

Quantum Chemistry

Lecture 29

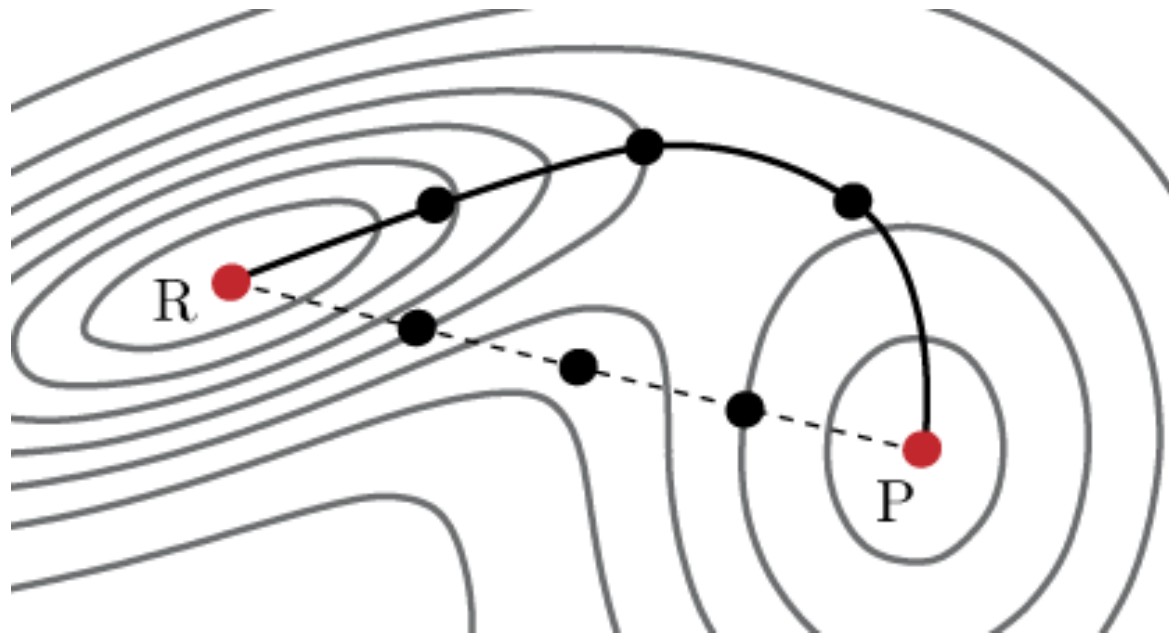
Transition State Methods
Minimum Energy Path
Nudged Elastic Band
Intrinsic Reaction Coordinate

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Minimum energy path

The transition state path can be thought of as the minimum energy path for a reaction. In transition state theory it is assumed that there is a high energy structure involved in the transition from reactants to products. The key assumption of the theory is that the transition state structure is in equilibrium with the reactant (and therefore also with the product). In considering a multi-dimensional space that involves all possible nuclear coordinates we can define one path as the reaction coordinate. The gradient will be zero for the coordinate perpendicular to this path. If one follows a minimum energy path (MEP) from reactants to products one must pass over a saddle point, which is a maximum along the reaction path.

Path along the PES



Depiction of a two-dimensional potential energy surface with two paths. The solid line represents the minimum energy path. The dashed line represents the shortest path.

Elastic band methods

There is group of methods that connect structures on a path between the reactant and product using a force constant. We call this collection of structures a chain. The chain is a series of linearly displaced structures that gradually alter reactant into product. The starting point for a calculation to find the minimum energy path using such a chain is shown as the dotted line on the previous slide. Clearly the dotted line does not pass through the transition state. The idea of maintaining a relationship between successive structures by the application of a force constant is called an elastic band. The goal of elastic band calculations is to move the chain so that it follows the MEP. However, there are many ways that a calculation can miss the transition state.

The nudged elastic band (NEB)

The innovation that leads to the success of elastic band methods is known as nudging. The nudged elastic band (NEB) method consists of a minimization of an elastic band in which the perpendicular component of the spring force and the parallel component of the true force are projected out. The force on each image is:

$$\vec{F}_i^0 = \vec{F}_i^\perp + \vec{F}_i^\parallel$$

where the perpendicular force is the gradient of the potential that pulls the system towards the true MEP.

$$\vec{F}_i^\perp = -\nabla(\vec{R}_i) + \nabla(\vec{R}_i) \cdot \hat{t}_\parallel \hat{t}_\parallel$$

The force parallel to the trajectory is the spring force

$$\vec{F}_i^\parallel = k(|\vec{R}_{i+1} - \vec{R}_i| - |\vec{R}_i - \vec{R}_{i-1}|)\hat{t}_i$$

Implementation of the NEB

The project of the perpendicular force $\nabla(R_i)$ and the parallel component of the spring force is called "nudging". The effect is to decouple the dynamics of the path from the particular chain of structures chosen to represent the path from reactants to products.

Bond breaking and other sudden changes along the reaction path can lead to slow convergence. Images trapped in the region of large parallel force try to move to lower energy. However, because nudging enforces equal spacing of the images, a lower energy can only occur by lengthening and, thereby, buckling of the chain in another region that has less applied force. The estimate of the local tangent is difficult at that point.

Switching function

One solution to this problem is the introduction of a smooth switching function that gradually turns on the perpendicular component.

$$\vec{F}_i^{\text{NEB}} = \vec{F}_i^0 + f(\phi_i)(\vec{F}_i^s - \vec{F}_i^s \cdot \hat{\tau}_{\parallel} \hat{\tau}_{\parallel})$$

$f(\phi_i)$ is a switching function which goes from 0 for a straight path to 1 if adjacent segments of the path form a right angle, for example

$$f(\phi_i) = \frac{1}{2}(1 + \cos(\pi(\cos \phi)))$$

The definition of the angle is

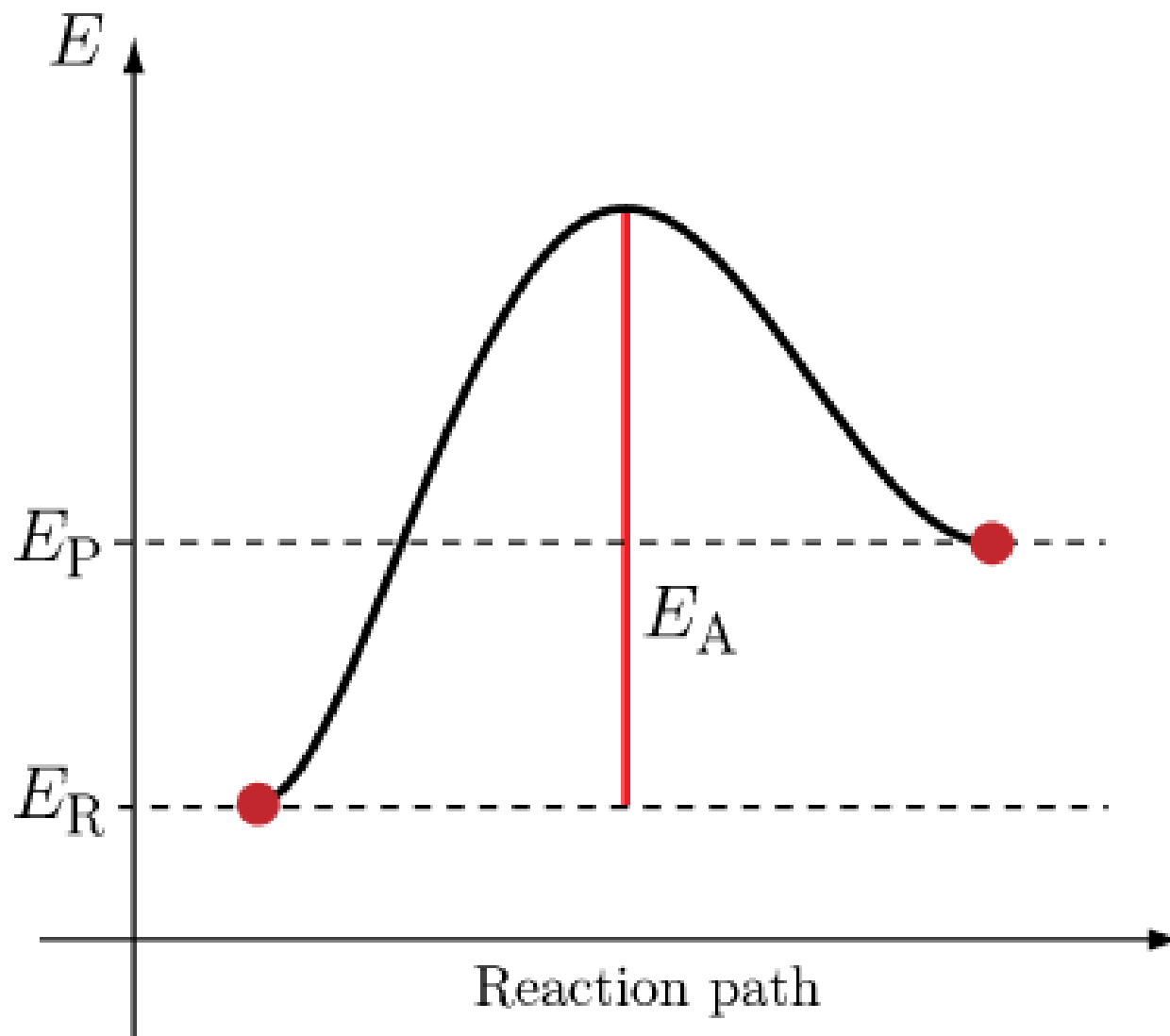
$$\cos \phi_i = \frac{(\vec{R}_{i+1} - \vec{R}_i) \cdot (\vec{R}_i - \vec{R}_{i-1})}{(|\vec{R}_{i+1} - \vec{R}_i| |\vec{R}_i - \vec{R}_{i-1}|)}$$

Criteria for transitions

The minimum energy path is the path over a transition state has negative curvature at the transition state. This provides an important check on a calculation. One can submit the transition state geometry for a vibrational frequency calculation. The result of the calculation should be that all of the eigenvalues are positive except the saddle point along the minimum energy path. There should also be six eigenvalues with a value of zero, which correspond to the translations and rotations of the molecule.

Although there should only be a single negative eigenvalue sometimes there is more than one. One common reason for this is the presence of methyl group rotations.

Transition state



Intrinsic Reaction Coordinate (IRC)

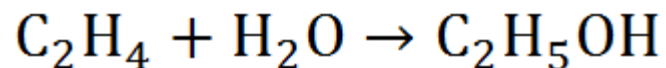
The IRC approach uses the Hessian matrix to predict the downhill direction. Then a constrained minimization is carried out following the normal mode coordinate with the negative eigenvalue. In theory, this mode should lead backward to the reactants and forward to the products.

One can also simply map out the potential energy surface of the normal model.

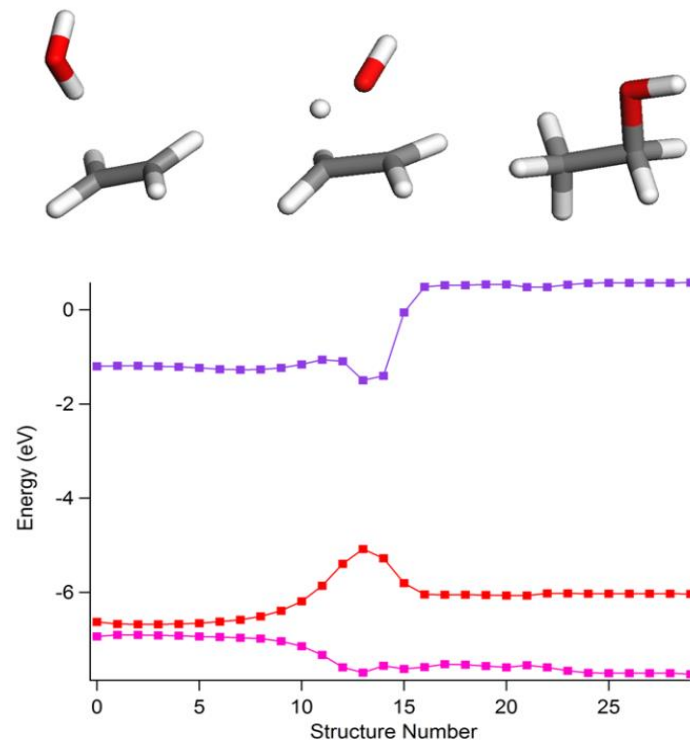
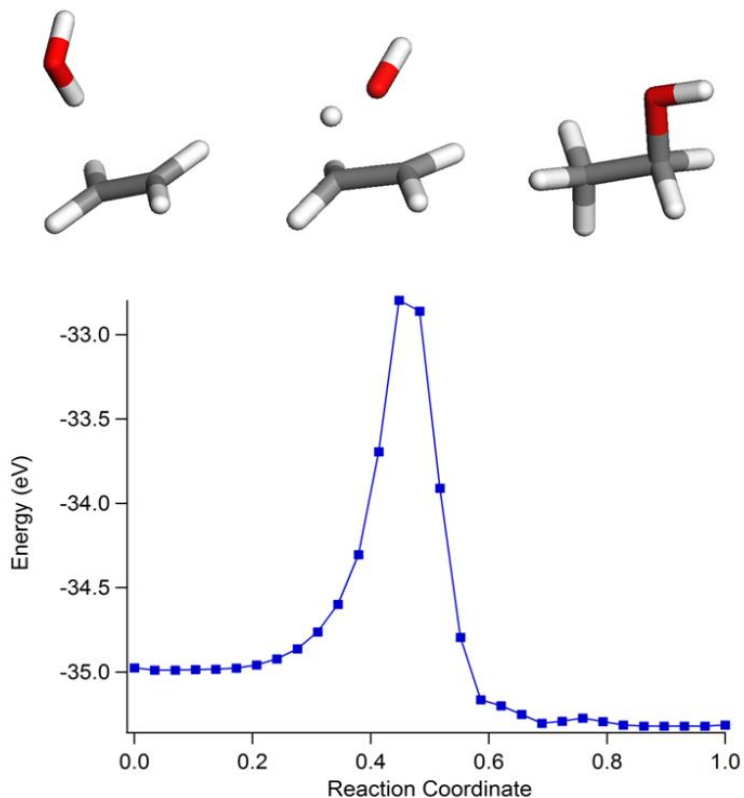
Example: hydration of ethene

Depiction of the minimum energy path from the energy of the reactants, E_R , to the products, E_P .

The hydration of ethene serves as a model system for NEB calculation. The reaction is,

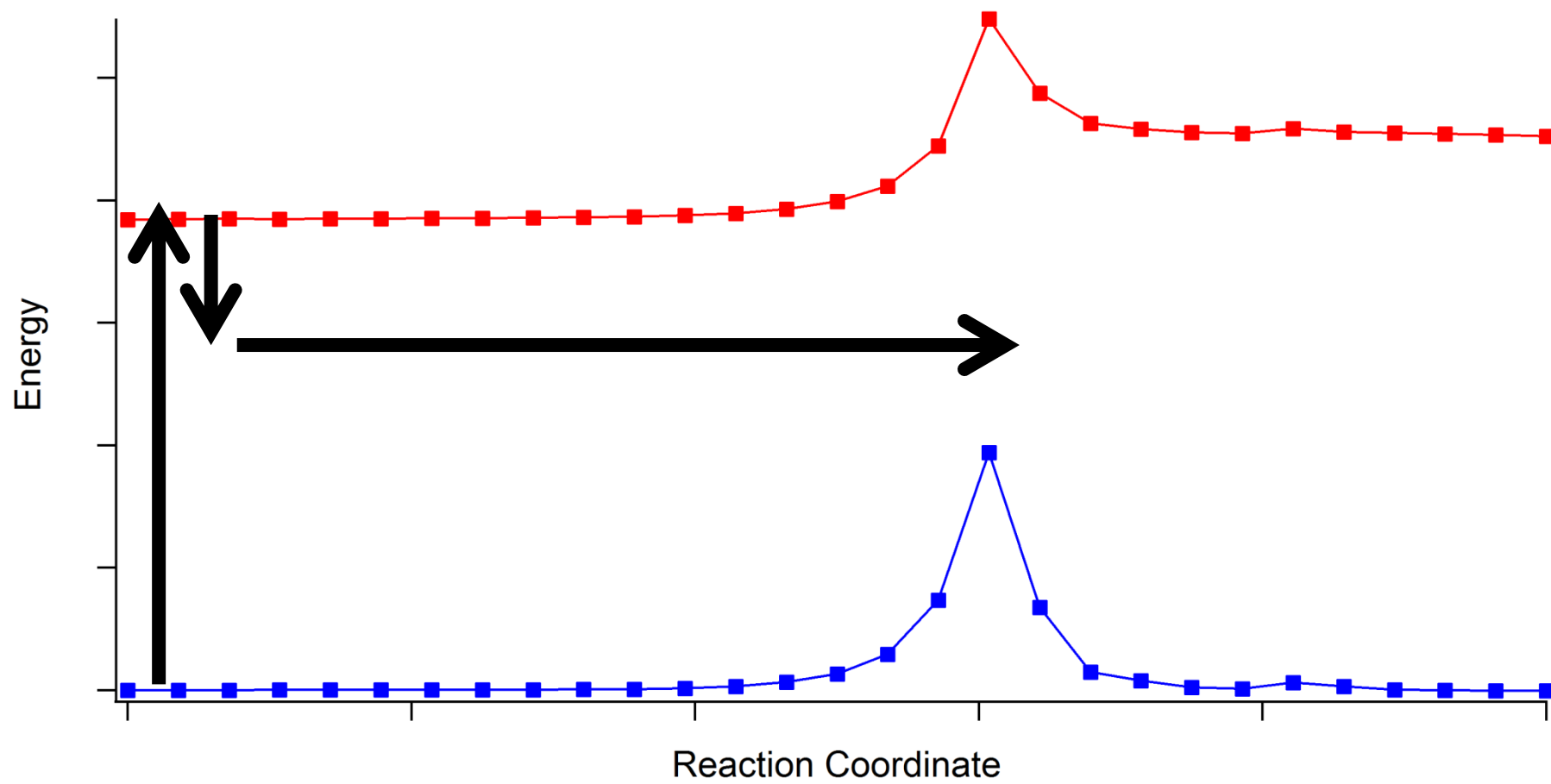
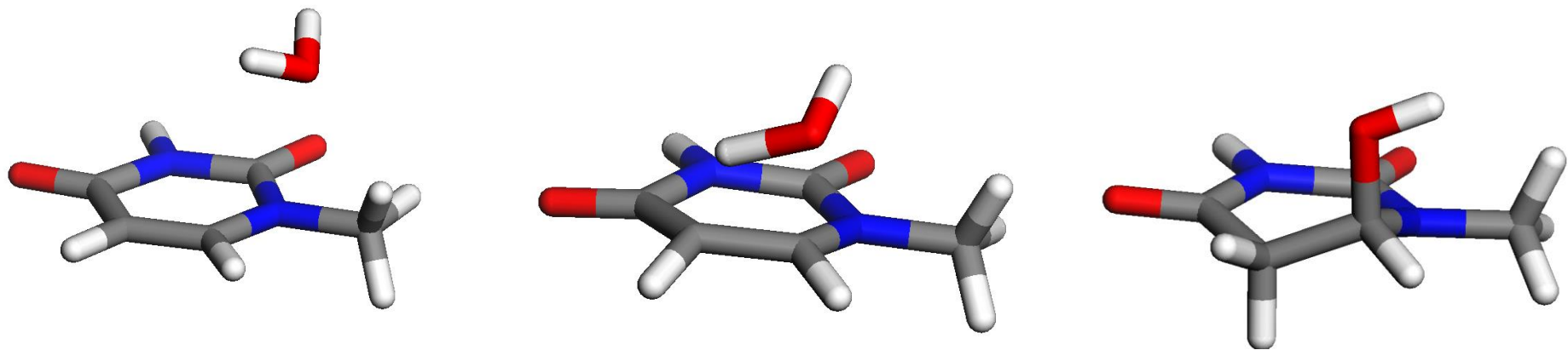


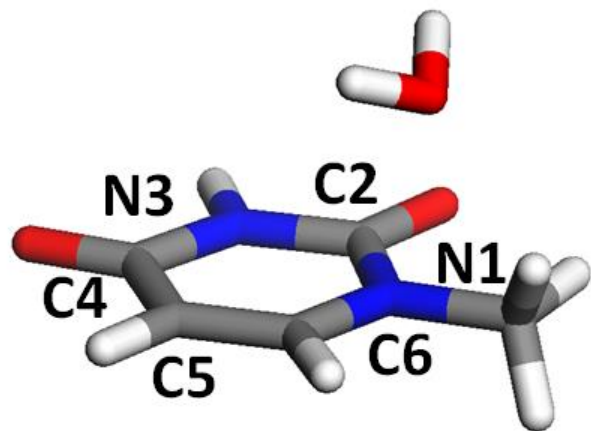
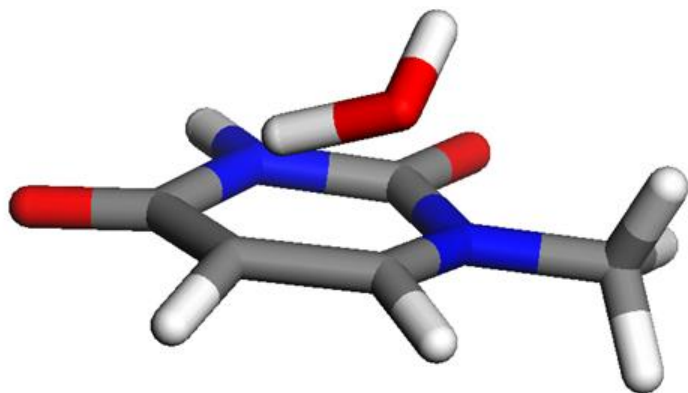
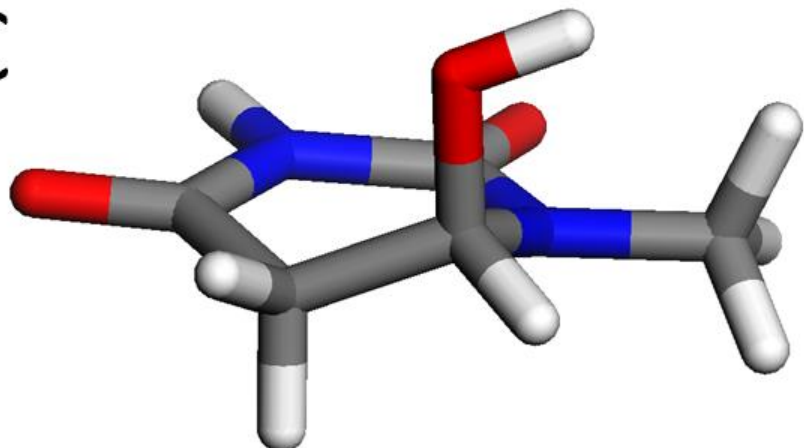
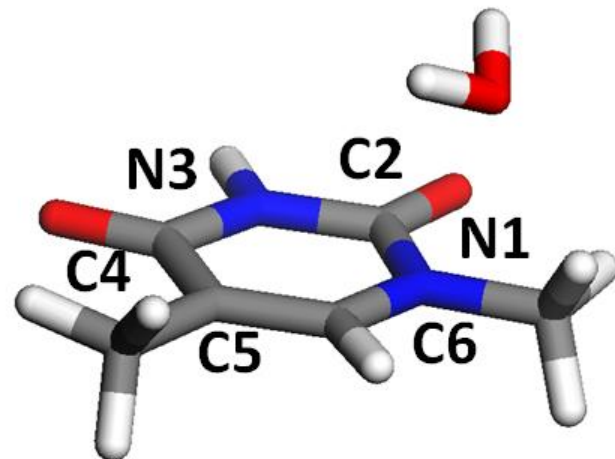
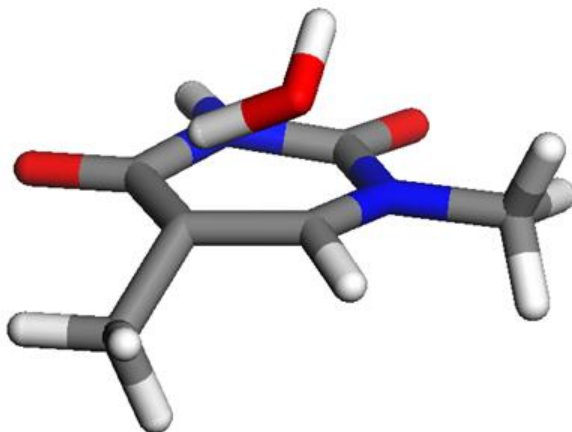
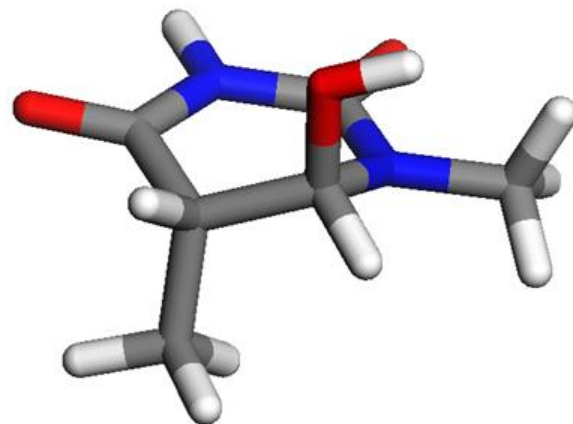
The structures above the NEB calculation represent reactant, transition state and product structures. A vibrational frequency calculation carried out on each of these structures shows that reactant and product are in stable minima, meaning that all of the eigenvalues in the normal mode calculation are positive and there are six zero eigenvalues corresponding to translation and rotation. By contrast the transition state has one negative eigenvalue, which corresponds to motion along the reaction path at the transition state. The a plot of the coordinate for this mode obtained from the eigenvector matrix column corresponding to the negative eigenvalue reveals that the hydrogen atom oscillates between the O atom of water and the C atom on the ethene. This means that it is the bond breaking and bond reforming coordinate.

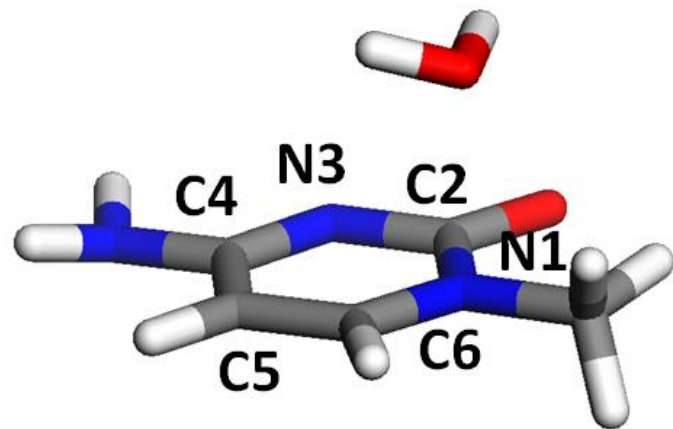
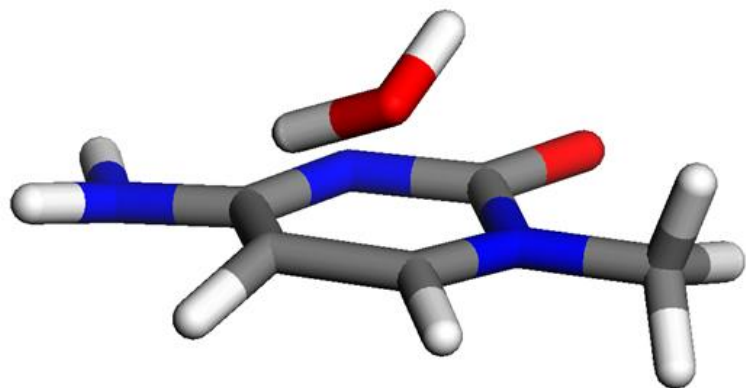
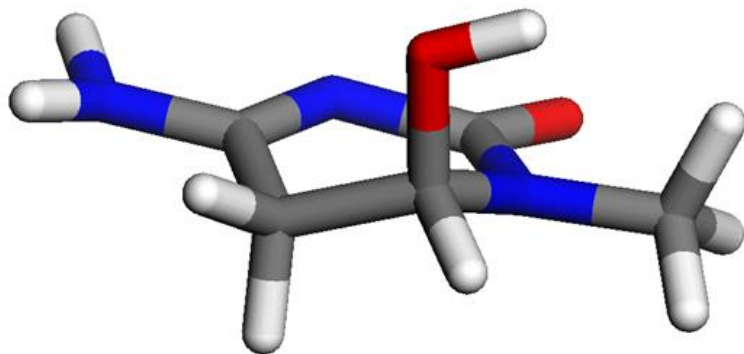
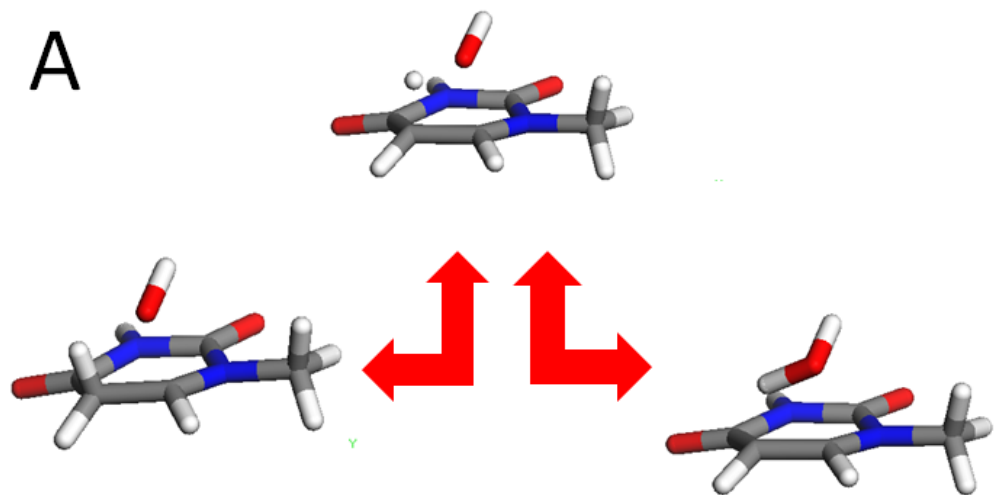
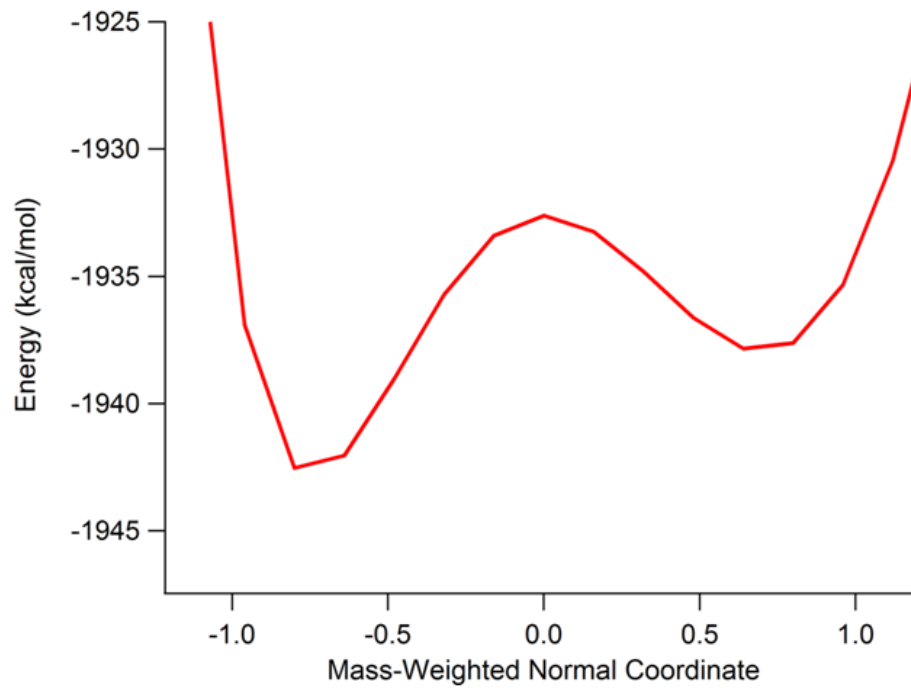


Ground state NEB trajectory for ethene hydration is shown in. Formation of ethanol via the hydrate addition is exothermic by -7.8 kcal/mol. The barrier for hydrate formation is 2.17 eV or 50.0 kcal/mol. The energies of the SHOMO, HOMO and LUMO are shown.

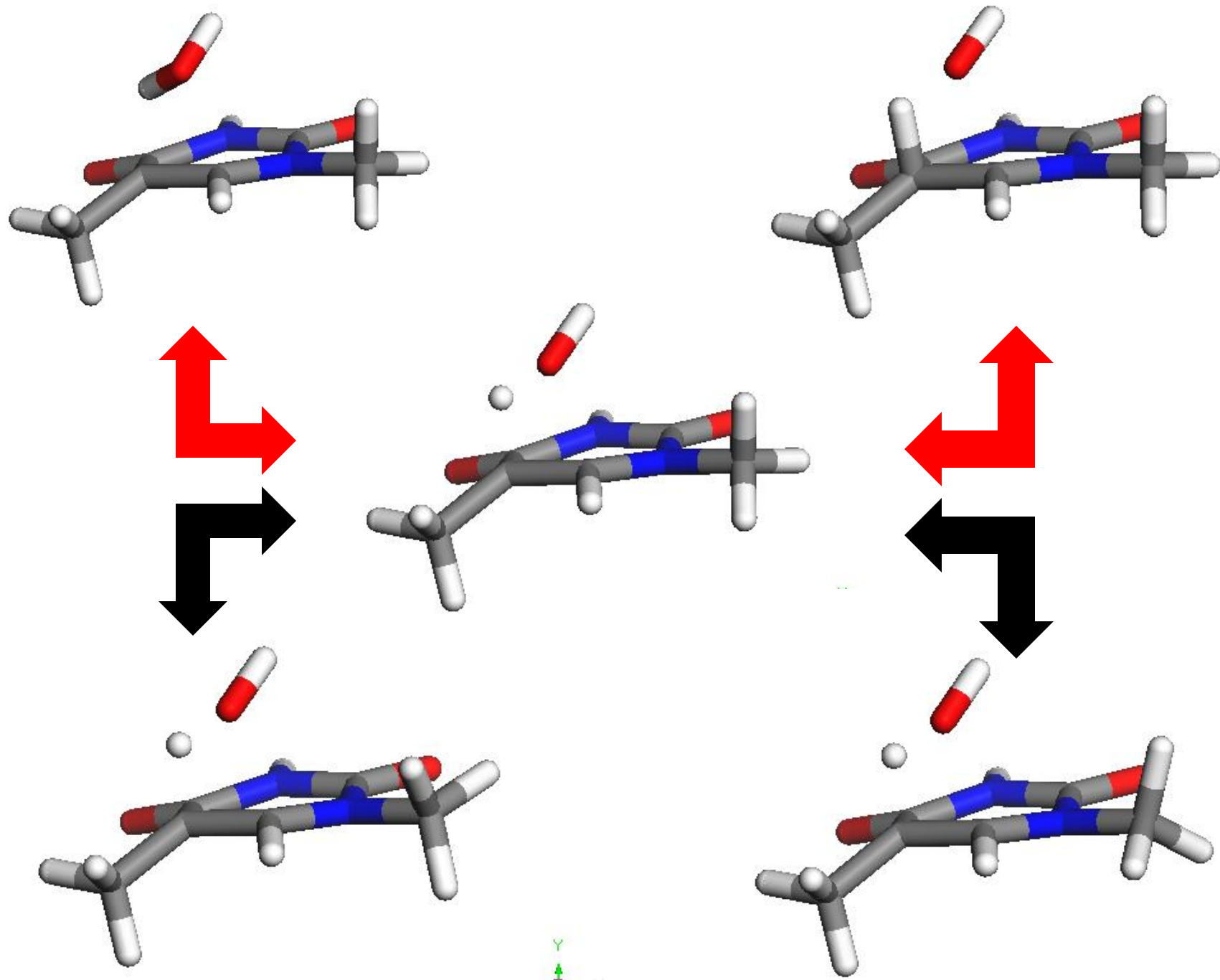
Study of the relationship of the MOs to the ground state energy barrier can provide information on the potential for a photochemical pathway. The barrier is high enough that thermal crossing from reactant to product is very slow. The photochemical addition of water, i.e. photohydrate reaction has been studied in a range of molecules with unsaturated bonds. Prominent examples include the pyrimidine nucleotides in DNA and RNA, thymine, cytosine and uridine. One fundamental question that has persisted in the study of photohydrate reactions is whether the reaction occurs via an excited state curve crossing or alternatively from a "hot" ground state following internal conversion from the excited state. The calculations shows no curve crossing. This observation suggests that the reaction occurs in the ground state manifold, but that it has sufficient excess energy to pass readily over the barrier.



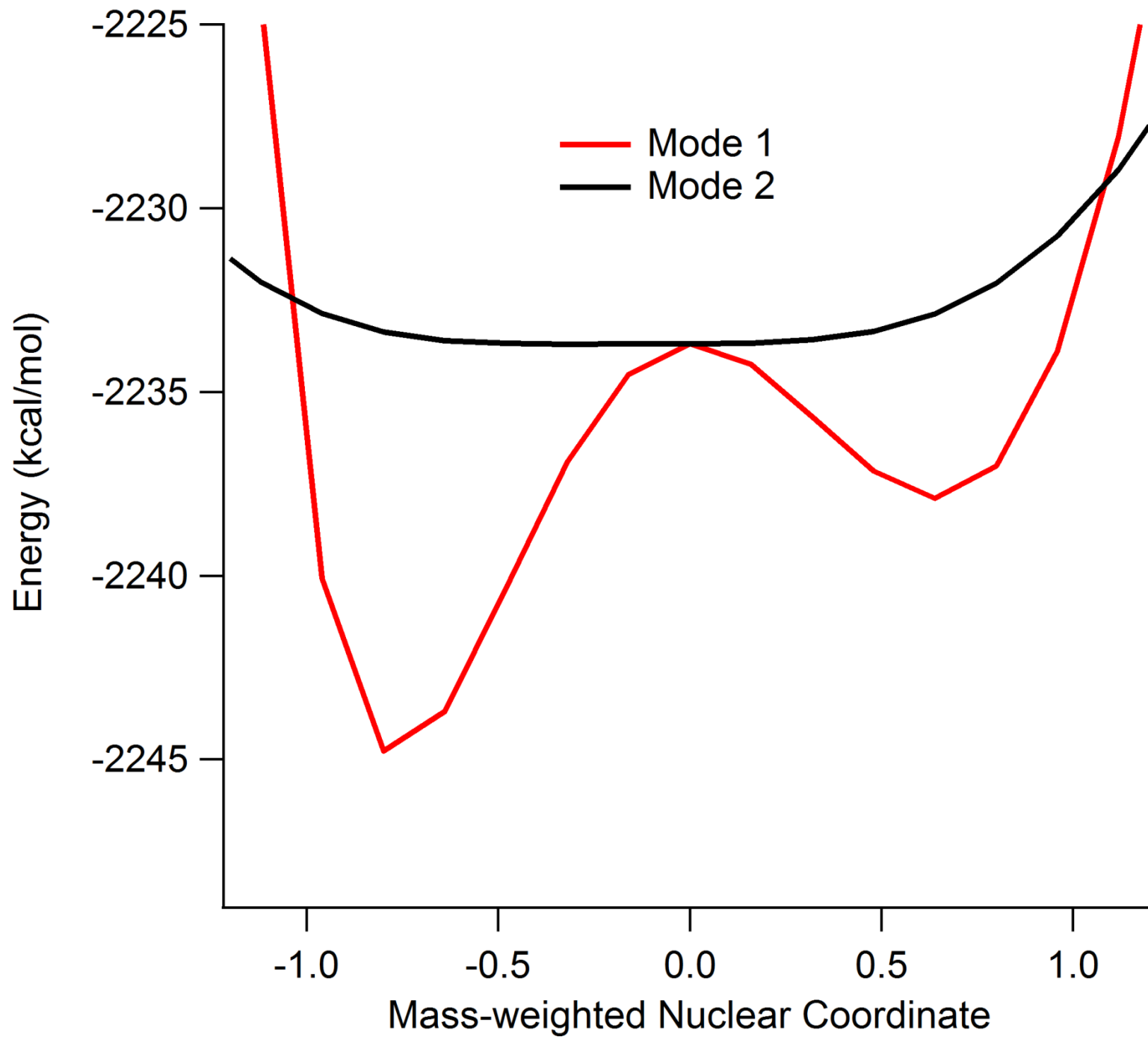
A**B****C****D****E****F**

G**H****I****A****B**

A



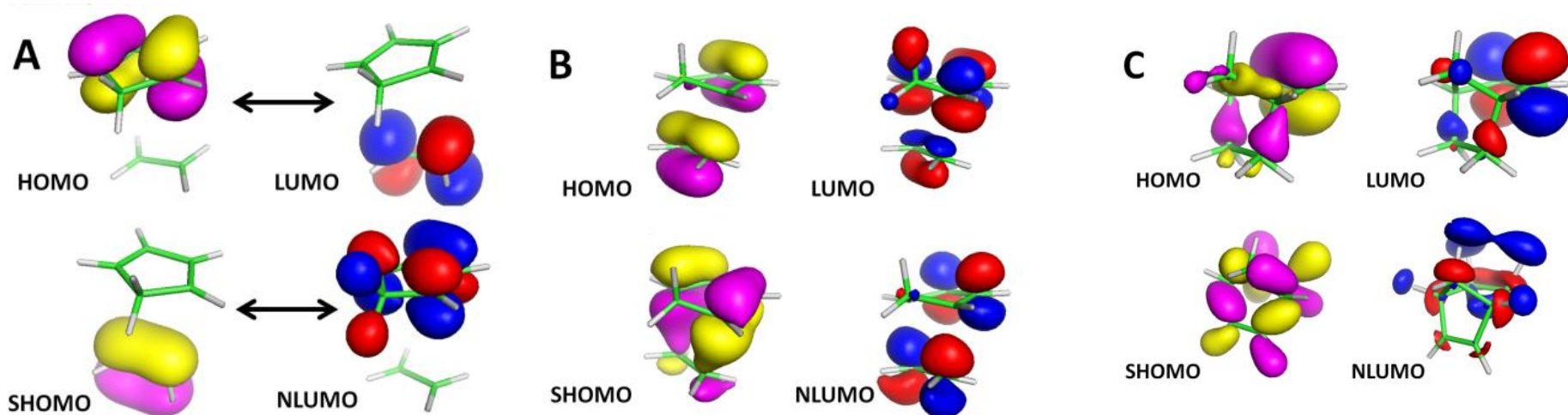
B



Diels-Alder using the NEB method

We return to the Diels-Alder reaction in order to further illustrate the power of the NEB method. We saw in the previous section that one brute force method of finding a transition state is to hypothesize that a particular coordinate must be important (e.g. a bond-breaking coordinate) and then to project along that coordinate. However, the brute force method builds bias into the search. The NEB method takes the reactant and product structures as the starting point and permits a search with significantly less bias. The nudging procedure further ensures that a MEP will be found, if one is present. This procedure was carried out for the Diels-Alder reaction and a transition state was identified. Figure 14.12 shows three structures with the four frontier orbitals.

Calculated Frontier Orbitals



Structures and molecular orbitals along the MEP for the Diels-Alder reaction. The three panels in the figure are A.) the reactant, B.) the transition state and C.) the product.