

Klopman-Salem equation

In the theory of [chemical reactivity](#), the **Klopman-Salem equation** describes the energetic change that occurs when two [species](#) approach each other in the course of a reaction and begin to interact, as their associated [molecular orbitals](#) begin to overlap with each other and atoms bearing [partial charges](#) begin to experience attractive or repulsive [electrostatic](#) forces. First described independently by [Gilles Klopman](#) and [Lionel Salem](#) in 1968, this relationship provides a mathematical basis for the key assumptions of [frontier molecular orbital theory](#) (i.e., theory of [HOMO-LUMO](#) interactions) and [hard soft acid base \(HSAB\) theory](#). Conceptually, it highlights the importance of considering both electrostatic interactions and orbital interactions (and weighing the relative significance of each) when rationalizing the selectivity or reactivity of a chemical process.

Formulation and interpretation

In modern form, the Klopman-Salem equation is commonly given as

$$\Delta E = \left(- \sum_{a,b} (q_a + q_b) \beta_{ab} S_{ab} \right) + \left(\sum_{k < l} \frac{Q_k Q_l}{\epsilon R_{kl}} \right) + \left(\sum_r^{\text{occ.}} \sum_s^{\text{unocc.}} - \sum_s^{\text{occ.}} \sum_r^{\text{unocc.}} \frac{2(\sum_{a,b} c_{ra} c_{sb} \beta_{ab})^2}{E_r - E_s} \right)$$

where

q_a is the electron population in atomic orbital a ,

β_{ab} , S_{ab} are the resonance and overlap integrals for the interaction of atomic orbitals a and b ,

Q_k is the total charge on atom k ,

ϵ is the local dielectric constant,

R_{kl} is the distance between the nuclei of atoms k and l ,

c_{ra} is the coefficient of atomic orbital a in molecular orbital r ,

and E_r is the energy of molecular orbital r .

Broadly speaking, the first term describes the closed-shell repulsion of the occupied molecular orbitals of the reactants (four-electron filled-filled interactions, *steric effects*). The second term describes the Coulombic attraction or repulsion

between the atoms of the reactants (ionic contribution, *electrostatic effects*). Finally, the third term accounts for all possible interactions between the occupied and unoccupied molecular orbitals of the reactants (two-electron filled-unfilled interactions, *stereoelectronic effects*). Although conceptually useful, the Klopman-Salem equation seldom serves as the basis for energetic analysis in modern quantum chemical calculations.

Because of the difference in MO energies appearing in the denominator of the third term, energetically close orbitals make the biggest contribution. Hence, approximately speaking, analysis can often be simplified by considering only the highest occupied and lowest unoccupied molecular orbitals of the reactants (the HOMO-LUMO interaction in frontier molecular orbital theory). The relative contributions of the second (ionic) and third (covalent) terms play an important role in justifying hard soft acid base theory (HSAB), with hard-hard interactions governed by the ionic term and soft-soft interactions governed by the covalent term.

^ Klopman, Gilles (1968-01-01). "Chemical reactivity and the concept of charge- and frontier-controlled reactions". *Journal of the American Chemical Society*. **90** (2): 223–234. doi:10.1021/ja01004a002. ISSN 0002-7863.

^ Salem, Lionel (1968-01-01). "Intermolecular orbital theory of the interaction between conjugated systems. I. General theory". *Journal of the American Chemical Society*. **90** (3): 543–552. doi:10.1021/ja01005a001. ISSN 0002-7863.

^ Fleming, Ian (1976). *Frontier Orbitals and Organic Chemical Reactions* (Reprinted 2006 ed.). Chichester, UK: Wiley. p. 27. ISBN 978-0471018209.

^ The term *steric effects* is broad and often includes the result of Coulombic repulsion as well, since, in practice, any method of dividing energetic contributions between repulsive electrostatic interactions and filled-orbital repulsion is artificial and arbitrary to varying degrees.

^ The term *stereoelectronic effects* usually refers to the consequence of energetically favorable, two-orbital, two-electron interactions; however, it can be used more broadly to refer to any effect originating from orbital interaction, including unfavorable two-orbital, four-electron interactions.

^ Fukui, Kenichi (1982). "Role of Frontier Orbitals in Chemical Reactions". *Science*. **218** (4574): 747–754. Bibcode:1982Sci...218..747F. doi:10.1126/science.218.4574.747. JSTOR 1689733. PMID 17771019.

^ Pearson, Ralph G. (1997). "The HSAB Principle". *Chemical Hardness*. Wiley-VCH Verlag GmbH & Co. KGaA. pp. 1–27. doi:10.1002/3527606173.ch1. ISBN 9783527606177.