SUPPLEMENTAL DATA

COORDINATE TRANSFORMATION FOR FORCE CALCULATIONS

β defines an internal coordinate system along the backbone of a protein based on relative positions of three contiguous C_α (refer to Fig. 2), where by the law of cosines:

$$\beta = \arccos \frac{|\vec{R}_{12}|^2 + |\vec{R}_{23}|^2 - |\vec{R}_{13}|^2}{2|\vec{R}_{12}||\vec{R}_{23}|} \tag{2}$$

$$\text{Let } B = \frac{|\vec{R}_{12}|^2 + |\vec{R}_{23}|^2 - |\vec{R}_{13}|^2}{2|\vec{R}_{12}||\vec{R}_{23}|} \quad \Rightarrow \quad \beta = \arccos B \tag{3}$$

With respect to the figure, we're interested in the force on on $C_{\alpha 2}$. From the chain rule we can introduce the coordinate β from eqs. 2 and 3:

$$\vec{F}_2 = -\frac{\partial U}{\partial \beta}\hat{r}|_{\vec{r}=\vec{r}_2} = -\frac{\partial U}{\partial \vec{r}_2} \cdot \frac{\partial \vec{r}_2}{\partial \beta}\hat{r} = -\left(\frac{\partial U}{\partial x_2}\frac{\partial x_2}{\partial \beta}\hat{\imath} + \frac{\partial U}{\partial y_2}\frac{\partial y_2}{\partial \beta}\hat{\jmath} + \frac{\partial U}{\partial z_2}\frac{\partial z_2}{\partial \beta}\hat{k}\right) \tag{4}$$

The $-\partial U/\partial \vec{r}_2$ term is solved by CHARMM in terms of Cartesian coordinates. The $\partial r_2/\partial \beta$ term is one that must be evaluated in terms of Cartesian coordinates, where $\partial \vec{r}_2/\partial \beta = 1/(\partial \beta/\partial \vec{r}_2)$. To evaluate $\partial \beta/\partial \vec{r}_2$, where $\beta = \arccos f(x_i, y_i, z_i)$ and $i = 1,2,3$, we see from derivative tables:

$$\frac{\mathrm{d}\ \arccos f(x)}{\mathrm{d}x} = -\frac{1}{\sqrt{1-f(x)^2}}\frac{\mathrm{d}f(x)}{\mathrm{d}x} \quad \Rightarrow \quad \frac{\partial \beta}{\partial \vec{r}_2} = -\frac{1}{\sqrt{1-B^2}}\frac{\partial B}{\partial \vec{r}_2} \tag{5}$$

In order to evaluate $\partial \beta/\partial \vec{r}_2$, we will let:

$$f(\vec{r}) = |\vec{R}_{12}|^2 + |\vec{R}_{23}|^2 - |\vec{R}_{13}|^2 \text{ and } g(\vec{r}) = 2|\vec{R}_{12}||\vec{R}_{23}| \Rightarrow B = \frac{f(\vec{r})}{g(\vec{r})} \tag{6}$$

We first evaluate $\partial \mathrm{f}(\vec{r})/\partial \vec{r}_2$:

$$\frac{\partial \mathrm{f}(\vec{r})}{\partial x_2} = 2(2x_2 - x_1 - x_3)\hat{\imath}, \quad \frac{\partial \mathrm{f}(\vec{r})}{\partial y_2} = 2(2y_2 - y_1 - y_3)\hat{\jmath}, \quad \frac{\partial \mathrm{f}(\vec{r})}{\partial z_2} = 2(2z_2 - z_1 - z_3)\hat{k} \tag{7}$$

Then evaluate $\partial \mathrm{g}(\vec{r})/\partial \vec{r}_2$:

$$\frac{\partial \mathrm{g}(\vec{r})}{\partial x_2} = 2(|\vec{R}_{12}|\frac{1}{2}[2(x_2-x_3)(1)] + |\vec{R}_{23}|\frac{1}{2}[2(x_1-x_2)(-1)]) = [2(x_2-x_3)|\vec{R}_{12}| - (x_1-x_2)|\vec{R}_{23}|]\hat{\imath}$$

$$\frac{\partial \mathrm{g}(\vec{r})}{\partial y_2} = [2(y_2-y_3)|\vec{R}_{12}| - (y_1-y_2)|\vec{R}_{23}|]\hat{\jmath}$$

$$\frac{\partial \mathrm{g}(\vec{r})}{\partial z_2} = [2(z_2-z_3)|\vec{R}_{12}| - (z_1-z_2)|\vec{R}_{23}|]\hat{k} \tag{8}$$

Together, we can evaluate $\partial \vec{r}_2/\partial \beta$:

$$\frac{\partial \beta}{\partial x_2} = -\frac{1}{\sqrt{1-B^2}}\frac{g(\vec{r})\frac{\partial f(\vec{r})}{\partial x_2} - f(\vec{r})\frac{\partial g(\vec{r})}{\partial x_2}}{g(\vec{r})^2} \quad \Rightarrow \quad \frac{\partial x_2}{\partial \beta} = -\sqrt{1-B^2}\frac{g(\vec{r})^2}{g(\vec{r})\frac{\partial f(\vec{r})}{\partial x_2} - f(\vec{r})\frac{\partial g(\vec{r})}{\partial x_2}} \tag{9}$$

with similar expressions for y_2 and z_2. Therefore,

$$\vec{F}_2 = g(\vec{r})^2\sqrt{1-B^2} \left(\frac{\partial U}{\partial x_2} \frac{1}{g(\vec{r})\frac{\partial f(\vec{r})}{\partial x_2} - f(\vec{r})\frac{\partial g(\vec{r})}{\partial x_2}} \hat{i} + \frac{\partial U}{\partial y_2} \frac{1}{g(\vec{r})\frac{\partial f(\vec{r})}{\partial y_2} - f(\vec{r})\frac{\partial g(\vec{r})}{\partial y_2}} \hat{j} + \frac{\partial U}{\partial z_2} \frac{1}{g(\vec{r})\frac{\partial f(\vec{r})}{\partial z_2} - f(\vec{r})\frac{\partial g(\vec{r})}{\partial z_2}} \hat{k} \right) \tag{10}$$

This gives an expression of the force on $C_{\alpha 2}$ in terms of a coordinate system defined by three adjoining C_α's and an angle β, which can be explicitly described in terms of Cartesian coordinates. This should allow us to use CHARMM's output to express this force as a function of an intrinsically defined coordinate system.