MDP.jl: Summary of the Implemented Equations - Draft

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Abstract

This draft presents a summary of the equations that are currently implemented in MDP.jl (and its auxiliary files). It is based on the file GOLFF.pdf (project name changed from GOLFF.jl to MDP.jl). Some of the terminology was slightly redefined in order to smooth the transition between the original equations and their computational implementation.

1 Input Variables/Parameters

The following table shows all the relevant input variables or parameters needed in the computational implementation. As mentioned above, some of them were slightly redefined and new definitions were added.

J	Number of configurations.	Ω_{ji}	Neighbors of the atom i in configuration j.
N_j	Number of atoms in configuration j.	Ω'_{jit}	Neighbors of the atom i in configuration j, whose atomic number type is t.
Z_{ji}	Atomic number of atom i in configuration j.	Ω''_{jit}	If the atomic number type of i is t, returns the neighbors of the atom i in configuration j, else it returns empty.
T_z	Type of the atomic number z. Each atomic number z is indexed in T.	K	?
N_z	Number of the different atomic numbers (or atomic number types) present in all configurations.	L	Degree
$\boldsymbol{r}_i^{N_j}$	Position of atom i in the configuration j.	M	Number of basis functions.
$\boldsymbol{r}^{N_j}$	Positions of all the atoms in configuration j ($N_j \times 3$).	$c_{tkk'l}$	Coefficient needed to calculate the potential/force. A linearized version c_m was finally used. See Equation 2.
$\boldsymbol{f}_{ji}^{\text{qm}}$	Quantum force associated to the atom i in the configuration j.	w_j	Weight associated to the configuration j.
r_{cut}	Cut radius needed to calculate the neighbors of each atom.	h	Finite difference increment.

2 Equation Summary

2.1 Main goal

The goal is to find an optimal coefficient vector $\boldsymbol{c}^*$ to match a set of input quantum mechanical (QM) forces. The optimization problem is formulated in the Equation 4 of the original manuscript. Here, the problem is formulated as follows:

$$\boldsymbol{c}^* = \arg\min_{\boldsymbol{c}\in\mathbb{R}^M} \sum_{j=1}^{J} w_j \sum_{i=1}^{N_j} \left| \boldsymbol{f}_{ji}(\boldsymbol{r}^{N_j}, \boldsymbol{c}) - \boldsymbol{f}_{ji}^{\text{qm}}(\boldsymbol{r}^{N_j}) \right|^2 . \tag{1}$$

where w_j are the user-defined weights in configuration j, $1 \leq j \leq J$, the default value of w_j is 1. $\boldsymbol{f}_{ji}$ depicts a (complex) atomic force, the definition of which can be found below. The value of this force depends on the configuration j, the atom i in the j-th configuration, the position of all atoms in the j-th configuration $\boldsymbol{r}^{N_j}$, and the variable for which the minimization is performed c. An analogous description is associated to the input QM forces $\boldsymbol{f}_{ji}^{\text{qm}}$, with the exception of the dependence of variable c.

Each atomic force $\boldsymbol{f}_{ji}$ is calculated through a set of basis functions, namely $d_{tkk'l}(\boldsymbol{r}^{N_j})$. In the original manuscript this force is defined in Equations 4 and 5. Here, the atomic force is formulated as follows:

$$\boldsymbol{f}_{ji}(\boldsymbol{r}^{N_j};\boldsymbol{c}) = \sum_{t=1}^{N_z}\sum_{k=1}^{K}\sum_{k'=k}^{K}\sum_{l=0}^{L} c_{tkk'l}\frac{\partial d_{tkk'l}(\boldsymbol{r}^{N_j})}{\partial \boldsymbol{r}_i^{N_j}} \tag{2}$$

Note that $\frac{\partial d_{tkk'l}(\boldsymbol{r}^{N^j})}{\partial \boldsymbol{r}_i}$ is the gradient vector of $d_{tkk'l}$ with respect to the position of the i-th atom in the j-configuration, i.e., f is a vector quantity.

Current Julia implementation uses "GalacticOptim" package to perform the optimization. In the computational implementation $c_{tkk'l}$ had to be linearized due to interface compatibility with the optimization library. The new coefficient is c_m, where the index m is just a one-dimension unrolling of the tuple index t,k,k',l. Therefore, $c \in \mathbb{R}^M$.

In future versions, neural networks will be used to perform the optimization.

2.2 Basis functions

The derivatives of the basis functions are defined in Equations 23 and 24 in the original manuscript. Here, it is formulated as:

$$\frac{\partial d_{tkk'l}(\boldsymbol{r}^{N_j})}{\partial \boldsymbol{r}_i^{N_j}} = \sum_{s\in\Omega'_{jit}} p^{\partial}_{iskk'l}(\boldsymbol{r}^{N_j}, j) - \sum_{s\in\Omega''_{jit}} p^{\partial}_{sikk'l}(\boldsymbol{r}^{N_j}, j), \tag{3}$$

where

$$\begin{aligned} p^{\partial}_{i_0 i_1 kk'l}(\boldsymbol{r}^{N_j}, j) = &\sum_{m=-l}^{l}\left(\frac{\partial u_{klm}(\boldsymbol{r}_{i_0}^{N_j} - \boldsymbol{r}_{i_1}^{N_j})}{\partial(\boldsymbol{r}_{i_0}^{N_j} - \boldsymbol{r}_{i_1}^{N_j})}\sum_{s\in\Omega_{j,i_1}}\left(u_{k'lm}(\boldsymbol{r}_s^{N_j} - \boldsymbol{r}_{i_1}^{N_j})\right)\right) + \\ &\sum_{m=-l}^{l}\left(\frac{\partial u_{k'lm}(\boldsymbol{r}_{i_0}^{N_j} - \boldsymbol{r}_{i_1}^{N_j})}{\partial(\boldsymbol{r}_{i_0}^{N_j} - \boldsymbol{r}_{i_1}^{N_j})}\sum_{s\in\Omega_{j,i_1}}\left(u_{klm}(\boldsymbol{r}_s^{N_j} - \boldsymbol{r}_{i_1}^{N_j})\right)\right) \end{aligned} \tag{4}$$

Ω, Ω', and Ω'' were introduced to simplify the notation and to have precomputed neighbor information. Two atoms, s and q, are neighbours if $s \neq q$ and $||\boldsymbol{r}_s^{N_j} - \boldsymbol{r}_q^{N_j}|| \leq r_{\text{cut}}$ **but this must take into account the periodic boundary conditions**.

The derivative of the (complex) function u_{klm} is not present in the original manuscript. Here, it is computed through the finite difference method.

$$\begin{aligned} \frac{\partial u_{klm}(\boldsymbol{r})}{\partial(\boldsymbol{r})} = \Bigg(&\frac{u_{klm}(\boldsymbol{r} + \boldsymbol{\Delta}x) - u_{klm}(\boldsymbol{r} - \boldsymbol{\Delta}x)}{2|\boldsymbol{\Delta}x|}, \\ &\frac{u_{klm}(\boldsymbol{r} + \boldsymbol{\Delta}y) - u_{klm}(\boldsymbol{r} - \boldsymbol{\Delta}y)}{2|\boldsymbol{\Delta}y|}, \\ &\frac{u_{klm}(\boldsymbol{r} + \boldsymbol{\Delta}z) - u_{klm}(\boldsymbol{r} - \boldsymbol{\Delta}z)}{2|\boldsymbol{\Delta}z|}\Bigg) \end{aligned} \tag{5}$$

where $\boldsymbol{\Delta}x = (h, 0, 0)$, $\boldsymbol{\Delta}y = (0, h, 0)$, and $\boldsymbol{\Delta}z = (0, 0, h)$.

The function $u_{klm} : \mathbb{R}^3 \to \mathbb{C}$ is defined in the Equation 11. Here, it is formulated as

$$u_{klm}(\boldsymbol{r}) = g_{lk}(r) Y_{lm}(\theta, \phi) \tag{6}$$

Note that $\boldsymbol{r}$ is expressed in cartesian coordinates (x, y, z), but spherical coordinates are needed to invoke g_{lk} and Y_{lm}. Then, the following transformations are used:

$$r = \sqrt{x^2 + y^2 + z^2}$$
$$\theta = \arccos(z/r)$$
$$\phi = \mathrm{atan}(y, x)^1$$

In Equation 6, g_{lk} is a radial basis functions. Currently, the Julia spherical Bessel function "sphericalbessely(l, r)" is used. Other functions should be implemented in the future, including polynomials and Gaussian functions.

Returning to Equation 6, the spherical harmonics of degree l and order m (Y_{lm}) is presented in Equation 12 in the original manuscript. Here, it is formulated as

$$Y_{lm}(\theta, \phi) = \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-m)!}{(l+m)!}} P_{lm}(\cos(\theta)) e^{im\phi} \tag{7}$$

P_{lm} are the associated Legendre polynomials. They are not included in the original manuscript. Here they are defined as

$$P_{lm}(x) = (-1)^m (1-x^2)^{m/2} \frac{\mathrm{d}^m}{\mathrm{d}x^m} P_l(x), \ if \ m \geq 0 \tag{8}$$

$$P_{lm}(x) = (-1)^{|m|} \frac{(l-|m|)!}{(l+|m|)!} P_{l|m|}, \ if \ m < 0 \tag{9}$$

P_l is the Legendre polynomial of degree l given by:

$$P_l(x) = \frac{1}{2^l l!} \frac{\mathrm{d}^l}{\mathrm{d}x^l} (x^2 - 1)^l \tag{10}$$

By combining Equations 8 and 10, we obtain the following expressions for $P_{lm}(x)$, $l \geq 0$, $0 \leq m \leq l$ (Equations 11 and 12). The case $-l \leq m < 0$ follows from Equation 9. See Appendix A for a brief proof.

$$P_{lm}(x) = (-1)^m (1-x^2)^{m/2} \left(\frac{1}{2!} \sum_{k=\lceil \frac{l+m}{2} \rceil}^{l} (-1)^{l-k} \binom{l}{k} \binom{2k}{l} \frac{(2k-l)!}{(2k-l-m)!} x^{2k-l-m} \right), \quad m > 0 \tag{11}$$

$$P_{lm}(x) = P_l(x) \quad m = 0. \tag{12}$$

In Equation 11, $\lceil . \rceil$ denotes the ceiling function.

[1]Use the Julia atan function with two arguments (y,x) that returns the angle in radians between the positive x-axis and the point (x, y) in the interval $[-\pi, \pi]$.

A Associated Legendre polynomials

In this Appendix, it is presented a derivation of Equation 11 from the definitions of Legendre polynomials (Equation 10) and associated Legendre polynomials (Equation 8).

By applying the binomial theorem:

$$P_l(x) = \frac{1}{2^l l!}\frac{\mathrm{d}^l}{\mathrm{d}x^l}(x^2-1)^l = \frac{1}{2^l l!}\sum_{k=0}^{l}\binom{l}{k}(-1)^{l-k}\frac{\mathrm{d}^l}{\mathrm{d}x^l}(x^{2k}). \tag{13}$$

The l-th derivative of x^{2k} can be written as:

$$\frac{\mathrm{d}^l}{\mathrm{d}x^l}(x^{2k}) = \begin{cases} 2k(2k-1)\ldots(2k-l+1)x^{2k-l} & \text{if } 2k \geq l \\ 0 & \text{if } 2k < l \end{cases}$$

Therefore, replacing the derivative in Equation 13:

$$P_l(x) = \frac{1}{2^l}\sum_{k=\lceil l/2\rceil}^{l}\binom{l}{k}(-1)^{l-k}\frac{(2k)!}{(2k-l)!l!}x^{2k-l}$$

$$P_l(x) = \frac{1}{2^l}\sum_{k=\lceil l/2\rceil}^{l}\binom{l}{k}(-1)^{l-k}\binom{2k}{l}x^{2k-l} \tag{14}$$

We proceed in a similar way to obtain the m-th derivative of $P_l(x)$ for $0 < m \leq l$ using Equation 14:

$$\frac{\mathrm{d}^m}{\mathrm{d}x^m}(x^{2k-l}) = \begin{cases} (2k-l)(2k-l-1)\ldots(2k-l-m+1)x^{2k-l-m} & \text{if } 2k-l \geq m \\ 0 & \text{if } 2k-l < m \end{cases}$$

Consequently:

$$P_{lm}(x) = (-1)^m(1-x^2)^{m/2}\frac{\mathrm{d}^m}{\mathrm{d}x^m}P_l(x) =$$

$$= (-1)^m(1-x^2)^{m/2}\frac{1}{2^l}\sum_{k=\lceil \frac{l+m}{2}\rceil}^{l}(-1)^{l-k}\binom{l}{k}\binom{2k}{l}\frac{(2k-l)!}{(2k-l-m)!}x^{2k-l-m}$$