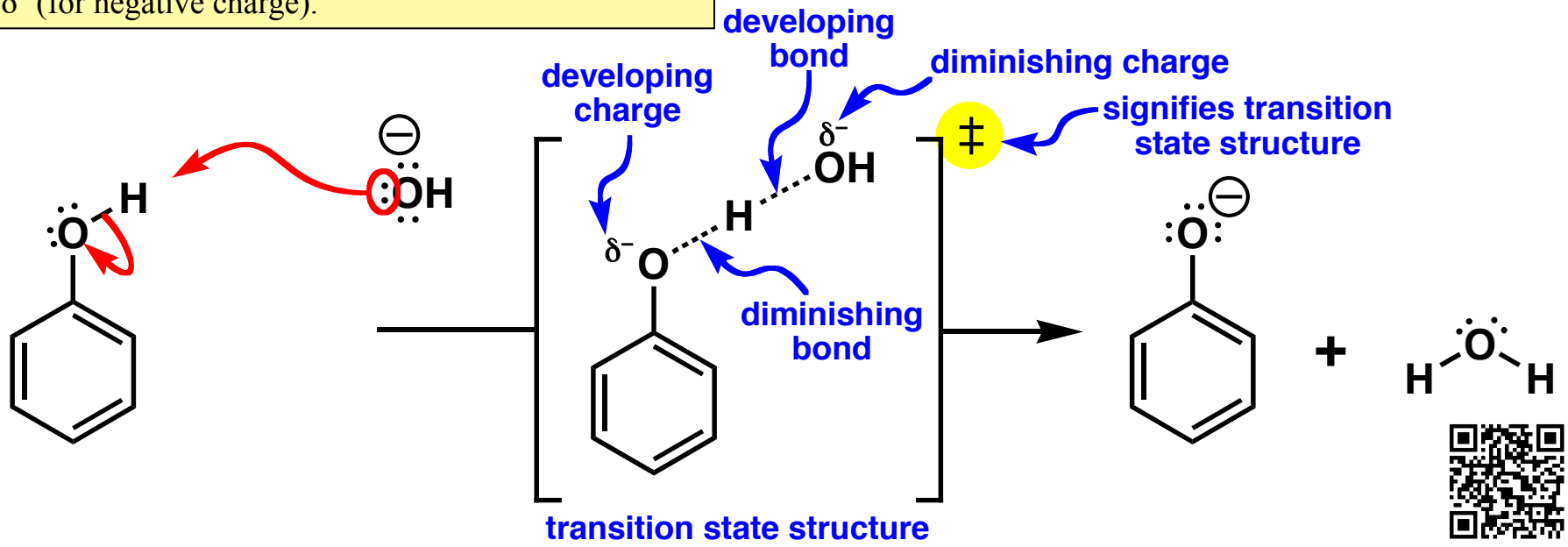
Structure of the Transition State

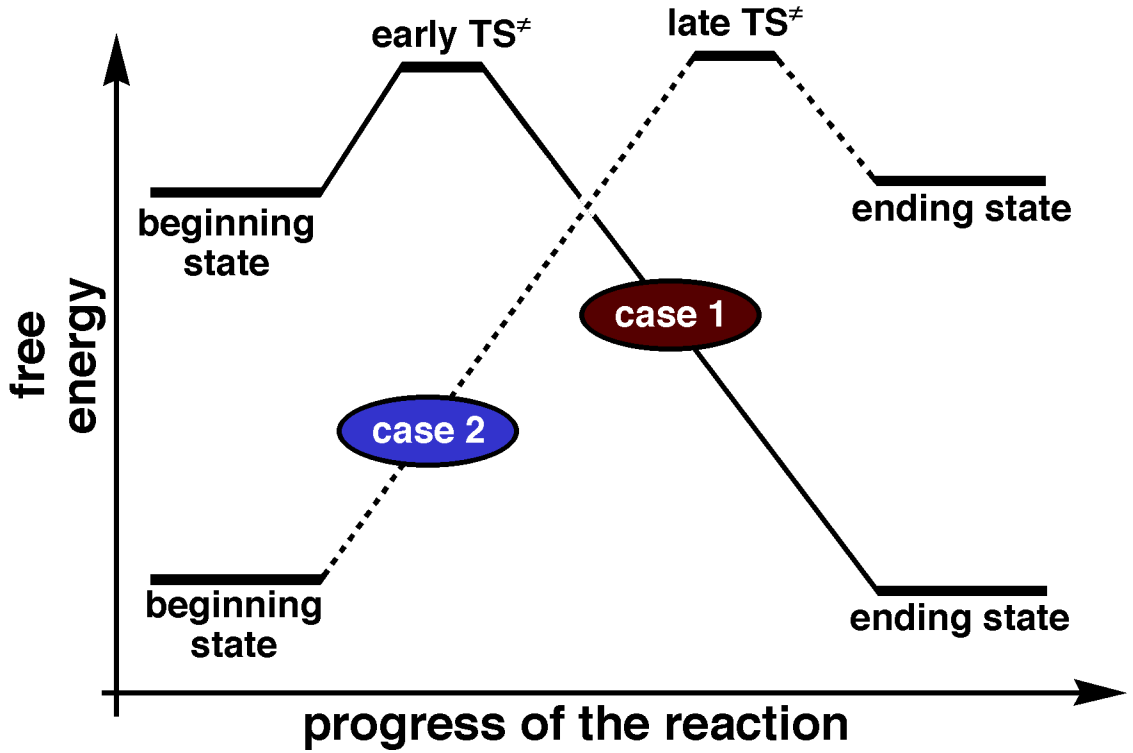
The transition state ($TS^{\neq}$) is a transient species lying on the reaction pathway that is undergoing the act of electron reconfiguration. But what does the structure of the $TS^{\neq}$ look like? We can generate a representation of the transition state structure using curved arrow notation as a guide. In representing the $TS^{\neq}$, lone pairs are not shown because the number of lone pairs often changes as part of the electron reconfiguration. Bonds being broken and bonds being made are represented as dashed lines. Changes in formal charge are important. In the $TS^{\neq}$ charges on one particular atom may be growing or diminishing and such charges are non-integer (i.e., they are partial charges). Partial charges, developing or diminishing, are represented as δ^+ (for positive charge) and δ^- (for negative charge).

For the proton transfer reaction shown below, notice the connection between the curved arrow notation and the representation of the $TS^{\neq}$. The tail of each curved arrow either corresponds to a lone pair whose electron density is being consumed as the reaction unfolds, or a bond that is being broken. The head of each arrow either corresponds to a lone pair being produced, or a bond being made. The changes in charge are determined by looking at the location of charge in the reactant and in the product. Each atom associated with a changing charge is given by a $\delta+$ or a $\delta-$. The entire structure is placed in square brackets with a double dagger ($\neq$) in the upper right sided to signify that the structure is transient.



Hammond's Postulate: Transition State Structure & Energy

Activated-rate theory says that the energy of a $TS^{\neq}$ must be known to predict reaction rates. Although $TS^{\neq}$ energies can accurately be calculated with modern computational tools like WebMO, $TS^{\neq}$'s cannot be studied experimentally because they only exist transiently. For building chemical intuition, a qualitative analysis may be better than sophisticated computation; thus, it is worthwhile to have some rules to help us rationalize the relationship between $TS^{\neq}$ energy and structure. In the $TS^{\neq}$, bonds are *being* made and bonds are *being* broken. How far along are the bond-formation and bond-breaking processes at the point the transition state is reached? Are bonds nearly fully developed or just beginning to form? Are bonds fully broken, or are they just beginning to weaken? The **Hammond postulate** helps to answer these questions. The Hammond postulate tells us that for any two minima connected via a $TS^{\neq}$, the structure of the transition state will more closely resemble the minimum that it is closer to in energy. This might sound complicated, but in reality there are only two possibilities to consider. Let's examine them with reference to the diagram.



Case 1: the beginning state is higher than the ending state – In this case Hammond's postulate tells us that the $TS^{\neq}$ will more closely resemble the beginning state. The energy of the $TS^{\neq}$ must be closer to the beginning state. There's just no other way to draw the diagram. We call this $TS^{\neq}$ "**early**" since the structure of the transition state has not evolved far from its starting point.

Case 2: the ending state is higher than the beginning state – In this case Hammond's postulate tells us that the $TS^{\neq}$ will more closely resemble the ending state. The energy of the $TS^{\neq}$ must be closer to the energy of the ending state. We call this $TS^{\neq}$ "**late**" since the structure of the transition state has nearly evolved to its ending point.