

Correction to Constant pH Molecular Dynamics in Explicit Solvent with λ -Dynamics

Serena Donnini, Florian Tegeler,[†] Gerrit Groenhof,* and Helmut Grubmüller*

Department of Theoretical and Computational Biophysics, Max Planck Institute for Biophysical Chemistry, Göttingen, Germany

Journal of Chemical Theory and Computation **2011**, 7, 1962–1978. DOI: 10.1021/ct200061r

With this erratum, we correct an error in the expressions for $V^{\text{chem}}(\lambda_1, \lambda_2)$ (eqs 31 and 32) and $V^{\text{transf}}(\lambda_1, \lambda_2)$ (eq 33) for chemically coupled titrating sites, in the aforementioned paper (*J. Chem. Theory Comput.* **2011**, 7, 1962–1978). The correct expressions for $V^{\text{chem}}(\lambda_1, \lambda_2)$ are

$$\begin{aligned} V^{\text{chem}}(\lambda_1, \lambda_2) = & (1 - \lambda_1)[(1 - \lambda_2)\Delta G_{\text{ref},00} + \lambda_2\Delta G_{\text{ref},01}^{\text{exp}}] \\ & + \lambda_1[(1 - \lambda_2)\Delta G_{\text{ref},10}^{\text{exp}} + \lambda_2\Delta G_{\text{ref},11}^{\text{exp}}] \\ & - \Delta \tilde{G}_{\text{ref}}^{\text{FF}}(\lambda_1, \lambda_2) \end{aligned}$$

with

$$\Delta G_{\text{ref},00} = 0$$

$$\Delta G_{\text{ref},01}^{\text{exp}} = (\ln 10)RT(\text{p}K_{\text{a,ref}}(00 \rightleftharpoons 01) - \text{pH})$$

$$\Delta G_{\text{ref},10}^{\text{exp}} = (\ln 10)RT(\text{p}K_{\text{a,ref}}(00 \rightleftharpoons 10) - \text{pH})$$

and

$$\Delta G_{\text{ref},11}^{\text{exp}} = (\ln 10)RT(\text{p}K_{\text{a,ref}}(00 \rightleftharpoons 11) - \text{pH})$$

which replace eqs 31 and 32.

The correct expression for $V^{\text{transf}}(\lambda_1, \lambda_2)$ is

$$\begin{aligned} V^{\text{transf}}(\lambda_1, \lambda_2) = & (1 - \lambda_1)[(1 - \lambda_2)\Delta G_{\text{AHH}^+} + \lambda_2\Delta G_{\text{AH}}] \\ & + \lambda_1[(1 - \lambda_2)\Delta G_{\text{AH}} + \lambda_2\Delta G_{\text{A}^-}], \end{aligned}$$

which replaces eq 33.

We note that in our implementation of the constant pH protocol, the expressions for the forces due to $V^{\text{chem}}(\lambda_1, \lambda_2)$ and $V^{\text{transf}}(\lambda_1, \lambda_2)$ were implemented correctly; thus the trajectories are unaffected. The above corrected expressions are required only to compute the total energy of the system (i.e., the real and λ particles together) during the simulation. As a test, we have computed a 1 ns constant pH trajectory of imidazole in water ($\approx 15\,700$ atoms) in the microcanonical ensemble. In the simulation, nonbonded interactions were evaluated with a 1.3 nm cutoff. Between 1 nm and the 1.3 nm cutoff, forces were smoothly shifted to zero using a shift function. We observed that the total energy of the complete system is constant with an average of $-177\,723 \text{ kJ mol}^{-1}$ and a standard deviation of 0.3 kJ mol^{-1} . As the time step was decreased from 0.5 fs to 0.25 fs and 0.1 fs, the standard deviation decreased from 0.3 kJ mol^{-1} to 0.07 kJ mol^{-1} and 0.01 kJ mol^{-1} , respectively, thus establishing proper conservation of total energy.

AUTHOR INFORMATION

Corresponding Author

*E-mail: hgrubmu@gwdg.de (H.G.), ggroenh@gwdg.de (G.G.).

Present Address

[†]Institute of Computer Science, Georg August University, Göttingen, Germany.

Published: June 12, 2013