Appendix C

Modified Shepard interpolation

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

$$U(X) \approx \sum_j W_j(X) \cdot U_j(X), \quad (C.1)$$

where the weights are given by:

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

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

Here $X^{(j)}$ 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 chosen.) Let $U^{(j)}$, $G^{(j)}$ and $H^{(j)}$ be the potential energy, the gradient and the Hessian at ab initio point $X^{(j)}$, respectively, then the contribution of each point is given by:

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

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

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

$$H_j(X) = H^{(j)}, \quad (C.6)$$

i.e., by using formula Eq. (C.1) and replacing the symbol $U$ by $G$ and $H$, respectively. The molecular dipole moment can be inter- and extrapolated in a similar fashion, that is, the potential value $U$ and the gradient $G$ has to be replaced by the related values for the dipoles $\mu_\alpha$ 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.
Modified Shepard interpolation