Appendix C

Modified Shepard interpolation

The modified Shepard interpolation of the potential at some point $\mathbf{X}$ is given by the weighted sum over all ab initio points j [153]:

$$U(\mathbf{X}) \approx \sum_j W_j(\mathbf{X})\, U_j(\mathbf{X}), \tag{C.1}$$

where the weights are given by:

$$W_j(\mathbf{X}) = \frac{w_j(\mathbf{X})}{\sum_k w_k(\mathbf{X})}, \tag{C.2}$$

$$w_j(\mathbf{X}) = \left[\left(\mathbf{X} - \mathbf{X}^{(j)}\right)^2\right]^{-p}. \tag{C.3}$$

Here $\mathbf{X}^{(j)}$ are the ab initio points and the formal arbitrary exponent p controls the smoothness of the interpolation. (As suggested in Ref. [43] a value $p = 21$ is choosen.) Let $U^{(j)}$, $\mathbf{G}^{(j)}$ and $\mathbf{H}^{(j)}$ be the potential energy, the gradient and the Hessian at ab initio point $\mathbf{X}^{(j)}$, respectively, then the contribution of each point is given by:

$$U_j(\mathbf{X}) = U^{(j)} + \mathbf{G}^{(j)} \cdot \left(\mathbf{X} - \mathbf{X}^{(j)}\right) + \frac{1}{2}\left(\mathbf{X} - \mathbf{X}^{(j)}\right)\mathbf{H}^{(j)}\left(\mathbf{X} - \mathbf{X}^{(j)}\right). \tag{C.4}$$

Neglecting changes in the weights, the first and second derivatives can be obtained by using weighted sums of:

$$\mathbf{G}_j(\mathbf{X}) = \mathbf{G}^{(j)} + \mathbf{H}^{(j)}\left(\mathbf{X} - \mathbf{X}^{(j)}\right), \tag{C.5}$$

$$\mathbf{H}_j(\mathbf{X}) = \mathbf{H}^{(j)}, \tag{C.6}$$

i.e., by using formula Eq. (C.1) and replacing the symbol U by $\mathbf{G}$ and $\mathbf{H}$, respectively. The molecular dipole moment can be inter- and extrapolated in a similar fashion, that is, the potential value U and the gradient $\mathbf{G}$ has to be replaced by the related values for the dipoles μ_α for each direction $\alpha = x$, y, or z. The Hessian of the dipole moment is not taken into account, thus the dipole surface is exact on the reaction plane and linearly approximated orthogonal to the reaction plane.