1 Hessians for the Lennard-Jones pair potential

Set

$$V(r) = 4\varepsilon\left((\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}\right) = 4\varepsilon\left(R^{12} - R^{6}\right), \qquad \text{with } R = \frac{\sigma}{r}, \tag{1}$$

and

$$r(\boldsymbol{p}, \boldsymbol{q}) = \|\boldsymbol{q} - \boldsymbol{p}\| = \sqrt{\sum_{i=1}^{d} r_i^2} \qquad \text{with } r_i \coloneqq (q_i - p_i). \tag{2}$$

1.1 Partial derivatives of r

We have ($r = r(\boldsymbol{p}, \boldsymbol{q})$):

$$\partial_{p_i} r(\boldsymbol{p}, \boldsymbol{q}) = -\frac{r_i}{r}, \tag{3}$$

$$\partial_{q_j} r(\boldsymbol{p}, \boldsymbol{q}) = \frac{r_j}{r}, \tag{4}$$

$$\partial_{q_i}\partial_{p_i} r(\boldsymbol{p}, \boldsymbol{q}) = -\partial_{p_i}\partial_{p_i} r(\boldsymbol{p}, \boldsymbol{q}) = \frac{r_i^2}{r^3} - \frac{1}{r}, \tag{5}$$

$$\partial_{q_j}\partial_{p_i} r(\boldsymbol{p}, \boldsymbol{q}) = -\partial_{p_j}\partial_{p_i} r(\boldsymbol{p}, \boldsymbol{q}) = \frac{r_i r_j}{r^3}, \tag{6}$$

$$\tag{7}$$

1.2 One dimensional derivatives of the Lennard-Jones potential

We have

$$V'(r) = \frac{24\varepsilon}{r} R^6 \left(1 - 2R^6\right) \tag{8}$$

$$V''(r) = \frac{24\varepsilon}{r^2} R^6 \left(26R^6 - 7\right). \tag{9}$$

1.3 Lennard-Jones forces and Hessians

We have

$$\partial_{p_i} V(r(\boldsymbol{p}, \boldsymbol{q})) = -\frac{24\varepsilon}{r^2} R^6 \left(1 - 2R^6\right) r_i \tag{10}$$

$$\partial_{q_i}\partial_{p_i} V(r(\boldsymbol{p}, \boldsymbol{q})) = -\partial_{p_i}\partial_{p_i} V(r(\boldsymbol{p}, \boldsymbol{q})) = \frac{24\varepsilon}{r^4} R^6 \left(8 - 28R^6\right) r_i^2 - \frac{24\varepsilon}{r^2} R^6 \left(1 - 2R^6\right) \tag{11}$$

$$\partial_{q_j}\partial_{p_i} V(r(\boldsymbol{p}, \boldsymbol{q})) = -\partial_{p_j}\partial_{p_i} V(r(\boldsymbol{p}, \boldsymbol{q})) = \frac{24\varepsilon}{r^4} R^6 \left(8 - 28R^6\right) r_i r_j \tag{12}$$