Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Reactive force fields made simple

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1 EVB-QMDFF with constant coupling term

As mentioned in the main text, to further simplify the EVB-QMDFF model it is possible to use the zero-order approach with a constant off-diagonal term. The results are somewhat less convincing quantitatively, as shown in Fig. 1, when compared to the EVB-QMDFF model with a Gaussian coupling term (see main text). Note that in this case the off-diagonal term leads to noticeable energy lowerings also at the minima; hence the EVB-QMDFF curve was shifted upwards by 25 kJ/mol, to guide the eye in comparing it to the DFT data. This shift is practically irrelevant since only energy differences between minima and TS determine the reaction dynamics. However, even after this shift, the deviations are clearly larger in this case, up to 6 kJ/mol. More importantly, they are non-uniform and thus also affect the shape of the potential, which in turn would influence the reaction dynamics.

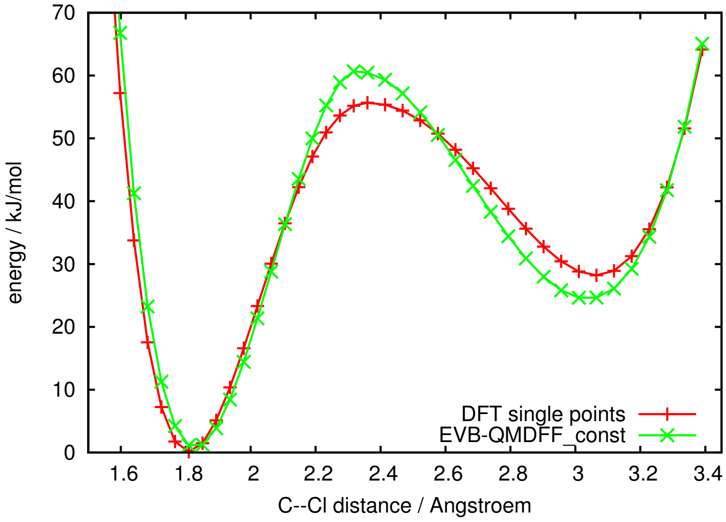

Figure 1: Energy profiles along the S_N2 reaction coordinate. Red: DFT single points, green: EVB-QMDFF with a constant off-diagonal term. The zero of energy is arbitrary and was chosen for clarity. The EVB-QMDFF curve was shifted upwards, as described in the text.

2 EVB-QMDFF in regions off the reaction path

Explorations of our EVB-QMDFF potential energy surfaces in directions orthogonal to the reaction coordinates reveal good agreement to the DFT reference data, and show the expected trends. This supplementary information demonstrates these claims, for the first two reactions of the main text.

Note that the QMDFF and EVB fits proceeded exactly as described in the main text; in particular, *no* effort was made (1) to include any reference data that do not reside near the reaction coordinate, and (2) to vary the very simple Gaussian coupling model explained in the main text, to improve the represenation in regions far away from the reaction coordinate.

Fig. 2 displays the DFT reference data (using ORCA with "PBE0 D3 def2-TZVPP grid5 tightscf opt") for a two-dimensional slice of the full-dimensional potential energy hypersurface of the S_N2 reaction between methyl bromide and a chloride ion, with all other coordinates being relaxed. In Fig. 3, we show the *differences* between these reference data and the corresponding EVB-QMDFF single-point values at the DFT-relaxed geometries. At lower energies, and hence in a fairly broad region around the whole reaction coordinate, agreement to the reference data is very good. The agreement deteriorates towards higher energies, which is tolerable since at typical chemical energies these high-energy regions are not important or not even visited.

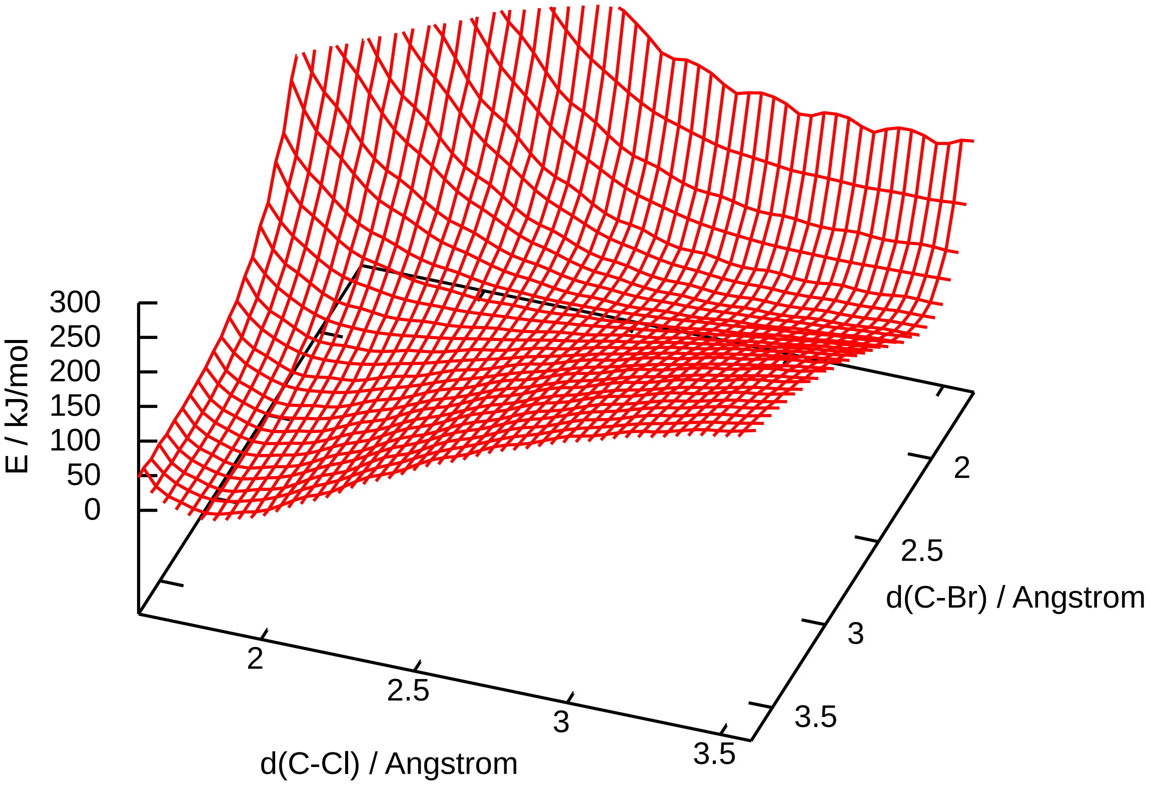

Figure 2: Reference DFT energies (in kJ/mol) for the S_N2 reaction shown in the main text, as a function of the two distances (in Å) between the central carbon atom and the chlorine and bromine atoms, respectively.

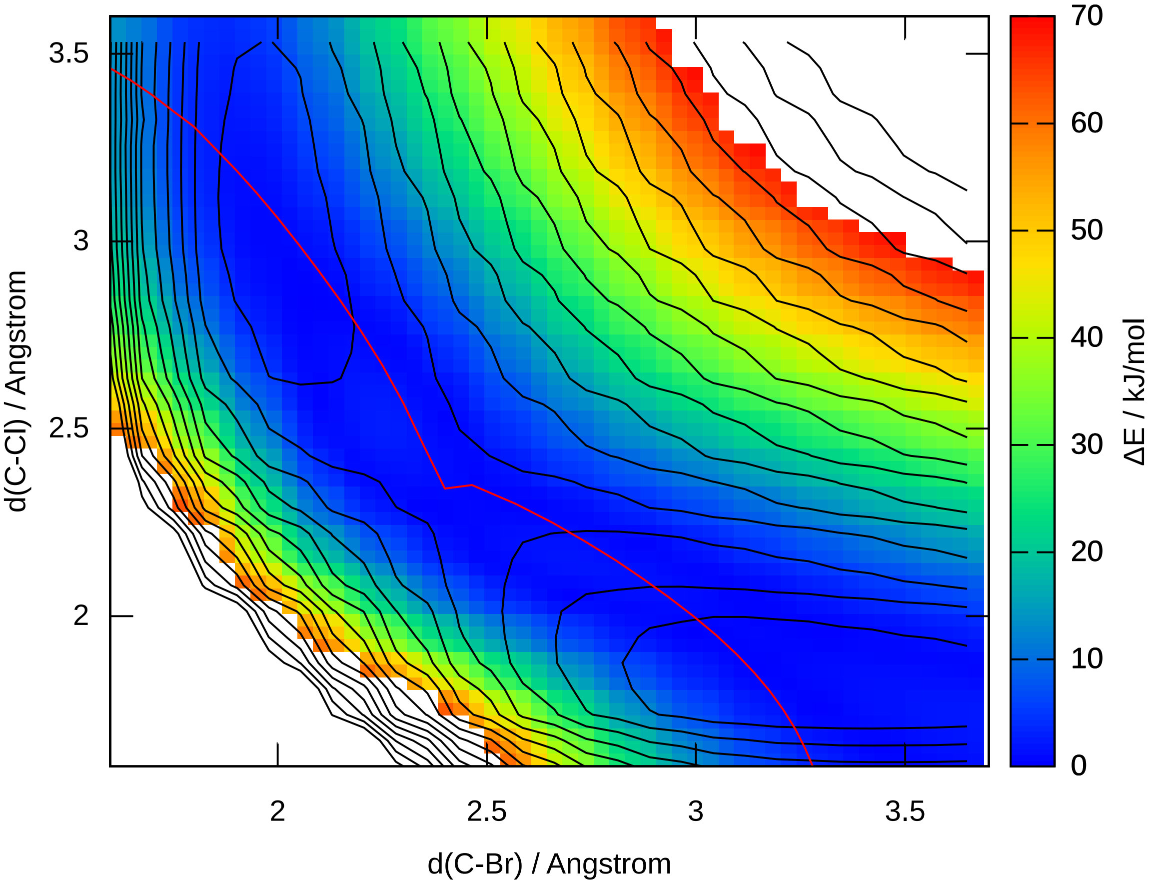

Figure 3: Color-coded energy differences in kJ/mol between the EVB-QMDFF potential energy surface and the DFT reference data, for the S_N2 reaction shown in the main text, as a function of the two distances (in Å) between the central carbon atom and the chlorine and bromine atoms, respectively. The red line indicates the one-dimensional trace used as approximation to the reaction coordinate in the corresponding figures of the main text.

Closer inspection of the data reveals that the area of small deviations is larger around the minima than around the transition state. Again, this is to be expected, for at least two reasons: (A) The functional form and the fitted parameters of the two QMDFFs are constructed to match broad regions of their respective minimum basins, with best agreement at the bottom; the EVB construction joining them is comparatively very simple and not system-specific. (B) The transition state region is higher in energy than the two minima, hence the accuracy of both QMDFFs is somewhat lower there.

For the Diels-Alder reaction of the main text, the overall impression is even better. Again, Fig. 4 displays the reference DFT data (as above, except that a def2-SVP basis was employed), and Fig. 5 the difference between these reference data and the EVB-QMDFF potential energy surface.

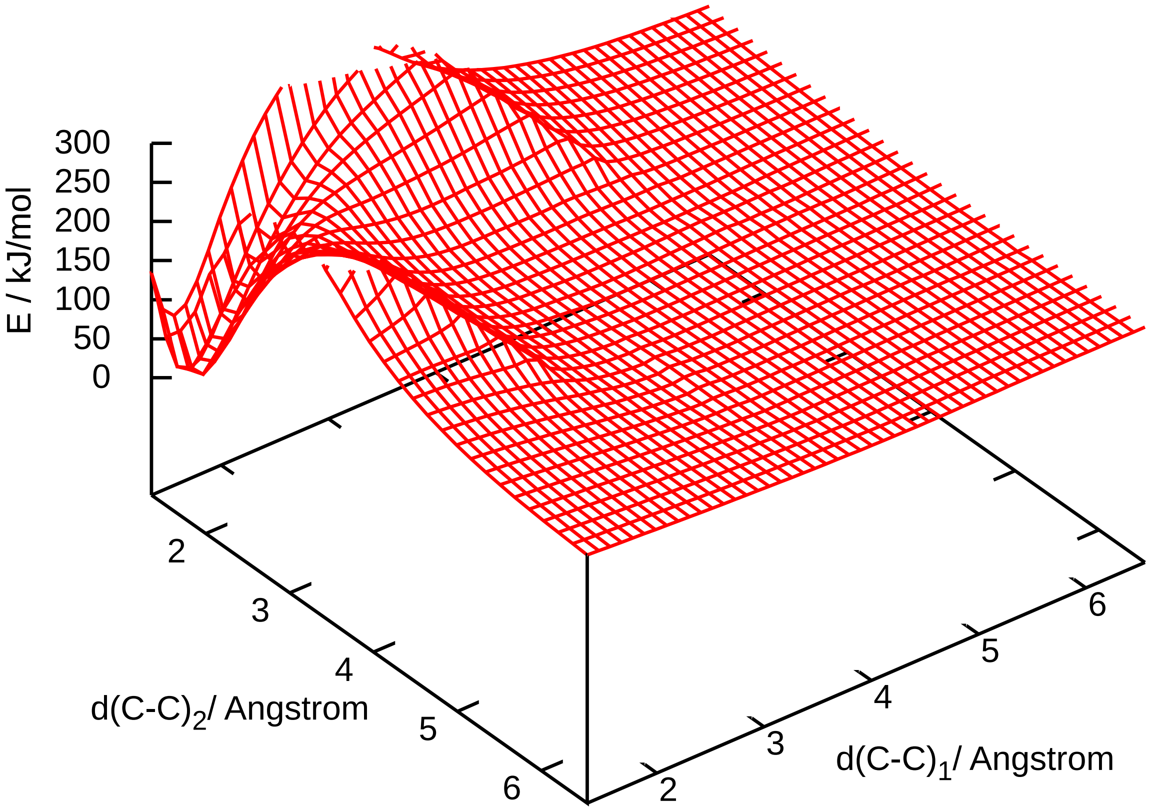

Figure 4: Reference DFT energies (in kJ/mol) for the Diels-Alder reaction shown in the main text, as a function of the two carbon–carbon distances (in Å) for which a bond is formed/broken during the reaction.

Clearly, there is room for improvement, for example by replacing the simple EVB coupling model used here with the more refined coupling models mentioned and cited in the main text. Nevertheless, these initial findings for this simple model already are very encouraging for our ongoing explorations of EVB-QMDFF potential energy surfaces, for several different reactions.

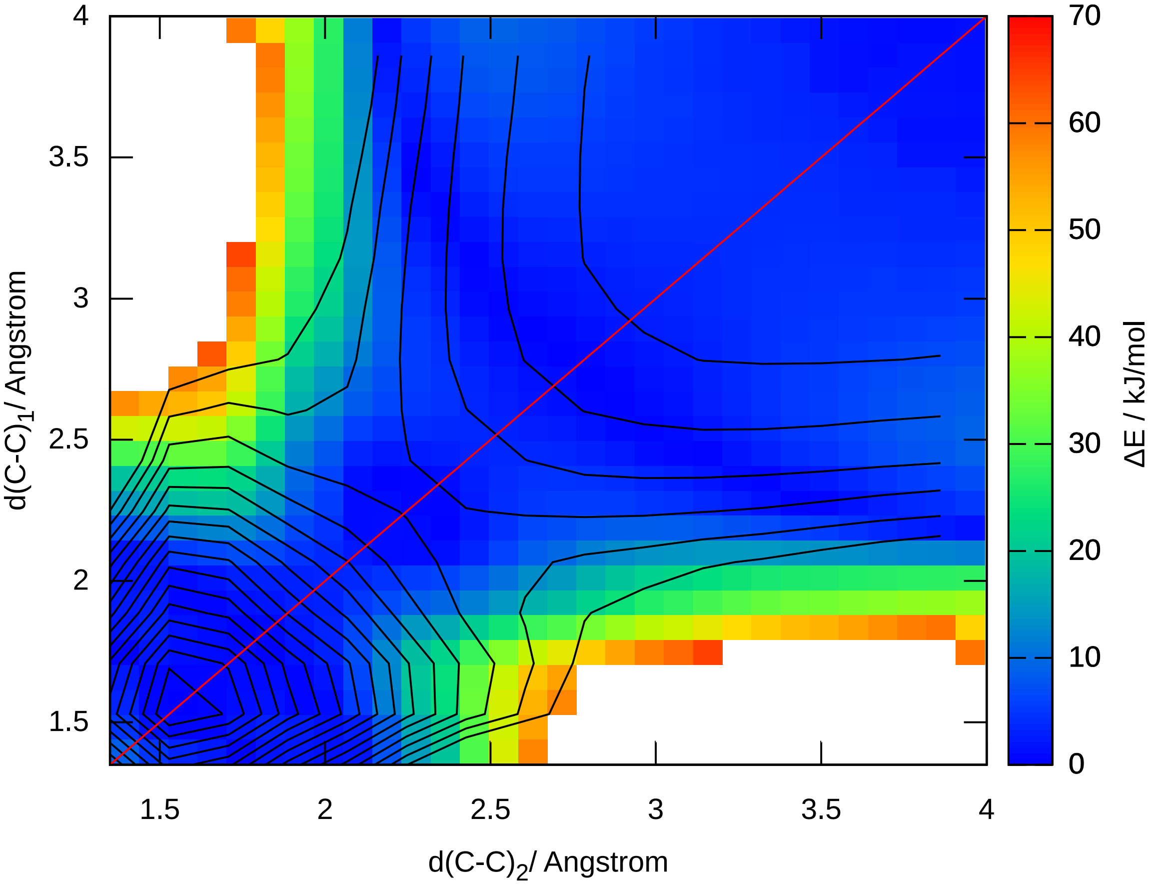

Figure 5: Color-coded energy differences in kJ/mol between the EVB-QMDFF potential energy surface and the DFT reference data, for the Diels-Alder reaction shown in the main text, as a function of the same two distances (in Å) as in Fig. 4. The red line indicates the one-dimensional trace used as approximation to the reaction coordinate in the corresponding figure of the main text.

Acknowledgement

BH thanks Julien Steffen for performing the calculations and preparing the figures shown in part 2 of this supplementary information.