Supporting Information for

The Effects of Computational Modeling Errors on the Estimation of Statistical Mechanical Variables

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1) Derivatives of A

$$A = -\frac{1}{\beta}\ln(\sum e^{-\beta E_i}) = -\frac{1}{\beta}\ln Q$$

1st order:

$$\frac{\partial A}{\partial E_i} = \frac{e^{-\beta E_i}}{Q} = P_i$$

2nd order:

$$\frac{\partial^2 A}{\partial E_i^2} = \frac{Q(-\beta)e^{-\beta E_i} - e^{-\beta E_i}(-\beta)e^{-\beta E_i}}{Q^2} =$$

$$\frac{\partial^2 A}{\partial E_i^2} = \beta(\frac{e^{-2\beta E_i}}{Q^2} - \frac{e^{-\beta E_i}}{Q}) =$$

$$\frac{\partial^2 A}{\partial E_i^2} = \beta(P_i^2 - P_i) = \frac{\partial P_i}{\partial E_i}$$

$$\frac{\partial^2 A}{\partial E_i \partial E_j} = \frac{Q(0) - e^{-\beta E_i}(-\beta)e^{-\beta E_j}}{Q^2} =$$

$$\frac{\partial^2 A}{\partial E_i \partial E_j} = \beta(P_i P_j) = \frac{\partial P_i}{\partial E_j}$$

3rd order:

$$\frac{\partial^3 A}{\partial E_i^3} = \beta(2P_i\beta(P_i^2 - P_i) - \beta(P_i^2 - P_i)) =$$

$$\frac{\partial^3 A}{\partial E_i^3} = \beta^2(2P_i^3 - 3P_i^2 + P_i)$$

$$\frac{\partial^3 A}{\partial E_i \partial E_j \partial E_k} = \frac{\partial}{\partial E_k}\left[\beta P_i P_j\right] =$$

$$\frac{\partial^3 A}{\partial E_i \partial E_j \partial E_k} = 2\beta^2 P_i P_k P_j$$

$$\frac{\partial^3 A}{\partial E_i^2 \partial E_j} = \frac{\partial}{\partial E_j}\beta(P_i^2 - P_i) =$$

$$\frac{\partial^3 A}{\partial E_i^2 \partial E_j} = \beta\left[2P_i\beta P_i P_j - \beta P_i P_j\right] =$$

$$\frac{\partial^3 A}{\partial E_i^2 \partial E_j} = \beta^2 P_i P_j\left[2P_i - 1\right]$$

4th order:

$$\frac{\partial^4 A}{\partial E_i^4} = \beta^3(6P_i^4 - 12P_i^3 + 7P_i^2 - P_i)$$

$$\frac{\partial^4 A}{\partial E_i^2 \partial E_j^2} = \frac{\partial}{\partial E_j}\beta^2 P_i P_j\left[2P_i - 1\right] =$$

$$\frac{\partial^4 A}{\partial E_i^2 \partial E_j^2} = \beta^2\left[\beta P_i P_j P_j[2P_i - 1] + P_i\beta(P_j^2 - P_j)[2P_i - 1] + P_i P_j 2\beta P_i P_j\right] =$$

$$\frac{\partial^4 A}{\partial E_i^2 \partial E_j^2} = \beta^3 P_i P_j\left[6P_i P_j - 2P_i - 2P_j + 1\right]$$

$$\frac{\partial^4 A}{\partial E_i^3 \partial E_j} = \frac{\partial}{\partial E_j}\beta^2(2P_i^3 - 3P_i^2 + P_i) =$$

$$\frac{\partial^4 A}{\partial E_i^3 \partial E_j} = \beta^2\left[6P_i^2\beta P_i P_j - 6P_i\beta P_i P_j + \beta P_i P_j\right] =$$

$$\frac{\partial^4 A}{\partial E_i^3 \partial E_j} = \beta^3 P_i P_j\left[6P_i^2 - 6P_i + 1\right]$$

$$\frac{\partial^4 A}{\partial E_i^2 \partial E_j \partial E_k} = \frac{\partial}{\partial E_k}\beta^2 P_i P_j\left[2P_i - 1\right] =$$

$$\frac{\partial^4 A}{\partial E_i^2 \partial E_j \partial E_k} = \beta^2\left[\beta P_i P_k P_j(2P_i - 1) + P_i\beta P_j P_k(2P_i - 1) + P_i P_j 2\beta P_i P_k\right] =$$

$$\frac{\partial^4 A}{\partial E_i^2 \partial E_j \partial E_k} = \beta^3 P_i P_k P_j\left[(6P_i - 2)\right]$$

$$\frac{\partial^4 A}{\partial E_i \partial E_j \partial E_k \partial E_l} = \frac{\partial}{\partial E_l}2\beta^2 P_i P_k P_j =$$

$$\frac{\partial^4 A}{\partial E_i \partial E_j \partial E_k \partial E_l} = 2\beta^2\left[\beta P_i P_l P_k P_j + P_i\beta P_k P_l P_j + P_i P_k \beta P_j P_l\right] =$$

$$\frac{\partial^4 A}{\partial E_i \partial E_j \partial E_k \partial E_l} = 6\beta^3 P_i P_l P_k P_j$$

2) First-order error propagation in A

$$A = -\frac{1}{\beta}\ln(\sum e^{-\beta E_i})$$

$$\frac{\partial A}{\partial E_i} = \frac{e^{-\beta E_i}}{Q} = P_i$$

$$\delta A_1 = \sum_i P_i \delta E_i^{Sys} \pm \sqrt{\sum_i \left(P_i \delta E_i^{Rand}\right)^2}$$

3) First-order error propagation in E

$$E = \frac{\sum_i E_i \exp(-\beta E_i)}{Q} = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)}$$

$$\frac{\partial E}{\partial E_j} = \frac{Q\left[\exp(-\beta E_j) + (-\beta)\exp(-\beta E_j)E_j\right] - (-\beta)\exp(-\beta E_j)\sum_i E_i \exp(-\beta E_i)}{Q^2}$$

$$\frac{\partial E}{\partial E_j} = \frac{\exp(-\beta E_j)}{Q} - \frac{(\beta)\exp(-\beta E_j)E_j}{Q} + (\beta)\frac{\exp(-\beta E_j)}{Q}\frac{\sum_i E_i \exp(-\beta E_i)}{Q}$$

$$\frac{\partial E}{\partial E_j} = P_j - \beta P_j E_j + \beta P_j E$$

$$\frac{\partial E}{\partial E_j} = P_j(1 - \beta E_j + \beta E)$$

$$\delta E = \sum_i \left|P_i(1 - \beta E_i + \beta E)\right| \delta E^{Sys}{}_i \pm \sqrt{\sum_i \left(P_i(1 - \beta E_i + \beta E)\delta E^{Rand}{}_i\right)^2}$$

4) First-order error propagation in S

$$S = -k\sum_i P_i \ln P_i$$

$$S = -k\sum_i \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} \ln\left(\frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}\right) = S_i + S_a$$

Since each term in the outer sum in S depends on every state (via the partition functions in the denominators), we break S into two parts: S_i for the outer sum term for state i, and S_a for all the remaining terms:

$$S_i = -k \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} \ln\left(\frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} \right) \qquad S_a = -k \sum_{a \neq i} \frac{e^{-\beta E_a}}{\sum_j e^{-\beta E_j}} \ln\left(\frac{e^{-\beta E_a}}{\sum_j e^{-\beta E_j}} \right)$$

Now,

$$\frac{\partial S}{\partial E_i} = \frac{\partial S_i}{\partial E_i} + \frac{\partial S_a}{\partial E_i}$$

$$\frac{\partial S_i}{\partial E_i} = -k\left[\left(\frac{(-\beta)e^{-\beta E_i}\sum_j e^{-\beta E_j} - (-\beta)e^{-2\beta E_i}}{\left(\sum_j e^{-\beta E_j}\right)^2}\right)\ln\left(\frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}\right) + \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}\left((-\beta) - \frac{(-\beta)e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}\right)\right]$$

$$\frac{\partial S_i}{\partial E_i} = -k(-\beta)\left[\left(\frac{e^{-\beta E_i}\sum_j e^{-\beta E_j} - e^{-2\beta E_i}}{\left(\sum_j e^{-\beta E_j}\right)^2}\right)\ln\left(\frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}\right) + \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}\left(1 - \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}\right)\right]$$

$$\frac{\partial S_i}{\partial E_i} = \frac{1}{T}\left[(P_i - P_i^2)\ln(P_i) + (P_i - P_i^2)\right]$$

$$\frac{\partial S_i}{\partial E_i} = \frac{(P_i - P_i^2)}{T}\left[\ln(P_i) + 1\right]$$

$$S_a = -k\sum_{a\neq i}\frac{e^{-\beta E_a}}{\sum_j e^{-\beta E_j}}\ln\left(\frac{e^{-\beta E_a}}{\sum_j e^{-\beta E_j}}\right)$$

$$S_a = -k\sum_{a\neq i}e^{-\beta E_a}\left(\sum_j e^{-\beta E_j}\right)^{-1}\ln\left(e^{-\beta E_a}\right) - e^{-\beta E_a}\left(\sum_j e^{-\beta E_j}\right)^{-1}\ln\left(\sum_j e^{-\beta E_j}\right)$$

$$\frac{\partial S_a}{\partial E_i} = -k\sum_{a\neq i}\left[\begin{array}{l} e^{-\beta E_a}\ln\left(e^{-\beta E_a}\right)(-1)\left(\sum_j e^{-\beta E_j}\right)^{-2}(-\beta)e^{-\beta E_i} + \\ -e^{-\beta E_a}(-1)\left(\sum_j e^{-\beta E_j}\right)^{-2}(-\beta)e^{-\beta E_i}\ln\left(\sum_j e^{-\beta E_j}\right) + \\ -e^{-\beta E_a}\left(\sum_j e^{-\beta E_j}\right)^{-1}\frac{(-\beta)e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} \end{array}\right]$$

$$\frac{\partial S_a}{\partial E_i} = -\frac{1}{T}\sum_{a\neq i}\left[\frac{e^{-\beta E_a}\ln\left(e^{-\beta E_a}\right)e^{-\beta E_i}}{\left(\sum_j e^{-\beta E_j}\right)^2} - \frac{e^{-\beta E_a}e^{-\beta E_i}\ln\left(\sum_j e^{-\beta E_j}\right)}{\left(\sum_j e^{-\beta E_j}\right)^2} + \frac{e^{-\beta E_a}e^{-\beta E_i}}{\left(\sum_j e^{-\beta E_j}\right)^2}\right]$$

$$\frac{\partial S_a}{\partial E_i} = -\frac{1}{T}\sum_{a\neq i}\left[P_iP_a\ln\left(e^{-\beta E_a}\right) - P_iP_a\ln\left(\sum_j e^{-\beta E_j}\right) + P_iP_a\right]$$

$$\frac{\partial S_a}{\partial E_i} = -\frac{1}{T}\sum_{a\neq i}\left[P_iP_a\ln\left(\frac{e^{-\beta E_a}}{\sum_j e^{-\beta E_j}}\right) + P_iP_a\right]$$

$$\frac{\partial S_a}{\partial E_i} = -\frac{1}{T}\sum_{a\neq i}P_iP_a\left[\ln\left(P_a\right)+1\right]$$

$$\frac{\partial S}{\partial E_i} = \frac{\partial S_i}{\partial E_i} + \frac{\partial S_a}{\partial E_i} = \frac{(P_i - P_i^2)}{T}\left[\ln(P_i)+1\right] - \frac{1}{T}\sum_{a\neq i}P_iP_a\left[\ln\left(P_a\right)+1\right]$$

$$\frac{\partial S}{\partial E_i} = \frac{(P_i - P_i^2)}{T}\left[\ln(P_i)+1\right] - \frac{P_i}{T}\sum_{a\neq i} P_a \ln(P_a) - \frac{P_i}{T}\sum_{a\neq i} P_a$$

Now use the fact that $P_i = 1 - \sum_{a\neq i} P_a$

$$\frac{\partial S}{\partial E_i} = \frac{(P_i - P_i^2)}{T}\left[\ln(P_i)+1\right] - \frac{P_i}{T}\sum_{a\neq i} P_a \ln(P_a) - \frac{P_i}{T}(1-P_i)$$

$$\frac{\partial S}{\partial E_i} = \frac{P_i}{T}\left[(1-P_i)\ln(P_i) + (1-P_i) - \sum_{a\neq i} P_a \ln(P_a) - (1-P_i)\right]$$

$$\frac{\partial S}{\partial E_i} = \frac{P_i}{T}\left[(1-P_i)\ln(P_i) - \sum_{a\neq i} P_a \ln(P_a)\right]$$

$$\frac{\partial S}{\partial E_i} = \frac{P_i}{T}\left[\ln(P_i) - \sum_{j} P_j \ln(P_j)\right]$$

$$\frac{\partial S}{\partial E_i} = \frac{P_i}{T}\left[\ln(P_i) + \frac{S}{k}\right]$$

$$\frac{\partial S}{\partial E_i} = \beta P_i\left[k\ln(P_i) + S\right]$$

$$\delta S = \sum_i \left|\beta P_i\left[k\ln(P_i)+S\right]\right|\delta E_i^{Sys} \pm \sqrt{\sum_i \left(\left(\beta P_i\left[k\ln(P_i)+S\right]\right)\delta E_i^{Rand}\right)^2}$$

5) Second-order error propagation in A. The following formulas were adapted from Ref. 9.

$$Err_{Sys} \approx \sum_i P_i \delta E_i^{Sys} + \frac{1}{2}\sum_i \frac{\partial^2 A}{\partial E_i^2}(\delta E_i^{Rand})^2$$

$$\left(Err_{Rand}\right)^2 \approx \sum_i \left(\frac{\partial A}{\partial E_i}\right)^2 \left(\delta E_i^{Rand}\right)^2 - \frac{1}{4}\left[\sum_i \frac{\partial^2 A}{\partial E_i^2}\left(\delta E_i^{Rand}\right)^2\right]^2$$

Replace the partial derivatives with the appropriate expressions from S1-S2:

$$\delta A_2 = \left[\sum_i P_i \delta E_i^{Sys} + \frac{1}{2} \sum_i \beta (P_i^2 - P_i)(\delta E_i^{Rand})^2 \right] \pm \left[\sum_i \left(P_i \delta E_i^{Rand} \right)^2 - \frac{1}{4} \left(\sum_i \beta (P_i^2 - P_i) \left(\delta E_i^{Rand} \right)^2 \right)^2 \right]^{1/2}$$

6) Fourth-order error propagation in A. The following formulas were adapted from Ref. 9.

$$Err_{Sys} \approx \sum_i P_i \delta E_i^{Sys} + \frac{1}{2} \sum_i \frac{\partial^2 A}{\partial E_i^2} (\delta E_i^{Rand})^2 + \frac{1}{4} \sum_i \sum_{j>i} \frac{\partial^4 A}{\partial E_i^2 \partial E_j^2} (\delta E_i^{Rand})^2 (\delta E_j^{Rand})^2$$

$$\begin{aligned} \left(Err_{Rand} \right)^2 \approx & \sum_i \left(\frac{\partial A}{\partial E_i} \right)^2 \left(\delta E_i^{Rand} \right)^2 + \\ & -\frac{1}{4} \left[\sum_i \frac{\partial^2 A}{\partial E_i^2} \left(\delta E_i^{Rand} \right)^2 \right]^2 + \\ & \sum_i \sum_{j \neq i} \frac{\partial A}{\partial E_i} \frac{\partial^3 A}{\partial E_i \partial E_j^2} \left(\delta E_i^{Rand} \right)^2 \left(\delta E_j^{Rand} \right)^2 + \\ & -\frac{1}{4} \sum_i \sum_{j>i} \frac{\partial^4 A}{\partial E_i^2 \partial E_j^2} \left(\delta E_i^{Rand} \right)^2 \left(\delta E_j^{Rand} \right)^2 \left[\frac{\partial^2 A}{\partial E_i^2} \left(\delta E_i^{Rand} \right)^2 + \frac{\partial^2 A}{\partial E_j^2} \left(\delta E_j^{Rand} \right)^2 + \frac{1}{4} \frac{\partial^4 A}{\partial E_i^2 \partial E_j^2} \left(\delta E_i^{Rand} \right)^2 \left(\delta E_j^{Rand} \right)^2 \right] \end{aligned}$$

Replace the partial derivatives with the appropriate expressions from S1-S2:

$$\begin{aligned} \delta A_4 = & \left[\sum_i P_i \delta E_i^{Sys} + \frac{1}{2} \sum_i \beta (P_i^2 - P_i)(\delta E_i^{Rand})^2 + \frac{1}{4} \sum_i \sum_{j>i} \beta^3 P_i P_j \left[6 P_i P_j - 2P_i - 2P_j + 1 \right] (\delta E_i^{Rand})^2 (\delta E_j^{Rand})^2 \right] \\ & \pm \left[\begin{aligned} & \sum_i \left(P_i \delta E_i^{Rand} \right)^2 - \frac{1}{4} \left(\sum_i \beta (P_i^2 - P_i) \left(\delta E_i^{Rand} \right)^2 \right)^2 + \sum_i \sum_{j \neq i} P_i \beta^2 P_i P_j \left[2P_j - 1 \right] \left(\delta E_i^{Rand} \right)^2 \left(\delta E_j^{Rand} \right)^2 + \\ & -\frac{1}{4} \sum_i \sum_{j>i} \beta^3 P_i P_j \left[6 P_i P_j - 2P_i - 2P_j + 1 \right] \left(\delta E_i^{Rand} \right)^2 \left(\delta E_j^{Rand} \right)^2 * \\ & \left(\beta (P_i^2 - P_i) \left(\delta E_i^{Rand} \right)^2 + \beta (P_j^2 - P_j) \left(\delta E_j^{Rand} \right)^2 + \frac{1}{4} \beta^3 P_i P_j \left[6 P_i P_j - 2P_i - 2P_j + 1 \right] \left(\delta E_i^{Rand} \right)^2 \left(\delta E_j^{Rand} \right)^2 \right) \end{aligned} \right]^{1/2} \end{aligned}$$