2D Morse

We are interested in restricting our target distribution $\mathbf{P}(\mathbf{x})$ within a cutoff contour defined by E_{cut}, we therefore define the distribution to be 0 if the Potential Energy ($\mathbf{V}$) is beyond the cutoff contour, and positive if the Potential Energy is within the contour.

$$\begin{cases} \mathbf{P}(\mathbf{x}) = 0 & \mathbf{V}(\mathbf{x}) > E_{cut} \\ \mathbf{P}(\mathbf{x}) > 0 & \mathbf{V}(\mathbf{x}) < E_{cut} \end{cases}$$

Following Garaschuk the 2D Morse Ecut=11.5, and the 3D is Ecut=7.5

To avoid numerical issues generated at 0 we introduce a finite parameter Δ such that

$$\mathbf{P}(\mathbf{x}) := \frac{E_{cut} + \Delta - \mathbf{V}(\mathbf{x})}{\int d\mathbf{x}\; E_{cut} + \Delta - \mathbf{V}(\mathbf{x})} \tag{1}$$

(where we make sure to normalize the target distribution). Again following Garaschuk we take Δ to be 1% of Ecut.

Consider the two-dimensional Morse Potential.

$$\mathbf{V}(x, y) := D\left[\left(e^{-w_x x} - 1\right)^2 + \left(e^{-w_y y} - 1\right)^2\right] \tag{2}$$

We are interested in $\mathbf{P}$ having regular spacing between gridpoints, we therefore introduce a quasi Lennard-Jones pairwise interaction ($\mathbf{U}_{ij}$) of the form.

$$\begin{gathered} \mathbf{U}_{ij}(\mathbf{x}_i, \mathbf{x}_j) := \left[\frac{\sigma_i(\mathbf{x}_i)}{|\mathbf{x}_{ij}|}\right]^{12} - \left[\frac{\sigma_i(\mathbf{x}_i)}{|\mathbf{x}_{ij}|}\right]^{6} \\ |\mathbf{x}_{ij}| = \sum \left(\mathbf{x}_i - \mathbf{x}_j\right)^2 \end{gathered} \tag{3}$$

σ represents the distance between nearest neighbors for our regularly distributed $\mathbf{P}$ gridpoints.

$$\sigma_i = \sigma(\mathbf{x}_i) := c \cdot \left[N \cdot P\left(\mathbf{x}_i\right)\right]^{-1/d} \tag{4}$$

The constant c should be on the order of 1. Our mmc algorithm uses the Pair-Potential to optimize the gridpoints

$$\mathcal{U} := \sum_{i,j} \mathbf{U}_{ij}(\mathbf{x}_i, \mathbf{x}_j) \tag{5}$$

I. BASIS CONSTRUCTION

Symmetric Gaussian Basis

Using Symmetric Gaussians as the basis we can reuse the derivations from DGB, removing the omega depedencies. Each quasi Lennard Jones grid point is associated with a basis function in the form of a symmetric multivariate Gaussian: A natural choice for α_i is

$$\alpha_i := \frac{\alpha_0}{\sigma_i^2} \tag{6}$$

where $\alpha_0 \sim 1$ is a constant to be specified later.

$$\bar{\mathbf{x}}^{ij} := \frac{\alpha_i \mathbf{x}^i + \alpha_j \mathbf{x}^j}{\alpha_i + \alpha_j} \tag{7}$$

$$A := \exp\left[-\frac{\alpha_i \alpha_j}{2(\alpha_i + \alpha_j)} \sum_k (\mathbf{x}_k^i - \mathbf{x}_k^j)^2\right] \tag{8}$$

$$S_k := \left[\frac{2\pi}{(\alpha_i + \alpha_j)}\right]^{1/2} \exp\left[-\frac{\alpha_i \alpha_j}{2(\alpha_i + \alpha_j)} (\mathbf{x}_k^i - \mathbf{x}_k^j)^2\right] \tag{9}$$

Note that the i, j-independent factor in Eq. 9 can be dropped as it does not affect the final generalized eigenvalue problem (*cf.* Eq. 21), i.e., we can safely use

$$S_k = \frac{1}{\sqrt{\alpha_i + \alpha_j}} \exp\left[-\frac{\alpha_i \alpha_j}{2(\alpha_i + \alpha_j)} (\mathbf{x}_k^i - \mathbf{x}_k^j)^2\right] \tag{10}$$

For convenience we will normalize our overlap matrix elements

$$S_k = \frac{(\alpha_i \alpha_j)^{1/4}}{(\alpha_i + \alpha_j)^{1/2}} \exp\left[-\frac{\alpha_i \alpha_j}{2(\alpha_i + \alpha_j)} (\mathbf{x}_k^i - \mathbf{x}_k^j)^2\right] \tag{11}$$

for the product of two Gaussians we have

$$\Phi_i(\mathbf{x}) \Phi_j(\mathbf{x}) = \mathbf{S}_{ij}\, P_{ij}(\mathbf{x}) \tag{12}$$

where

$$P_{ij}(\mathbf{x}) = \prod_{k=1}^{d} P_{ij}^{(k)}(\mathbf{x}_k) \tag{13}$$

$$P_{ij}^{(k)}(\mathbf{x}_k) := \left[\frac{(\alpha_i + \alpha_j)}{2\pi}\right]^{1/2} \exp\left(-\frac{(\alpha_i + \alpha_j)}{2} (\mathbf{x}_k - \bar{\mathbf{x}}_k^{ij})^2\right)$$

is a normalized Gaussian distribution ($\int d\mathbf{x}_k\, P_{ij}^{(k)}(\mathbf{x}_k) = 1$)

In seperable coordinates the overlap matrix can be computed as

$$\mathbf{S}_{ij} = \prod_{k=1}^{d} S_k = \left(\frac{\sqrt{\alpha_i \alpha_j}}{\alpha_i + \alpha_j}\right)^{d/2} \exp\left[\sum_{k=1}^{d} \frac{-\alpha_i \alpha_j (\mathbf{x}_k^i - \mathbf{x}_k^j)^2}{2(\alpha_i + \alpha_j)}\right] \tag{14}$$

Kinetic Energy

$$\mathbf{T}_{ij} = \mathbf{S}_{ij} \sum_{k=1}^{d} \frac{\alpha_i \alpha_j}{2(\alpha_i + \alpha_j)} \left[1 - \frac{\alpha_i \alpha_j (\mathbf{x}_k^i - \mathbf{x}_k^j)^2}{\alpha_i + \alpha_j}\right] \tag{15}$$

Potential Energy

$$\mathbf{V}_{ij} = \mathbf{S}_{ij} \int_{\mathbb{R}^d} d\mathbf{x}\ P_{ij}(\mathbf{x}) V(\mathbf{q}_0 + \mathbf{M}^{-1/2}\mathbf{U}\mathbf{x}) \tag{16}$$

The integral in Eq. 16 can be computed by the quasi-Monte Carlo method as following. First, generate a quasi-random sequesnce $\mathbf{z}^{(l)},\ l = 1, ..., L\}$ sampled from the standard normal distribution $(2\pi)^{-d/2} \exp\left(-\frac{1}{2}\mathbf{z}^{\mathrm{T}}\mathbf{z}\right)$. Then use

$$\int_{\mathbb{R}^d} d\mathbf{r}\ P_{ij}(\mathbf{x}) V(\mathbf{q}_0 + \mathbf{M}^{-1/2}\mathbf{U}\mathbf{x}) \approx \frac{1}{L} \sum_{l=1}^{L} V(\mathbf{q}^{(l)}) \tag{17}$$

with

$$\mathbf{x}_k^{(l)} = \bar{\mathbf{x}}_k^{ij} + [(\alpha_i + \alpha_j)]^{-1/2}\, \mathbf{z}_k^{(l)} \tag{18}$$

and

$$\begin{aligned} \mathbf{q}^{(l)} &= \mathbf{q}_0 + \mathbf{M}^{-1/2}\mathbf{U}\mathbf{x}^{(l)}, \\ \mathbf{q}_:^{(l)} &= \mathbf{q}_0 + \mathbf{M}_:^{-1/2} \sum_k \mathbf{U}_{k,:}\mathbf{x}_:^{(l)}, \end{aligned} \tag{19}$$

Generalized Eigenvalue Problem

Finally, the vibrational eigenenergies E and eigenfunctions

$$\Psi(\mathbf{r}) = \sum_j c_j \Phi_j(\mathbf{x}) \tag{20}$$

can be obtained from solving the generalized eigenvalue problem:

$$\sum_j (\mathbf{V}_{ij} + \mathbf{T}_{ij} - E\mathbf{S}_{ij}) c_j = 0 \tag{21}$$

II. QUADRATURE

To directly compare accuracy with Garashchuk we are going to modify the general approach presented about.

First we will consider a uniform grid generated within the contour defined by Ecut. Because the grid is completly uniform we can define our Gaussian Basis Functions to have a constant alpha (the same for every basis function).

Analytic Results

To test the code consider our 2D morse potential with a single atom (x,y cartesian coordinates) and a mass of 1 (Assume atomic units), D defines the morse parameter.

$$V := D\left(\exp\left[-c_x x\right]-1\right)^2 + D\left(\exp\left[-c_y y\right]-1\right)^2 \tag{22}$$

Evaluating the standard terms we find

$$\begin{aligned}
\left(\frac{\partial V}{\partial x}\right)_y &= 2Dc_x e^{-2c_x x}\left(e^{c_x x}-1\right)\ \Big|_{x=0} = 0 \\
\left(\frac{\partial V}{\partial y}\right)_x &= 2Dc_y e^{-2c_y y}\left(e^{c_y y}-1\right)\ \Big|_{y=0} = 0 \\
\frac{\partial^2 V}{\partial y \partial x} &= 0 \\
\frac{\partial^2 V}{\partial x \partial y} &= 0
\end{aligned} \tag{23}$$

The forces are given by

$$F(x,y) = -\nabla V(x,y) = \begin{bmatrix} \left(-\frac{\partial V}{\partial x}\right)_y \\ \left(-\frac{\partial V}{\partial y}\right)_x \end{bmatrix} = \begin{bmatrix} -2Dc_x e^{-2c_x x}\left(e^{c_x x}-1\right) \\ -2Dc_y e^{-2c_y y}\left(e^{c_y y}-1\right) \end{bmatrix} \tag{24}$$

For reference we can compute the Hessian Analytically,

$$\text{Hessian} = \begin{bmatrix} \frac{\partial^2 V}{\partial x^2} & \frac{\partial^2 V}{\partial x \partial y} \\ \frac{\partial^2 V}{\partial y \partial x} & \frac{\partial^2 V}{\partial y^2} \end{bmatrix} = \begin{bmatrix} -2c_x^2 D e^{-2c_x x}\left(e^{c_x x}-2\right) & 0 \\ 0 & -2c_y^2 D e^{-2c_y y}\left(e^{c_y y}-2\right) \end{bmatrix} \tag{25}$$