LOCALISING TRANSITION STATES OF DIFFUSION CONTROLLED REACTIONS - APPLICATION TO INORGANIC COMPLEXES

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The dissociation of a compound into two molecular fragments is a fundamental chemical reaction. To the chemist, both the bond dissociation energy (BDE) and the transition state for of this type of reaction is of interest and quantum chemistry can provide these insights.

Locating the transition states of dissociation reactions could be challenging in quantum chemistry because the calculated electronic energy often increases monotonously upon separation of the fragments (see Figure 1). However, when considering the Gibbs free energy, the dissociation is accompanied by an onset of rotational and translational entropy of the fragments resulting in a transition state. To be able to account for this in a quantum chemical calculation and to localize such transition states, we need to define when the bond is broken. Therefore, finding a suitable descriptor, which indicates complete bond cleavage, is essential. Testing different options, descriptors depicting bond orders proved to be most suitable.

With the help of this descriptor, we developed a methodology to model the onset of entropy and to estimate the free energy surface (denoted as ΔG_{fit} in Figure 1). Our results showed excellent agreement with available experimental and high-level computational data. We showcased the applicability of our methodology at several organometallic and inorganic complexes such as the $Pd(P^tBu_3)_2$ complex depicted below.
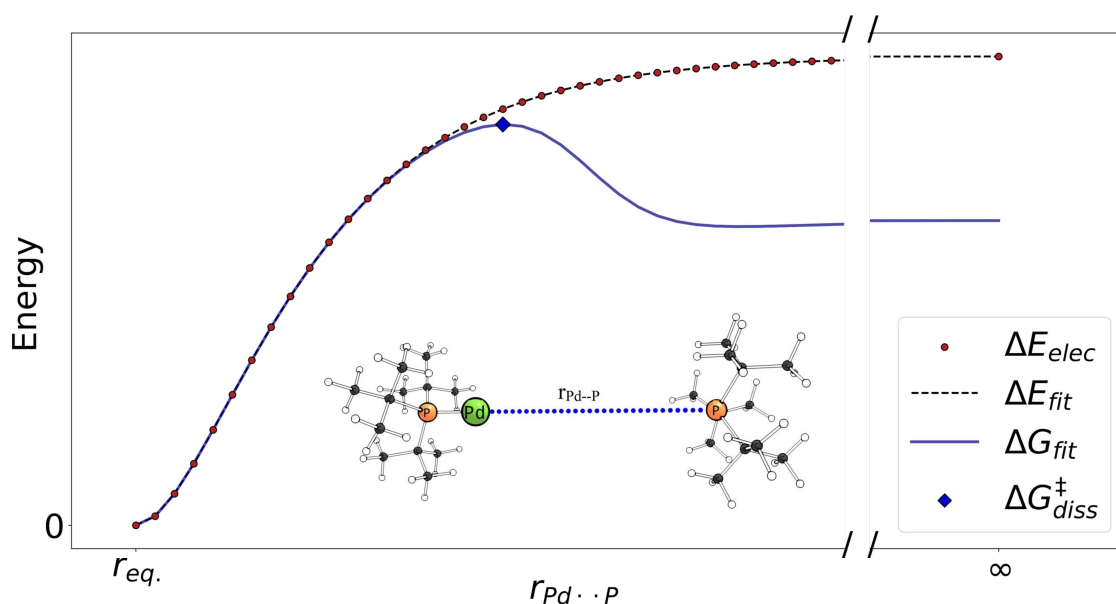

Figure 1: Calculated electronic energies and estimated dissociation barrier for the dissociation of an organometallic complex $(Pd(P^tBu_3)_2)$.