

Klopman/Salem Equation

$$\Delta E = \underbrace{- \sum_{ab} (q_a + q_b) \beta_{ab} S_{ab}}_{\text{first term}} + \underbrace{\sum_{k < l} \frac{Q_k Q_l}{\epsilon R_{kl}}}_{\text{second term}} + \underbrace{\sum_r^{\text{occ.}} \sum_s^{\text{unocc.}} - \sum_s^{\text{occ.}} \sum_r^{\text{unocc.}} \frac{2(\sum_{ab} c_{ra} c_{sb} \beta_{ab})^2}{E_r - E_s}}_{\text{third term}}$$

q_a and q_b	electron populations in atomic orbitals a and b
β and S	resonance and overlap integrals
Q_k and Q_l	total charges on atoms k and l
ϵ	local dielectric constant
R_{kl}	distance between atoms k and l
c_{ra}	coefficient of atomic orbital a in molecular orbital r
c_{sb}	coefficient of atomic orbital b in molecular orbital s
E_r	Energy of molecular orbital r
E_s	Energy of molecular orbital s

Simplified Form

$$\Delta E = - \underbrace{\frac{Q_{nuc} Q_{elec}}{\epsilon R}}_{\text{second term}} + \underbrace{\frac{2(c_{nuc} c_{elec} \beta)^2}{E_{HOMO} - E_{LUMO}}}_{\text{third term}}$$

Hard nucleophiles have a low-energy HOMO and usually a negative charge

Soft nucleophiles have a high-energy HOMO but do not necessarily have a negative charge

Hard electrophiles have a high-energy LUMO and usually a positive charge

Soft electrophiles have a low-energy LUMO but do not necessarily have a positive charge

A hard-hard reaction is fast because of a large Coulombic attraction - the second term is large and the third term is small

A soft-soft reaction is fast because of a large interaction between the HOMO of the nucleophile and the LUMO of the electrophile - the second term is small and the third term is large

The larger the coefficient the softer the reagent