Metadynamics of Gas Phase Zundel Ion

Proton Transfer Coordinate CV

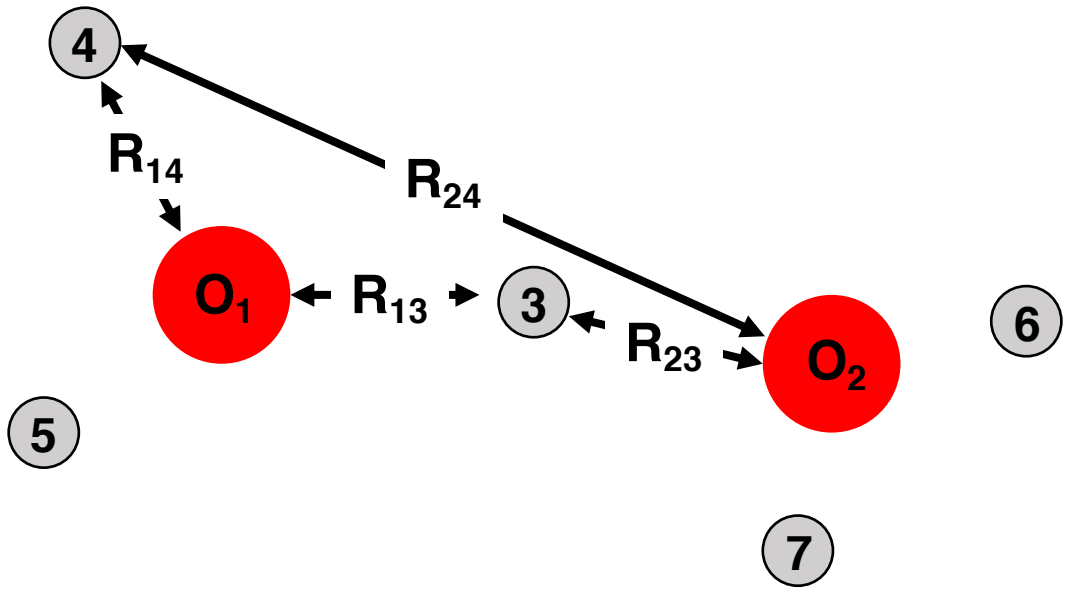
The proton transfer coordinate (PTC) is defined as:

$$s = R_{O_1H^*} - R_{O_2H^*}$$

with $R_{O_jH^*}$ being the distance between oxygen, j, and the shared proton.

However, when the protons exchange (which will happen if we add a bias potential with respect to the PTC), our definition must be generalized, defining the shared proton to have the smallest PTC value:

$$s = \min_k \left| R_{O_1H_k} - R_{O_2H_k} \right|$$



The value of the PTC in the above example would be:

$$s = \min(\,|R_{13} - R_{23}|, |R_{14} - R_{24}|, \ldots\,)$$

$$= |R_{13} - R_{23}|$$

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Unfortunately, our generalized PTC:

$$s = \min_k \left| R_{O_1 H_k} - R_{O_2 H_k} \right| = \min_k s_k$$

is not differentiable, and therefore can't be used as a CV in metadynamics. Instead, we need to use a "smooth minimum" function (see: https://en.wikipedia.org/wiki/Smooth_maximum). Note that we can add a negative sign to the arguments of a "smooth maximum" to make it a smooth minimum.

A familiar choice of smooth minimum is the LogSumExp (LSE) minimum function:

$$\mathrm{LSE}(s_1, s_2, \ldots, s_N) = -\frac{1}{\beta} \log\left(\sum_k e^{-\beta s_k} \right) \sim \min_k s_k \ \ (\text{as } \beta \to \infty)$$

where β is a fixed parameter. When β is 'large,' it effectively lessens the contributions of the larger s_k values (since the exponential of a large negative number is small). Notice that the Helmholtz free energy is a smooth minimum of the possible energies of a system at constant temperature (T), and is exactly equal to the minimum energy in the limit of $T \to 0$ ($\beta \to \infty$), as expected.

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While LogSumExp,

$$\mathrm{LSE}(s_1, s_2, \ldots, s_N) = -\frac{1}{\beta}\log\left(\sum_k e^{-\beta s_k}\right) \sim \min_k s_k \ \ (\text{as } \beta \to \infty)$$

works well on paper, I've discovered that there are practical issues with it. I believe that the default floating point arithmetic used by PLUMED, python, etc. will evaluate exp(-[very large number]) = 0.0, which then gives us log(0) which is undefined.

For some reason, this error shows up in the MBX electrostatics (in stderr):

```
gammq: x = -nan, a = 0.75
driver: $MBX_HOME/src/potential/electrostatics/gammq.cpp:156: double
elec::gammq(double, double): Assertion `x >= 0.0 && a > 0.0' failed.
```

I'm not sure why this is being passed to the gamma function since it is just a CV for metadynamics, so this might be worth remembering in case problems arise in the future.

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We can choose a different smooth minimum function (taken from the PLUMED documentation),

$$\mathrm{SMIN}(s_1, s_2, \ldots, s_N) = \beta \left[\log \left(\sum_k \exp \left[\frac{\beta}{s_k} \right] \right) \right]^{-1} \sim \min_k s_k \ (\text{as } \beta \to \infty)$$

but this function has an even bigger problem than LSE, since when any $s_k = 0$, we have to divide by 0. This is obviously bad because $s_k = 0$ is the PTC value of the minimum-energy Zundel!

However, there is a nice duct tape fix to this by adding a small fixed number, σ, to each argument, and subtracting σ from the result:

$$\mathrm{SMIN}(s_1, s_2, \ldots, s_N) = -\sigma + \beta \left[\log \left(\sum_k \exp \left[\frac{\beta}{s_k + \sigma} \right] \right) \right]^{-1} \sim \min_k s_k \ (\text{as } \beta \to \infty)$$

This new PTC should be stable (as far as I can tell). The only downside is that we might deviate from the true minimum by tenths of an Angstrom in some pathological cases. I am printing out all values of s_k along with the SMIN values, so we can double check the accuracy if needed.