0.1 Adaptive Path

The adaptive path algorithm in *autodE* attempts to traverse the minimum energy pathway from reactants to products with constrained optimisations using a gradient dependent step size. The initial constraints for the first point are

$$r_b^{(1)} = r_b^{(0)} + \text{sgn}(r_b^{\text{final}} - r_b^{(0)})\Delta r_{\text{init}} \tag{1}$$

for a bond b, where the superscript denotes the current step. Δr_{init} is an initial step size, e.g. 0.2 Å. Constraints for subsequent steps are then given by

$$r_b^{(k)} = r_b^{(k-1)} + \text{sgn}(r_b^{\text{final}} - r_b^{(0)})\Delta r_b^{(k-1)} \tag{2}$$

$$\Delta r_b^{(k)} = \begin{cases} \Delta r_{\text{max}} & \text{if } \text{sgn}(r_b^{\text{final}} - r_b^{(0)})\nabla E_j \cdot \boldsymbol{r}_{ij} > 0 \\ \Delta r_{\text{m}} \exp\left[-\left(\nabla E_j^{(k)} \cdot \boldsymbol{r}_{ij}/g \right)^2 \right] + \Delta r_{\text{min}} & \text{otherwise} \end{cases} \tag{3}$$

where $\Delta r_{\text{m}} = \Delta r_{\text{max}} - \Delta r_{\text{min}}$, E the total potential energy (in the absence of any harmonic constraints) and g a parameter to control the interpolation between Δr_{max} and Δr_{min} e.g. 0.05 Ha Å^{-1}. Atom indices i, j form part of the bond indexed by b with j being an atom not being substituted. In the case that neither i nor j are being substituted the gradient is taken as an average over i and j.