^{-1} = -\left(\mathbf{A}^{\alpha_q} + \mathbf{A}^{\beta_q}\right) = \sum\nolimits_t X_t^{a,q}\mathbf{M}_t\end{aligned}} \quad \text{(S3.8)}$$

where $X_t^{\mathrm{N1},q} \equiv X_t^{\alpha_q}$, $X_t^{\mathrm{N2},q} \equiv X_t^{\beta_q}$, and $X_t^{a,q} \equiv -\left(X_t^{\alpha_q} + X_t^{\beta_q}\right)$.

S6) Wigner Function Derivatives $\partial D^l_{m'm}/\partial\Omega$ and Infinitesimal Rotation Matrices

Recall the expressions for $\partial D^l_{m'm}/\partial\Omega$ from eqns. 22 and 24 of the main text

$$\frac{\partial}{\partial\Omega} D^l_{m',m}[\mathbf{R}(\Omega)] = \sum_{i=-1}^{1}\sum_{k=-1}^{1} B^k_{l-1,m-i} C^i_{lm} D^1_{ki}[\mathbf{R}^{-1}\frac{\partial \mathbf{R}}{\partial\Omega}] D^l_{m',m-i+k}[\mathbf{R}]. \quad (22)$$

$$\frac{\partial}{\partial\Omega} D^l_{m'm}[\mathbf{R}(\Omega)] = \sum_{i=-1}^{1}\sum_{k=-1}^{1} B^k_{l-1,m'-i} C^i_{lm'} D^1_{ik}[\frac{\partial \mathbf{R}}{\partial\Omega}\mathbf{R}^{-1}] D^l_{m'-i+k,m}[\mathbf{R}]. \quad (24)$$

where the constants B^k_{lm} and C^k_{lm} are defined in eqns. A.8 and A.10 of the appendix, respectively.

$$B^{\pm1}_{lm} \equiv \sqrt{\frac{(l \pm m + 1)(l \pm m + 2)}{2(2l+1)(2l+3)}}, \quad B^0_{lm} \equiv \sqrt{\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}}. \quad (A.8)$$

$$C^{\pm1}_{lm} \equiv \sqrt{\frac{2l+1}{2l-1}}\sqrt{\frac{(l \pm m)(l \pm m - 1)}{2}}, \qquad C^0_{lm} \equiv \sqrt{\frac{2l+1}{2l-1}}\sqrt{(l+m)(l-m)}. \quad (A.10)$$

As a first step in the calculation of $\partial D^l_{m'm}/\partial\Omega$, either $\mathbf{A}^\Omega \equiv (\partial\mathbf{R}/\partial\Omega)\mathbf{R}^{-1}$ or $\bar{\mathbf{A}}^\Omega \equiv \mathbf{R}^{-1}(\partial\mathbf{R}/\partial\Omega)$ is inserted into eqns. A.14 – A.16 in order to arrive at the expressions for $D^1[\mathbf{A}^\Omega]$ and $D^1[\bar{\mathbf{A}}^\Omega]$, respectively. For many cases of Ω (e.g. Ω is an Euler angles, atomic position), $\mathbf{A}^\Omega$ and $\bar{\mathbf{A}}^\Omega$ are antisymmetric (see section S1). If $\mathbf{A}^\Omega$ is antisymmetric, then $\mathbf{A}^\Omega$ can be expanded in the basis of infinitesimal rotation matrices $\mathbf{M}_p$ (eqn. S1.4) $\mathbf{A}^\Omega = \sum_{p=1}^{3} a_p \mathbf{M}_p$. Since the $D^1[\mathbf{R}]$ is a linear function of $\mathbf{R}$ from eqns. A.14 – A.16,

$$D^1[\mathbf{A}^\Omega] = \sum_{p=1}^{3} a_p D^1[\mathbf{M}_p] \quad \text{(S6.1)}$$

and the expression for $\partial D^l_{m'm}/\partial\Omega$ from eqn. 24 is given by

$$
\begin{aligned}
\frac{\partial}{\partial\Omega} D^l_{m'm}[\mathbf{R}(\Omega)] &= \sum_{p=1}^{3} a_p \sum_{i=-1}^{1}\sum_{k=-1}^{1} B^k_{l-1,m'-i} C^i_{lm'} D^1_{ik}[\mathbf{M}_p] D^l_{m'-i+k,m}[\mathbf{R}] \\
&= \sum_{p=1}^{3} a_p \left(\frac{\partial D^l_{m'm}[\mathbf{R}]}{\partial\Phi} \right)_{\hat{x}_p}
\end{aligned} \tag{S6.2}
$$

where $\left(\partial D^l_{m'm}/\partial\Phi\right)_{\hat{x}_p}$ is the derivative of $D^l{}_{m'm}$ with respect to rotation about the $\hat{x}_p$ coordinate axis defined by

$$
\left(\frac{\partial D^l_{m'm}[\mathbf{R}]}{\partial\Phi} \right)_{\hat{x}_p} \equiv \sum_{i=-1}^{1}\sum_{k=-1}^{1} B^k_{l-1,m'-i} C^i_{lm'} D^1_{ik}[\mathbf{M}_p] D^l_{m'-i+k,m}[\mathbf{R}] \tag{S6.3}
$$

A similar result holds by inserting $\bar{\mathbf{A}}^{\Omega} \equiv \mathbf{R}^{-1}(\partial\mathbf{R}/\partial\Omega)$ into eqn. 22.

The infinitesimal rotation matrix derivatives of Wigner functions $\left(\partial D^l_{m'm}/\partial\Phi\right)_{\hat{x}_p}$ defined in eqn. S6.3 will be derived as follows. First the results for $D^1[\mathbf{M}_p]$ are found by inserting $\mathbf{M}_p$ given in eqn. 28 into eqns. A14 – A16 to arrive at

$$
D^1[\mathbf{M}_1] = \frac{-i}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix},\ D^1[\mathbf{M}_2] = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix},\ D^1[\mathbf{M}_3] = i \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \tag{S6.4}
$$

In component form, $D^1[\mathbf{M}_p]$ appears as

$$
D^1_{ik}[\mathbf{M}_1] = \frac{-i}{\sqrt{2}} \left(\delta_{i,-1}\delta_{k,0} + \delta_{i,0}\delta_{k,-1} + \delta_{i,0}\delta_{k,1} + \delta_{i,1}\delta_{k,0} \right) \tag{S6.5}
$$

$$
D^1_{ik}[\mathbf{M}_2] = \frac{1}{\sqrt{2}} \left(\delta_{i,-1}\delta_{k,0} - \delta_{i,0}\delta_{k,-1} + \delta_{i,0}\delta_{k,1} - \delta_{i,1}\delta_{k,0} \right) \tag{S6.6}
$$

$$
D^1_{ik}[\mathbf{M}_3] = i\left(\delta_{k,-1}\delta_{i,-1} - \delta_{k,1}\delta_{i,1} \right) \tag{S6.7}
$$

After inserting eqns. S6.5 – S6.7, B^k_{lm} (eqn. A.8), and C^k_{lm} (eqn. A.10) into eqn. S6.3, the results for $\left(\partial D^l_{m'm}/\partial\Phi\right)_{\hat{x}_p}$ are given by

$$
\left(\frac{\partial D^l_{m'm}[\mathbf{R}]}{\partial\Phi} \right)_{\hat{x}_1} = \frac{-i}{2} \left(K^-_{lm'} D^l_{m'-1,m}[\mathbf{R}] + K^+_{lm'} D^l_{m'+1,m}[\mathbf{R}] \right) \tag{S6.8}
$$

$$
\left(\frac{\partial D^l_{m'm}[\mathbf{R}]}{\partial\Phi} \right)_{\hat{x}_2} = -\frac{1}{2} \left(K^-_{lm'} D^l_{m'-1,m}[\mathbf{R}] - K^+_{lm'} D^l_{m'+1,m}[\mathbf{R}] \right) \tag{S6.9}
$$

$$\left(\frac{\partial D^l_{m'm}[\mathbf{R}]}{\partial \Phi}\right)_{\hat{x}_3} = -im' D^l_{m'm}[\mathbf{R}] \qquad \text{(S6.10)}$$

where $K^{\pm}_{lm} \equiv \sqrt{(l \pm m + 1)(l \mp m)}$. If **R** is set equal to the identity matrix **I**, $D^l_{m',m}[\mathbf{I}] = \delta_{m'm}$, and eqns. S6.8 – S6.10 become

$$\left(\frac{\partial D^l_{m'm}[\mathbf{I}]}{\partial \Phi}\right)_{\hat{x}_1} = \frac{-i}{2}\left(K^-_{lm}\delta_{m',m-1} + K^+_{lm}\delta_{m',m+1}\right) \qquad \text{(S6.11)}$$

$$\left(\frac{\partial D^l_{m'm}[\mathbf{I}]}{\partial \Phi}\right)_{\hat{x}_2} = \frac{1}{2}\left(K^-_{lm}\delta_{m',m-1} - K^+_{lm}\delta_{m',m+1}\right) \qquad \text{(S6.12)}$$

$$\left(\frac{\partial D^l_{m'm}[\mathbf{I}]}{\partial \Phi}\right)_{\hat{x}_3} = -im\delta_{m',m} \qquad \text{(S6.13)}$$

where $K^{\mp}_{lm\pm1} = K^{\pm}_{lm}$ was used. Eqns. S6.11 – S6.13 agree with eqns. 5 – 7, respectively on page 116 of Varshalovich et al.[53]

The expressions for $\left(\partial D^l_{m'm} / \partial \Phi\right)_{\hat{x}_p}$ given in eqns. S6.8 – S6.10 can be used to find derivatives of spherical tensors T_{lm} with respect to an infinitesimal rotation. Suppose $T_{lm}(\hat{r})$ transforms to $T_{lm}(\hat{r}')$ under a rotation **R** where $\hat{\mathbf{r}}' = \mathbf{R}\hat{\mathbf{r}}$, i.e.

$$T_{lm}(\hat{r}') = \sum_{m'=-l}^{l} D^l_{m'm}[\mathbf{R}^{-1}] T_{lm'}(\hat{r}). \qquad \text{(S6.14)}$$

The derivative of $T_{lm}' \equiv T_{lm}(\hat{r}')$ with respect to an infinitesimal rotation about the $\hat{x}_p$ axis is given by

$$\left(\frac{\partial T_{lm}'}{\partial \Phi}\right)_{\hat{x}_p} = \sum_{m'=-l}^{l} T_{lm'}(\hat{r}) \left(\frac{\partial D^l_{mm'}[\mathbf{R}]}{\partial \Phi}\right)^*_{\hat{x}_p}. \qquad \text{(S6.15)}$$

For p = 1, 2, 3, $\left(\partial T_{lm}' / \partial \Phi\right)_{\hat{x}_p}$ is found by inserting eqns. S6.8 – S6.10 into eqn. S6.15

$$\left(\frac{\partial T_{lm}'}{\partial \Phi}\right)_{\hat{x}_1} = \frac{i}{2}\left(K^-_{lm}T_{lm-1}' + K^+_{lm}T_{lm+1}'\right), \qquad \text{(S6.16)}$$

$$\left(\frac{\partial T_{lm}'}{\partial \Phi}\right)_{\hat{x}_2} = -\frac{1}{2}\left(K^-_{lm}T_{lm-1}' - K^+_{lm}T_{lm+1}'\right), \qquad \text{(S6.17)}$$

$$\left(\frac{\partial T_{lm}'}{\partial \Phi}\right)_{\hat{x}_3} = imT_{lm}'. \qquad \text{(S6.18)}$$

The expressions for torque in eqns. 31 – 33 of the main text can be found by letting $T_{lm} = Q_{lm}$ be the multipole moment and inserting eqns. S6.16 – S6.18 into eqn. 25.

S7) Wigner Matrix Derivatives for Euler Angles

In this section, $\partial D^l_{m'm}/\partial\Omega$ is derived for the case when Ω is an Euler angle using the expressions given in eqns. 22 and 24 of the main text by first calculating $\mathbf{R}^{-1}(\partial\mathbf{R}/\partial\Omega)$ or $(\partial\mathbf{R}/\partial\Omega)\mathbf{R}^{-1}$, respectively. The Cartesian rotation matrix as a function of Euler angles[53-56] $\mathbf{R}(\alpha, \beta, \gamma)$ is formed from the product three successive rotations. First, the $\hat{x}_i$ coordinate system is rotated about the $\hat{x}_3$ axis by an angle α to arrive at the $\hat{x}_i'$ coordinate system, i.e. $\hat{x}_k' = \sum_j \mathbf{R}_{jk}(\alpha\hat{x}_3)\hat{x}_j'$. Next, the $\hat{x}_i'$ coordinate system is rotated about the $\hat{x}_2'$ axis by an angle β to arrive at the $\hat{x}_i''$ coordinate system, i.e. $\hat{x}_l'' = \sum_k \mathbf{R}_{kl}(\beta\hat{x}_2')\hat{x}_k'$. Lastly, the $\hat{x}_i''$ coordinate system is rotated about the $\hat{x}_3''$ axis by an angle γ to arrive at the $\hat{x}_i'''$ coordinate system, i.e. $\hat{x}_i''' = \sum_l \mathbf{R}_{li}(\gamma\hat{x}_3'')\hat{x}_l'$. The total transformation is given by $\hat{x}_i''' = \sum_j \mathbf{R}_{ji}(\alpha,\beta,\gamma)\hat{x}_j$, where $\mathbf{R}_{ji}(\alpha,\beta,\gamma) \equiv \sum_{lk} \mathbf{R}_{kj}(\alpha\hat{x}_3)\mathbf{R}_{kl}(\beta\hat{x}_2')\mathbf{R}_{li}(\gamma\hat{x}_3'')$. In matrix form, $\mathbf{R}(\alpha, \beta, \gamma)$ is given by

$$\mathbf{R}(\alpha,\beta,\gamma) = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\beta & 0 & \sin\beta \\ 0 & 1 & 0 \\ -\sin\beta & 0 & \cos\beta \end{pmatrix} \begin{pmatrix} \cos\gamma & -\sin\gamma & 0 \\ \sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
$$= \begin{pmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma & -\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma & \cos\alpha\sin\beta \\ \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma & -\sin\alpha\cos\beta\sin\gamma + \cos\alpha\cos\gamma & \sin\alpha\sin\beta \\ -\sin\beta\cos\gamma & \sin\beta\sin\gamma & \cos\beta \end{pmatrix}. \quad \text{(S7.1)}$$

Symbolically, eqn. S7.1 can be expressed as

$$\mathbf{R}(\alpha,\beta,\gamma) = \mathbf{R}_z(\alpha)\mathbf{R}_y(\beta)\mathbf{R}_z(\gamma) \quad \text{(S7.2)}$$

The inverse of $\mathbf{R}(\alpha, \beta, \gamma)$ is given by

$$\mathbf{R}^{-1}(\alpha,\beta,\gamma) = \mathbf{R}(-\gamma,-\beta,-\alpha) = \mathbf{R}_z(-\gamma)\mathbf{R}_y(-\beta)\mathbf{R}_z(-\alpha). \quad \text{(S7.3)}$$

The expression for $(\partial\mathbf{R}/\partial\alpha)\mathbf{R}^{-1}$ is given by

$$\frac{\partial\mathbf{R}}{\partial\alpha}\mathbf{R}^{-1} = \frac{\partial\mathbf{R}_z(\alpha)}{\partial\alpha}\mathbf{R}_z(-\alpha) = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \mathbf{M}_3. \quad \text{(S7.4)}$$

Similarly, the results for $\mathbf{R}^{-1}(\partial\mathbf{R}/\partial\beta)$ and $\mathbf{R}^{-1}(\partial\mathbf{R}/\partial\gamma)$ are given by

$$\mathbf{R}^{-1}\frac{\partial\mathbf{R}}{\partial\beta} = \sin\gamma\,\mathbf{M}_1 + \cos\gamma\,\mathbf{M}_2 \quad \text{(S7.5)}$$

$$\mathbf{R}^{-1}\frac{\partial\mathbf{R}}{\partial\gamma} = \mathbf{M}_3 \quad \text{(S7.6)}$$

After inserting eqn. S7.4 into eqn. S6.2 or eqn. 24, $\partial D^l_{m'm}/\partial\alpha$ is given by

$$\frac{\partial D^l_{m',m}}{\partial \alpha} = \left(\frac{\partial D^l_{m'm}}{\partial \Phi}\right)_{\hat{x}_1} = -im' D^l_{m'm} \tag{S7.10}$$

Similarly, after inserting eqns. S7.5 and S7.6 into eqn. 22, the results for $\partial D^l_{m'm}/\partial\beta$ and $\partial D^l_{m'm}/\partial\gamma$ are given by

$$\frac{\partial D^l_{m'm}}{\partial \beta} = \frac{e^{-i\gamma}}{2}\sqrt{(l+m)(l-m+1)}D^l_{m',m-1} - \frac{e^{i\gamma}}{2}\sqrt{(l-m)(l+m+1)}D^l_{m',m+1}\,. \tag{S7.11}$$

$$\frac{\partial D^l_{m',m}}{\partial \gamma} = -imD^l_{m'm} \tag{S7.12}$$

A second equation for $\partial D^l_{m'm}/\partial\beta$ can be found by taking the complex conjugate of eqn. S7.11, interchanging m' with m, and interchanging **R** with $\mathbf{R}^{-1}$ (see eqn. S7.3)

$$\frac{\partial D^l_{m'm}}{\partial \beta} = -\frac{e^{-i\alpha}}{2}\sqrt{(l+m')(l-m'+1)}D^l_{m'-1,m} + \frac{e^{i\alpha}}{2}\sqrt{(l-m')(l+m'+1)}D^l_{m'+1,m}\,. \tag{S7.13}$$

Eqns. S7.10 – S7.13 agree with eqns. 8, 3, 9, and 2, respectively on page 94 of Varshalovich et al.[53]

S8) Wigner Matrix Derivatives for Quaternions

In this section, derivatives of Wigner rotation matrices with respect to quaternions $\partial D^l_{m'm}\big/\partial q_\mu$ are derived. Expressions for $(\partial\mathbf{R}/\partial q_\mu)\mathbf{R}^{-1}$ are found and then inserted into eqn. 24 to arrive a set of equations for $\partial D^l_{m'm}\big/\partial q_\mu$. The Cartesian rotation matrix **R** can be parameterized explicitly[55] in terms of quaternions $q_\mu \equiv (q_0, q_1, q_2, q_3)$ by

$$\mathbf{R} = \begin{pmatrix} q_0^2+q_1^2-q_2^2-q_3^2 & 2(q_1q_2-q_0q_3) & 2(q_1q_3+q_0q_2) \\ 2(q_1q_2+q_0q_3) & q_0^2-q_1^2+q_2^2-q_3^2 & 2(q_2q_3-q_0q_1) \\ 2(q_1q_3-q_0q_2) & 2(q_2q_3+q_0q_1) & q_0^2-q_1^2-q_2^2+q_3^2 \end{pmatrix}. \tag{S8.1}$$

The inverse matrix is given by letting $(q_0, q_1, q_2, q_3) \to (q_0, -q_1, -q_2, -q_3)$

$$\mathbf{R}^{-1}(q_0,q_1,q_2,q_3) = \mathbf{R}(q_0,-q_1,-q_2,-q_3)\,. \tag{S8.2}$$

and the quaternions satisfy a normalization condition

$$\sum_{\mu=0}^{3} q_\mu^2 = 1\,. \tag{S8.3}$$

Since quaternions satisfy a constraint condition, $(\partial\mathbf{R}/\partial q_\mu)\mathbf{R}^{-1}$ is not antisymmetric. Nevertheless, $(\partial\mathbf{R}/\partial q_\mu)\mathbf{R}^{-1}$ can still be calculated and inserted into eqn. 24 to arrive $\partial D^l_{m'm}\big/\partial q_\mu$.

In order to calculate $(\partial\mathbf{R}/\partial q_\mu)\mathbf{R}^{-1}$, one could simply differentiate eqn. S8.1 with respect to q_μ to get $\partial\mathbf{R}/\partial q_\mu$, and then right multiply by $\mathbf{R}^{-1}$. The result would be an expression which involves cubic powers of q_μ. This expression could be simplified by the normalization condition, eqn. S8.3, into an expression which is linear in q_μ.

However, a more economical derivation of $(\partial\mathbf{R}/\partial q_\mu)\mathbf{R}^{-1}$ can be found by first noting the quaternion multiplication formulae for successive rotations. First, note that quaternions can be expressed in vector notation by $q_\mu \equiv (q_0, q_1, q_2, q_3) \equiv (q_0, \vec{q})$. Suppose q_μ, p_μ, and r_μ are three different quaternions related by

$$\mathbf{R}(q_\mu)\mathbf{R}(p_\mu) = \mathbf{R}(r_\mu) \ . \tag{S8.4}$$

It can be shown[55] that $r \equiv q * p$ is given by $r_0 = p_0 q_0 - \vec{p}\cdot\vec{q}$, and $\vec{r} = p_0\vec{q} + q_0\vec{p} + \vec{p}\times\vec{q}$. In component form, this appears as

$$r_0 = q_0 p_0 - \sum_{i=1}^{3} q_i p_i\,, \qquad r_i = q_0 p_i + p_0 q_i + \sum_{j=1}^{3}\sum_{k=1}^{3} q_j p_k \varepsilon_{ijk} \quad i = 1, 2, 3, \tag{S8.5}$$

where ε_{ijk} is the Levi-Cita symbol defined by 1 for an even permutation of (1,2,3) , –1 for an odd permutation of (1,2,3), and 0 if any index is repeated. Recall the inverse relation for quaternions in eqn. S8.2. The expression $(\partial\mathbf{R}/\partial q_\mu)\mathbf{R}^{-1}$ can be derived from eqns. S8.1 and S8.2 by noting

$$\begin{aligned}\frac{\partial\mathbf{R}(q)}{\partial q_\mu}\mathbf{R}^{-1}(q) &= \lim_{p\to q^{-1}}\frac{\partial}{\partial q_\mu}\mathbf{R}(q)\mathbf{R}(p) = \lim_{p\to q^{-1}}\frac{\partial}{\partial q_\mu}\mathbf{R}(r) \\ &= \lim_{p\to q^{-1}}\sum_{\nu=0}^{3}\frac{\partial\mathbf{R}(r)}{\partial r_\nu}\frac{\partial r_\nu}{\partial q_\mu}\end{aligned}\ , \tag{S8.6}$$

where the limit of $p \to q^{-1}$ is short for $(p_0, p_1, p_2, p_3) \to (q_0, -q_1, -q_2, -q_3)$. The following expressions for r_ν and $\partial r_\nu/\partial q_\mu$ can be found from eqn. S8.5. It is important to first evaluate the derivative and then apply the limit.

$$\lim_{p\to q^{-1}} r_0 = 1\,, \qquad \lim_{p\to q^{-1}} r_i = 0\,, \tag{S8.7}$$

$$\lim_{p\to q^{-1}}\frac{\partial r_0}{\partial q_0} = q_0\,, \qquad \lim_{p\to q^{-1}}\frac{\partial r_0}{\partial q_i} = q_i\,, \tag{S8.8}$$

$$\lim_{p\to q^{-1}}\frac{\partial r_i}{\partial q_0} = -q_i\,, \qquad \lim_{p\to q^{-1}}\frac{\partial r_i}{\partial q_j} = q_0\delta_{ij} + \sum_k \varepsilon_{ijk} q_k \tag{S8.9}$$

where i,j = 1,2,3. The derivative of $\mathbf{R}(r)$ with respect to r_0 can be found by simply replacing the q's with r's in eqn. S8.1 and then differentiate with respect to r_0. After taking the limit of $p \to q^{-1}$ and applying eqn. S8.7, the result becomes

$$\lim_{p\to q^{-1}}\frac{\partial\mathbf{R}(r)}{\partial r_0} = 2\mathbf{I}\ . \tag{S8.10}$$

A similar procedure can be applied for the derivative $\mathbf{R}(r)$ with respect to r_i (i = 1,2,3) to yield the following result

$$\lim_{p \to q^{-1}} \frac{\partial \mathbf{R}(r)}{\partial r_i} = 2\mathbf{M}_i \, , \tag{S8.11}$$

where $\mathbf{M}_i$ are the infinitesimal rotation matrices. Eqns. S8.7 – S8.11 can be inserted into eqn. S8.6 to arrive at the result for $(\partial\mathbf{R}/\partial q_\mu)\mathbf{R}^{-1}$

$$\frac{\partial \mathbf{R}}{\partial q_0}\mathbf{R}^{-1} = 2(q_0\mathbf{I} - \sum_i q_i \mathbf{M}_i) \tag{S8.12}$$

$$\frac{\partial \mathbf{R}}{\partial q_i}\mathbf{R}^{-1} = 2(q_i\mathbf{I} + q_0\mathbf{M}_i - \sum_{jk} \varepsilon_{ijk} q_j \mathbf{M}_k) \tag{S8.13}$$

Eqn. S8.13 can be written out explicitly for i = 1, 2, 3 by

$$\frac{\partial \mathbf{R}}{\partial q_1}\mathbf{R}^{-1} = 2(q_1\mathbf{I} + q_0\mathbf{M}_1 + q_3\mathbf{M}_2 - q_2\mathbf{M}_3) \tag{S8.14}$$

$$\frac{\partial \mathbf{R}}{\partial q_2}\mathbf{R}^{-1} = 2(q_2\mathbf{I} + q_0\mathbf{M}_2 + q_1\mathbf{M}_3 - q_3\mathbf{M}_1) \tag{S8.15}$$

$$\frac{\partial \mathbf{R}}{\partial q_3}\mathbf{R}^{-1} = 2(q_3\mathbf{I} + q_0\mathbf{M}_3 + q_2\mathbf{M}_1 - q_1\mathbf{M}_2) \tag{S8.16}$$

Note $(\partial\mathbf{R}/\partial q_\mu)\mathbf{R}^{-1}$ is *not* antisymmetric due to the presence of the terms containing **I**.

In order to arrive at the final expression for $\partial D^l_{m'm} \big/ \partial q_\mu$, the following intermediate result is needed

$$\sum_{i=-1}^{1}\sum_{k=-1}^{1} B^k_{l-1,m'-i} C^i_{lm'} D^1_{ik}[\mathbf{I}] D^l_{m'-i+k,m}[\mathbf{R}] = l D^l_{m',m}[\mathbf{R}] \, , \tag{S8.17}$$

where **I** is the identity matrix. After inserting eqns. S8.12 – S8.16 for $(\partial\mathbf{R}/\partial q_\mu)\mathbf{R}^{-1}$ into eqn. 24 for $\partial D^l_{m'm} \big/ \partial q_\mu$, and using eqns. S8.17, S6.8 – S6.10, the final results for $\partial D^l_{m'm} \big/ \partial q_\mu$ becomes

$$\frac{\partial D^l_{m'm}}{\partial q_0} = 2(q_0 l + im' q_3) D^l_{m'm} + (q_2 + iq_1) K^-_{lm'} D^l_{m'-1,m} + (-q_2 + iq_1) K^+_{lm'} D^l_{m'+1,m} \tag{S8.18}$$

$$\frac{\partial D^l_{m'm}}{\partial q_1} = 2(q_1 l + im' q_2) D^l_{m'm} + (-q_3 - iq_0) K^-_{lm'} D^l_{m'-1,m} + (q_3 - iq_0) K^+_{lm'} D^l_{m'+1,m} \tag{S8.19}$$

$$\frac{\partial D^l_{m'm}}{\partial q_2} = 2(q_2 l - im' q_1) D^l_{m'm} + (-q_0 + iq_3) K^-_{lm'} D^l_{m'-1,m} + (q_0 + iq_3) K^+_{lm'} D^l_{m'+1,m} \tag{S8.20}$$

$$\frac{\partial D^l_{m'm}}{\partial q_3} = 2(q_3 l - im' q_0) D^l_{m'm} + (q_1 - iq_2) K^-_{lm'} D^l_{m'-1,m} + (-q_1 - iq_2) K^+_{lm'} D^l_{m'+1,m} \tag{S8.21}$$

A second set of equations for $\partial D^l_{m'm} \big/ \partial q_\mu$ can be found by taking the complex conjugate of eqns. S8.18 – S8.21, interchanging m' with m, and interchanging **R** with $\mathbf{R}^{-1}$ (eqn. S8.2)

$$\frac{\partial D^l_{m'm}}{\partial q_0} = 2(q_0 l + imq_3)D^l_{m'm} + (-q_2 + iq_1)K^-_{lm}D^l_{m'm-1} + (q_2 + iq_1)K^+_{lm}D^l_{m'm+1} \tag{S8.22}$$

$$\frac{\partial D^l_{m'm}}{\partial q_1} = 2(q_1 l - imq_2)D^l_{m'm} + (-q_3 - iq_0)K^-_{lm}D^l_{m'm-1} + (q_3 - iq_0)K^+_{lm}D^l_{m'm+1} \tag{S8.23}$$

$$\frac{\partial D^l_{m'm}}{\partial q_2} = 2(q_2 l + imq_1)D^l_{m'm} + (q_0 - iq_3)K^-_{lm}D^l_{m'm-1} + (-q_0 - iq_3)K^+_{lm}D^l_{m'm+1} \tag{S8.24}$$

$$\frac{\partial D^l_{m'm}}{\partial q_3} = 2(q_3 l - imq_0)D^l_{m'm} + (q_1 + iq_2)K^-_{lm}D^l_{m'm-1} + (-q_1 + iq_2)K^+_{lm}D^l_{m'm+1} \,. \tag{S8.25}$$

Eqns. S8.22 – S8.25 could have also been derived by calculating $\mathbf{R}^{-1}(\partial\mathbf{R}/\partial q_\mu)$ and inserting these results into eqn. 22.

S9) Proof of $\boldsymbol{\tau}_a = \boldsymbol{\alpha}\times\mathbf{F}^{orient}_{a\to \mathrm{N1}} + \boldsymbol{\beta}\times\mathbf{F}^{orient}_{a\to \mathrm{N2}}$

The expressions for $\mathbf{F}^{orient}_{a\to \mathrm{N1}}$ and $\mathbf{F}^{orient}_{a\to \mathrm{N2}}$ are given by inserting eqn. 37 into eqn. 39

$$\begin{aligned}\mathbf{F}^{orient}_{a\to \mathrm{N1},q} &= -\left(\frac{1}{\boldsymbol{\alpha}^2}(\hat{\mathbf{x}}_q\times\boldsymbol{\alpha})\cdot\boldsymbol{\tau}_a + \frac{\boldsymbol{\alpha}\cdot\boldsymbol{\beta}}{\boldsymbol{\alpha}^2[\boldsymbol{\alpha}^2\boldsymbol{\beta}^2-(\boldsymbol{\alpha}\cdot\boldsymbol{\beta})^2]}\left(\boldsymbol{\alpha}\times\boldsymbol{\beta}\right)_q\boldsymbol{\alpha}\cdot\boldsymbol{\tau}_a\right)\\ &= -\left(\frac{1}{\boldsymbol{\alpha}^2}\hat{\mathbf{x}}_q\cdot(\boldsymbol{\alpha}\times\boldsymbol{\tau}_a) + \frac{(\boldsymbol{\alpha}\cdot\boldsymbol{\beta})(\boldsymbol{\alpha}\cdot\boldsymbol{\tau}_a)}{\boldsymbol{\alpha}^2[\boldsymbol{\alpha}^2\boldsymbol{\beta}^2-(\boldsymbol{\alpha}\cdot\boldsymbol{\beta})^2]}\left(\boldsymbol{\alpha}\times\boldsymbol{\beta}\right)_q\right)\end{aligned} \tag{S9.1}$$

or

$$\mathbf{F}^{orient}_{a\to \mathrm{N1}} = -\left(\frac{1}{\boldsymbol{\alpha}^2}\boldsymbol{\alpha}\times\boldsymbol{\tau}_a + \frac{(\boldsymbol{\alpha}\cdot\boldsymbol{\beta})(\boldsymbol{\alpha}\cdot\boldsymbol{\tau}_a)}{\boldsymbol{\alpha}^2[\boldsymbol{\alpha}^2\boldsymbol{\beta}^2-(\boldsymbol{\alpha}\cdot\boldsymbol{\beta})^2]}\boldsymbol{\alpha}\times\boldsymbol{\beta}\right) \tag{S9.2}$$

Similarly,

$$\mathbf{F}^{orient}_{a\to \mathrm{N2}} = \frac{\boldsymbol{\alpha}\cdot\boldsymbol{\tau}_a}{\boldsymbol{\alpha}^2\boldsymbol{\beta}^2-(\boldsymbol{\alpha}\cdot\boldsymbol{\beta})^2}\boldsymbol{\alpha}\times\boldsymbol{\beta} \tag{S9.3}$$

Using the property $\mathbf{A}\times(\mathbf{B}\times\mathbf{C}) = \mathbf{B}(\mathbf{A}\cdot\mathbf{C}) - \mathbf{C}(\mathbf{A}\cdot\mathbf{B})$, $\boldsymbol{\alpha}\times\mathbf{F}^{orient}_{a\to \mathrm{N1}}$ and $\boldsymbol{\beta}\times\mathbf{F}^{orient}_{a\to \mathrm{N2}}$ become

$$\boldsymbol{\alpha}\times\mathbf{F}^{orient}_{a\to \mathrm{N1}} = -\left(\frac{1}{\boldsymbol{\alpha}^2}\left(\boldsymbol{\alpha}(\boldsymbol{\alpha}\cdot\boldsymbol{\tau}_a) - \boldsymbol{\tau}_a\boldsymbol{\alpha}^2\right) + \frac{(\boldsymbol{\alpha}\cdot\boldsymbol{\beta})(\boldsymbol{\alpha}\cdot\boldsymbol{\tau}_a)}{\boldsymbol{\alpha}^2[\boldsymbol{\alpha}^2\boldsymbol{\beta}^2-(\boldsymbol{\alpha}\cdot\boldsymbol{\beta})^2]}\left(\boldsymbol{\alpha}(\boldsymbol{\alpha}\cdot\boldsymbol{\beta}) - \boldsymbol{\beta}\boldsymbol{\alpha}^2\right)\right) \tag{S9.4}$$

$$\boldsymbol{\beta}\times\mathbf{F}^{orient}_{a\to \mathrm{N2}} = \frac{\boldsymbol{\alpha}\cdot\boldsymbol{\tau}_a}{\boldsymbol{\alpha}^2\boldsymbol{\beta}^2-(\boldsymbol{\alpha}\cdot\boldsymbol{\beta})^2}\left(\boldsymbol{\alpha}\boldsymbol{\beta}^2 - \boldsymbol{\beta}(\boldsymbol{\alpha}\cdot\boldsymbol{\beta})\right) \tag{S9.5}$$

Adding eqns. S9.4 and S9.5 gives the final result for $\boldsymbol{\tau}_a$.

$$\boldsymbol{\alpha}\times\mathbf{F}^{orient}_{a\to \mathrm{N1}}+\boldsymbol{\beta}\times\mathbf{F}^{orient}_{a\to \mathrm{N2}}=\frac{1}{\boldsymbol{\alpha}^2}\left(\boldsymbol{\tau}_a\boldsymbol{\alpha}^2-\boldsymbol{\alpha}(\boldsymbol{\alpha}\cdot\boldsymbol{\tau}_a)\right)+\frac{(\boldsymbol{\alpha}\cdot\boldsymbol{\tau}_a)}{\boldsymbol{\alpha}^2}\boldsymbol{\alpha}=\boldsymbol{\tau}_a \tag{S9.6}$$

S10) Proof of $\sum_{a'}\mathbf{r}_{a'}\times\partial\eta/\partial\mathbf{r}_{a'}=0$

The variable η denotes any bond length r, bond angle θ, or torsion angle ω. For all cases, η can be expressed as a function of a scalar product of relative atomic positions. For example, the bond length r_{ab} between two atoms a and b is given by

$$r_{ab}=\sqrt{\mathbf{r}_{ab}\cdot\mathbf{r}_{ab}} \tag{S10.1}$$

where $\mathbf{r}_{ab}\equiv\mathbf{r}_a-\mathbf{r}_b$ is the relative displacement between atoms a and b. Similarly, the bond angle θ_{abc} between atoms a, b, c is given by

$$\theta_{abc}=\cos^{-1}\left(\frac{\mathbf{r}_{ab}\cdot\mathbf{r}_{cb}}{r_{ab}r_{cb}}\right) \tag{S10.2}$$

and the torsion angle ω_{abcd} between atoms a, b, c, d is given by

$$\omega_{abcd}=\cos^{-1}\left(\frac{\mathbf{r}_{ab}\cdot\mathbf{r}_{dc}}{r_{ab}r_{dc}}-\frac{(\mathbf{r}_{ab}\cdot\mathbf{r}_{cb})(\mathbf{r}_{dc}\cdot\mathbf{r}_{cb})}{r_{ab}r_{dc}r_{cb}^2}\right) \tag{S10.3}$$

Thus, the generic variable η is a function of the dot product $\mathbf{r}_{ab}\cdot\mathbf{r}_{cd}$, i.e. $\eta=\eta\ (\mathbf{r}_{ab}\cdot\mathbf{r}_{cd})$. Letting $x\equiv\mathbf{r}_{ab}\cdot\mathbf{r}_{cd}$,

$$\mathbf{r}_a\times\frac{\partial\eta}{\partial\mathbf{r}_a}=\frac{\partial\eta}{\partial x}\mathbf{r}_a\times\mathbf{r}_{cd} \tag{S10.4}$$

Therefore, $\sum_{a'}\mathbf{r}_{a'}\times\partial\eta/\partial\mathbf{r}_{a'}$ is given by

$$\begin{aligned}\sum_{a'}\mathbf{r}_{a'}\times\frac{\partial\eta}{\partial\mathbf{r}_{a'}}&=\mathbf{r}_a\times\frac{\partial\eta}{\partial\mathbf{r}_a}+\mathbf{r}_b\times\frac{\partial\eta}{\partial\mathbf{r}_b}+\mathbf{r}_c\times\frac{\partial\eta}{\partial\mathbf{r}_c}+\mathbf{r}_d\times\frac{\partial\eta}{\partial\mathbf{r}_d}\\&=\frac{\partial\eta}{\partial x}(\mathbf{r}_a\times\mathbf{r}_{cd}-\mathbf{r}_b\times\mathbf{r}_{cd}+\mathbf{r}_c\times\mathbf{r}_{ab}-\mathbf{r}_{cd}\times\mathbf{r}_{ab})\\&=0\end{aligned} \tag{S10.5}$$