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Supporting Information for:

**Global Potential Energy Surfaces with Correct Permutation Symmetry by Multi-Configuration Molecular Mechanics**

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This appendix (four pages, including this page) gives the derivatives of the coupling term $V_{12}^S$ with respect to internal coordinates.

The gradient and Hessian of $V_{12}^S$ of eq 24 with respect to internal coordinates are given by:

$$\mathbf{g}^S(\mathbf{r}) \equiv \frac{\partial V_{12}^S(\mathbf{r})}{\partial \mathbf{r}} = \sum_{k=1}^{N} \sum_{i=1}^{m!} \left[ \frac{\partial W_{ki}}{\partial \mathbf{r}} V_{12}'(\mathbf{r};k;i) + W_{ki} \mathbf{g}_{12}(\mathbf{r};k;i) \right] \tag{S1}$$

$$\begin{aligned} \mathbf{f}^S(\mathbf{r}) \equiv \frac{\partial^2 V_{12}^S(\mathbf{r})}{\partial \mathbf{r}^2} = & \sum_{k=1}^{N} \sum_{i=1}^{m!} \left( \frac{\partial^2 W_{ki}}{\partial \mathbf{r}^2} V_{12}'(\mathbf{r};k;i) + \frac{\partial W_{ki}}{\partial \mathbf{r}} \mathbf{g}_{12}(\mathbf{r};k;i)^\mathsf{T} + \right. \\ & \left. \mathbf{g}_{12}(\mathbf{r};k;i) \left( \frac{\partial W_{ki}}{\partial \mathbf{r}} \right)^\mathsf{T} + W_{ki} \mathbf{f}_{12}(\mathbf{r};k;i) \right), \end{aligned} \tag{S2}$$

where

$$\begin{aligned} \mathbf{g}_{12}(\mathbf{r};k;i) \equiv \frac{\partial V_{12}'(\mathbf{r};k;i)}{\partial \mathbf{r}} = & \\ & \frac{D^{(k,i)}}{2V_{12}'(\mathbf{r};k;i)} (\mathbf{b}^{(k,i)} + \mathbf{C}^{(k,i)} \boldsymbol{\Delta}\mathbf{r}^{(k,i)}) u(\mathbf{r};k;i) \\ & \times \left( 1 + \frac{\delta}{(V_{12}(\mathbf{r};k;i))^2} \right) \end{aligned} \tag{S3}$$

and

$$\begin{aligned} \mathbf{f}_{12}(\mathbf{r};k;i) \equiv & \frac{\partial^2 V_{12}'(\mathbf{r};k;i)}{\partial \mathbf{r}^2} = \\ & \frac{1}{V_{12}'(\mathbf{r};k;i)} \left( -\mathbf{g}_{12}(\mathbf{r};k;i) \mathbf{g}_{12}(\mathbf{r};k;i)^\mathsf{T} + \frac{D^{(k,i)} u(\mathbf{r};k;i)}{2} \left\{ \frac{\mathbf{C}^{(ki)} \delta}{(V_{12}(\mathbf{r};k;i))^2} + \right. \right. \\ & \left. \left. \frac{D^{(k,i)} \delta^2 (\mathbf{b}^{(k,i)} + \mathbf{C}^{(k,i)} \boldsymbol{\Delta}\mathbf{r}^{(k,i)})(\mathbf{b}^{(k,i)} + \mathbf{C}^{(k,i)} \boldsymbol{\Delta}\mathbf{r}^{(k,i)})^\mathsf{T}}{(V_{12}(\mathbf{r};k;i))^6} + \mathbf{C}^{(k,i)} \right\} \right), \end{aligned} \tag{S4}$$

where the coefficients $D^{(k,i)}$, $\mathbf{b}^{(k,i)}$, and $\mathbf{C}^{(k,i)}$ are given in eqs 20–22.

The functional form for the unnormalized weight function $w_{ki}$ is given in eq 37. The normalized weight function used in eq 24, $W(\mathbf{r})$ at point $(k,i)$, is

$$W_{ki} = \frac{w_{ki}(\mathbf{s})}{w(\mathbf{s})}, \tag{S5}$$

where $w$ is defined by

$$w(\mathbf{s}) = \sum_{k=1}^{N+2} \sum_{i=1}^{m!} w_{ki}(\mathbf{s}). \tag{S6}$$

The derivatives required in eqs S1 and S2 are given by

$$\frac{\partial W_{ki}}{\partial r_\alpha} = \sum_{\gamma=1}^{\Gamma} \frac{\partial W_{ki}}{\partial s_\gamma} \frac{\partial s_\gamma}{\partial r_\alpha} \tag{S7}$$

$$\frac{\partial^2 W_{ki}}{\partial r_\alpha \partial r_\beta} = \sum_{\gamma=1}^{\Gamma} \sum_{\gamma=1'}^{\Gamma} \frac{\partial s_\gamma}{\partial r_\alpha} \frac{\partial^2 W_{ki}}{\partial s_\gamma \partial s_{\gamma'}} \frac{\partial s_{\gamma'}}{\partial r_\beta} + \sum_{\gamma=1}^{\Gamma} \frac{\partial W_{ki}}{\partial s_\gamma} \frac{\partial^2 s_\gamma}{\partial r_\alpha \partial r_\beta} \tag{S8}$$

$$\frac{\partial W_{ki}}{\partial s_\gamma} = \frac{\partial w_{ki}}{\partial s_\gamma} \frac{1}{w(\mathbf{s})} - \frac{w_{ki}(\mathbf{s})}{w(\mathbf{s})^2} \sum_{k=1}^{N} \sum_{i=1}^{m!} \frac{\partial w_{ki}}{\partial s_\gamma} \tag{S9}$$

and

$$\begin{aligned}\frac{\partial^2 W_{ki}}{\partial s_\gamma \partial s_{\gamma'}} =& \frac{\partial^2 w_{ki}}{\partial s_\gamma \partial s_{\gamma'}} \frac{1}{w(\mathbf{s})} - \frac{\partial w_{ki}}{\partial s_\gamma} \frac{1}{w(\mathbf{s})^2} \sum_{i=1}^{m!} \sum_{k=1}^{N} \frac{\partial w_{ki}}{\partial s_{\gamma'}} - \frac{\partial w_{ki}}{\partial s_{\gamma'}} \frac{1}{w(\mathbf{s})^2} \sum_{i=1}^{m!} \sum_{k=1}^{N} \frac{\partial w_{ki}}{\partial s_\gamma} + \\ & \frac{2 w_{ki}(\mathbf{s})}{w(\mathbf{s})^3} \sum_{i=1}^{m!} \sum_{k=1}^{N} \frac{\partial w_{ki}}{\partial s_{\gamma'}} \sum_{i=1}^{m!} \sum_{k=1}^{N} \frac{\partial w'_{ki}}{\partial s_{\gamma'}} - \frac{w_{ki}(\mathbf{s})}{w(\mathbf{s})^2} \sum_{i=1}^{m!} \sum_{k=1}^{N} \frac{\partial^2 w_{ki}}{\partial s_\gamma \partial s_{\gamma'}}\end{aligned} \tag{S10}$$

The Jacobians $\frac{\partial s_\gamma}{\partial r_\alpha}$ and $\frac{\partial^2 s_\gamma}{\partial r_\alpha \partial r_\beta}$ in eqs S7 and S8 are trivial if either $\mathbf{s}$ is the same as $\mathbf{r}$ (as in the present application) or the set $\mathbf{r}$ is non-redundant and $\mathbf{s}$ is a subset of $\mathbf{r}$. In either of these cases

$$\frac{\partial s_\gamma}{\partial r_\alpha} = \delta_{\alpha\gamma} \tag{S11}$$

and

$$\frac{\partial^2 s_\gamma}{\partial r_\alpha \partial r_\beta} = \delta_{\alpha\gamma}\delta_{\alpha\beta} \tag{S12}$$

where $\delta_{\gamma\gamma'}$ is a Kronecker delta. Other cases require additional considerations to obtain these derivatives, regardless of whether one uses the algorithm presented here or the unsymmetrized MCMM method. Note also that $V_{12}$ is assumed to be essentially zero at the two MM minima, therefore the sums in eqs S9 and S10 run over $N$ rather than over $N + 2$.

The derivatives of the unnormalized weights $w_{ki}$ are given by differentiating eq 37:

$$\frac{\partial w_{ki}}{\partial \mathbf{s}} = \frac{1}{d_{ki}(\mathbf{s})} \boldsymbol{\Delta}\mathbf{s}^{(ki)} \frac{d w_{ki}(\mathbf{s})}{d d_{ki}} \tag{S13}$$

$$\frac{\partial^2 w_{ki}}{\partial \mathbf{s}^2} = \frac{1}{d_{ki}(\mathbf{s})}\frac{dw_{ki}(\mathbf{s})}{dd_{ki}} + \frac{1}{(d_{ki}(\mathbf{s}))^2}\left(\frac{d^2 w_{ki}(\mathbf{s})}{dd_{ki}^2} - \frac{1}{d_{ki}(\mathbf{s})}\frac{dw_{ki}(\mathbf{s})}{dd_{ki}}\right)\boldsymbol{\Delta}\mathbf{s}^{(ki)}\boldsymbol{\Delta}\mathbf{s}^{(ki)\intercal} \tag{S14}$$

$$\frac{dw_{ki}}{dd_{ki}} = \frac{4(d_{ki}(\mathbf{s}))^{-5}}{\sum_{k=1}^{N+2}\sum_{i=1}^{m!}\frac{1}{(d_{ki}(\mathbf{s}))^4}}\left(\frac{(d_{ki}(\mathbf{s}))^{-4}}{\sum_{k=1}^{N+2}\sum_{i=1}^{m!}\frac{1}{(d_{ki}(\mathbf{s}))^4}} - 1\right) \tag{S15}$$

$$\frac{d^2 w_{ki}}{dd_{ki}^2} = \frac{4(d_{ki}(\mathbf{s}))^{-6}}{\sum_{k=1}^{N+2}\sum_{i=1}^{m!}\frac{1}{(d_{ki}(\mathbf{s}))^4}}\left(\frac{8(d_{ki}(\mathbf{s}))^{-8}}{\left(\sum_{k=1}^{N+2}\sum_{i=1}^{m!}\frac{1}{(d_{ki}(\mathbf{s}))^4}\right)} - \frac{13(d_{ki}(\mathbf{s}))^{-4}}{\sum_{k=1}^{N+2}\sum_{i=1}^{m!}\frac{1}{(d_{ki}(\mathbf{s}))^4}} + 5\right) \tag{S16}$$

$$\frac{\partial d_{ki}}{\partial \mathbf{s}} = \frac{\boldsymbol{\Delta}\mathbf{s}^{(ki)}}{d_{ki}(\mathbf{s})} \tag{S16}$$

$$\frac{\partial^2 d_{ki}}{\partial \mathbf{s}^2} = \frac{1}{d_{ki}(\mathbf{s})}\mathbf{1} - \frac{\boldsymbol{\Delta}\mathbf{s}^{(ki)}\boldsymbol{\Delta}\mathbf{s}^{(ki)\intercal}}{(d_{ki}(\mathbf{s}))^3} \tag{S17}$$