Supporting Information for:

Adaptive Partitioning in Combined Quantum Mechanical and Molecular Mechanical Calculations of Potential Energy Functions for Multiscale Simulations

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Functional form of sorted smoothing function. To evaluate the quality of a number of functional forms for the smoothing functions Φ_i, we performed multiple tests using the sorted adaptive partitioning (sorted AP) method with different smoothing functions Φ_i.

The test system used for the testing presented here consists of 15 particles (simulations performed with a different number of particles did not alter our conclusions). We used an IMMMM-type scheme to define the multilevel energy. For the low-level interaction potential we chose the Lennard-Jones potential:

$$V_{ij} = 4\varepsilon\left(\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right) \tag{S1}$$

For the high-level interaction potential, we chose the Morse potential:

$$V_{ij} = D\left[1 - e^{-a\left(r_{ij} - r_e\right)}\right]^2 - D \tag{S2}$$

with the same well depth ($D = \varepsilon$), position of the well depth ($r_e = 2^{\frac{1}{6}}\sigma$), and force constant at the minimum as in the Lennard-Jones potential.

One of the particles is defined as the primary group. The radius of the active zone is $r_{\min} = 2\sigma$. The buffer zone is 0.5σ thick. A particle is initially positioned randomly on the boundary between buffer and environmental zone. Zero to three particles are randomly placed in the buffer zone. The rest of the particles are randomly positioned up to 3σ away from the primary group in the active and environmental zones. During the tests the particle that is initially on the boundary between buffer and environmental zone is moved along a straight-line path to the boundary between active and buffer zone. No other particles are moved during the test. To avoid unrealistic geometries during the tests, paths are eliminated if any point along the path, two particles approach each other closer than 0.9σ. The procedure was repeated until statistics were accumulated for 5000 paths.

A good smoothing function Φ_i for the sorted AP method minimizes rapid changes in the force components on a particle both when there is only one particle in the buffer zone and also when there are multiple particles present in the buffer zone. Figure S1 illustrates the average maximum difference in a force component on a particle determined during our tests (averaged over 5000 random paths) for several possible choices of the smoothing function $\Phi_i(X_i)$. X_i is here defined as:

$$X_i = \sum_{j=1}^{i-1} \frac{1-P_j}{P_j - P_i} + \frac{1-P_i}{P_i} + \sum_{j=i+1}^{N} \frac{1-P_i}{P_i - P_j} P_j \tag{S3}$$

where

$$P_i(\alpha_i) = -6\alpha_i^5 + 15\alpha_i^4 - 10\alpha_i^3 + 1, \tag{S4}$$

and α_i is given by:

$$\alpha_i = \frac{r_i - r_{\min}}{r_{\max} - r_{\min}}, \qquad \text{for} \qquad r_{\min} < r_i < r_{\max}. \tag{S5}$$

The better functional forms minimize rapid changes in a force component on a particle during the tests. Depending on the number of particles in the buffer zone, different functional forms for Φ_i give the smallest average maximum difference in a force component. Figure S1a shows that if there is only one particle in the buffer zone

$$\Phi_i = (1 + X_i/2)^{-3} \tag{S6}$$

is the optimal functional form (out of the tested functional forms) for the sorted AP method. Figure S1b illustrates that if there are three particles in the buffer zone

$$\Phi_i = (1 + 5X_i)^{-3} \tag{S7}$$

is the optimal functional form (out of the tested functional forms) for the sorted AP method. Both, Figure S1a and S1b show that the functional form for Φ_i,

$$\Phi_i = (1 + X_i)^{-3}, \tag{S8}$$

results in small changes in a force component during the passage of a particle through the buffer zone for both one particle and multiple particles present in the buffer zone. Therefore, this functional form was chosen as the smoothing function for the sorted AP simulations in this article.

The tests performed in this study are not exhaustive enough to define an optimal functional form for the smoothing functions Φ_i for all possible cases, and in fact the optimal form may depend on the case, and a more optimal form may emerge with experience. However, the form used here, equation S8, appears to be robust enough for use in a variety of applications.

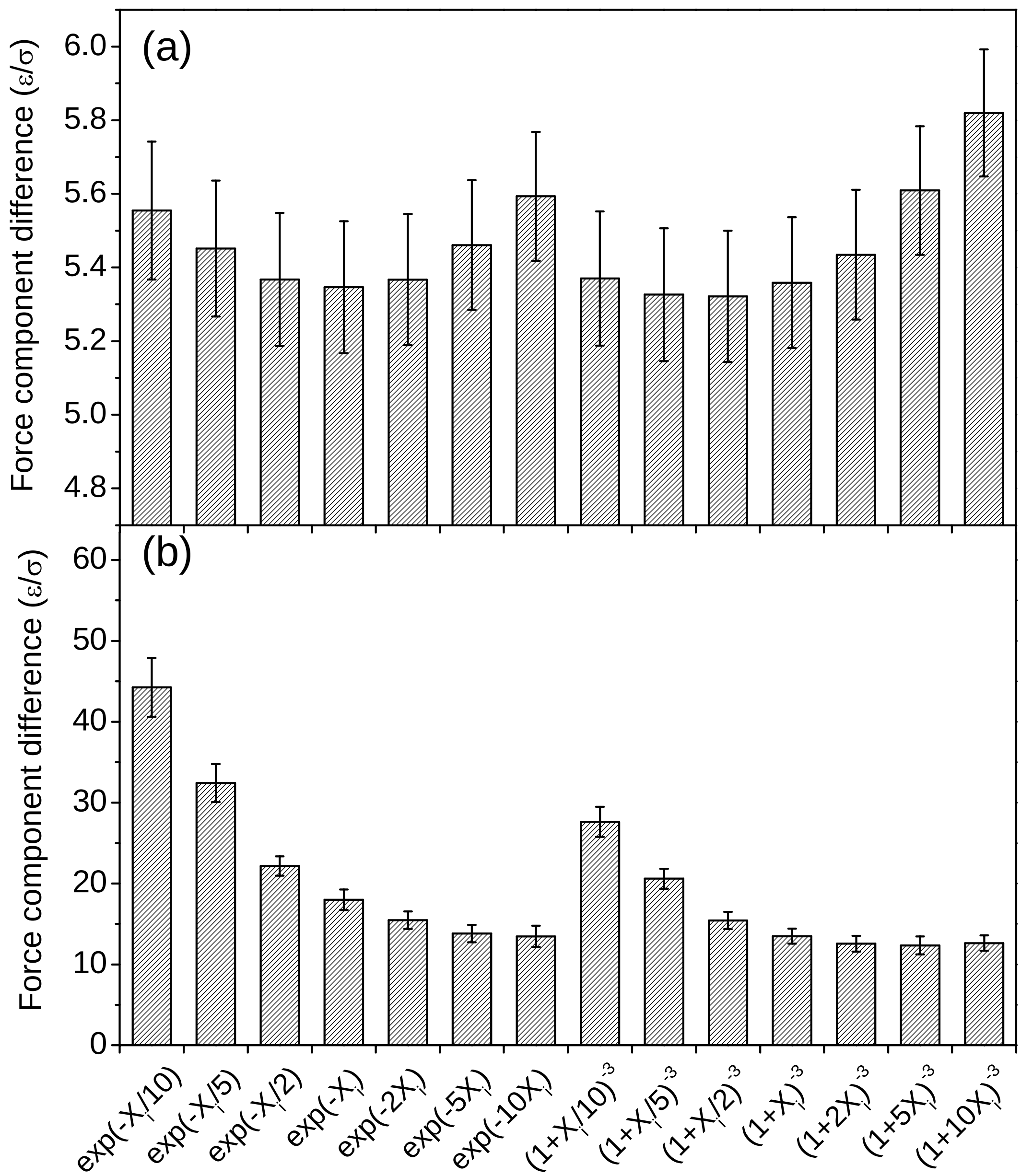

Fig. S1 Average maximum difference in a force component (and 95% confidence interval) on a particle during a sorted AP test simulation using different smoothing functions Φ_i. Altogether 5000 random paths were analyzed. Each system consists of 15 particles, with (a) 1 of them in the buffer zone, (b) 3 of them in the buffer zone. Confidence intervals are computed by dividing the 5000 paths into five groups of 1000 paths.