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Theoretical
Chemistry Accounts

Perspective

Perspective on "Intermolecular orbital theory of the interactions between conjugated systems." I General theory; II Thermal and photochemical cycloadditions

Salem L (1968) J Am Chem Soc 90: 543, 553

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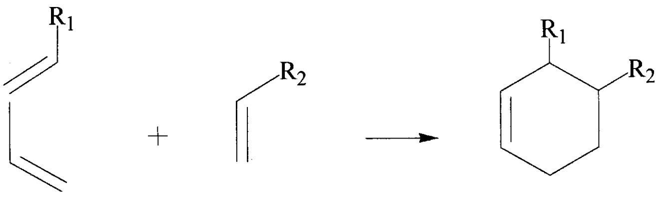
Abstract. At the time where a reaction path between molecules could not be calculated easily, the interaction between conjugated molecules was calculated using perturbation theory. The theory of Lionel Salem gave a very interesting approximation to a reaction path between rather large conjugated systems.

Key words: Molecular orbitals – Perturbation theory – Intermolecular interactions

1 Personal historical perspective

It was the fall of 1968. Universities opened late this term in France. Paris-Jussieu (called Halles aux Vins because the university was built on the site of an old wine whole sale market) was still closed and I registered at the University of Orsay, 25 km southwest of the city. Nice trees, plenty of grass, a stream going through the campus, it was one of the most beautiful campuses in France. In the program of chemical physics, I sat through classes of quantum mechanics, spectroscopy, thermodynamics, kinetics, and structure and bonding of molecules. The professor for "structure and bonding of molecules" was young, tall and thin. He looked at us with piercing eyes under dark bushy eyebrows. He came to class with heavy piles of yellow scratch papers covered with handwritten notes but hardly looked through them except for writing something in the middle of his presentation. His name was Lionel Salem. As we went through the material during the semester, he often repeated "Molecular orbitals, they don't exist but that should not stop us from drawing and using them". In the following semester, during the class for organic chemistry, I discovered the full meaning of this sentence. Very luckily for us, the professor, Nguyen Trong Anh, decided on a very unusual program. In place of the expected order stereochemistry, organic functions and "if time permits modern approaches", he started with the last section. This is why we were introduced to organic chemistry through the Woodward–Hoffmann rules. Nothing could have been better and we learned what nonexisting molecular orbitals could do for chemistry. At the end of this year I had my BA. I joined Nguyen Trong Anh's research group under the condition that I was going to work on a project related to Woodward–Hoffmann rules, and I was going to "play" with these nonexisting molecular orbitals which could still be drawn.

In my project, I had to understand the regiochemistry of the addition of unsymmetrically substituted dienes and dienophiles. The major product (shown in Scheme 1 for one type of reactants) could not be explained by classical electrostatic arguments since new bonds were made between carbon centers with identical charges. Steric effects were also in contradiction with the nature of the major isomer [1, 2].



$R_1 = NEt_2, Ph, CO_2H, {}^tBu$

$R_2 = CO_2R, Ph, CN$

The selection rules of the pericyclic reactions were established for idealized nonsubstituted molecules [3]. In the particular case of cycloaddition, the two bonds were thus supposed to form in a synchronous manner. There was certainly no reason for the two bonds to be made synchronously for unsymmetrically substituted molecules although the reaction was concerted, i.e. there was no detectable intermediate. There was in fact proof that the two bonds were not formed synchronously [4, 5]. The use of perturbation theory and frontier orbitals within the hypothesis of synchronous formation of the two bonds gave disastrous results for "predicting" the major isomer. I had to assume asynchronicity . How to determine the amount of asynchronicity? This is how I came to the paper of Lionel Salem.

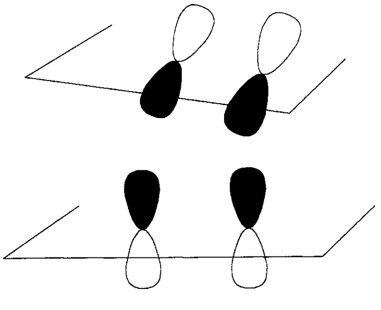
In the1960s, reaction mechanisms were not studied through localization of transition states as has been done since the 1980s. Two methods were possible at this time. The extended Hückel method [6] could be as easily used for a single molecule as for two molecules in interaction considered as a composite system, sometimes also called a super-system [3, 7, 8]. However, to quote Lionel, "the numerical resolution of a large secular equation does not provide any information on the important atom–atom or orbital–orbital interactions..." and "It is difficult, without repeating the entire diagonalisation at many different interatomic distances to establish whether a given bond closure is more favorable than another one and whether a given reaction must proceed symmetrically or not". It is a mark of the time that Lionel also wrote, "Furthermore for very large molecules, the secular determinant procedure itself becomes unwieldy. The interaction of two pyrene molecules requires the resolution of a 132 × 132 determinant for each dimer configuration when there is no plane of symmetry allowing for its factorization".

2 General theory

Lionel Salem developed "a theory which provides explicit expressions for the interaction energy of two conjugated molecules as a function of the various atomic orbital overlaps (a reaction surface of sorts). Such a theory should provide insight into the important orbital interactions and should allow ready calculations of reaction paths". The essential features of the proposed theory were as follows.

1. The wave functions were built out of intermolecular orbitals covering the entire system of interacting molecules. The Hamiltonian was an effective one-electron Hamiltonian.
2. The molecular orbitals and experimental energies of the separate molecules were chosen as starting points. This theory was going to seek only the small changes brought about by the interaction.
3. Perturbation theory was used to determine the changes in the molecular orbitals and in the energies of states.
4. Expansion in powers of the overlap allows for explicit analytical energy expressions which were numerically tractable.

The theory was thus developed for conjugated systems with well-separated σ and π orbitals. While this approximation is not strictly true for small olefinic systems such as ethylene, it is valid for larger conjugated molecules. Coulombic repulsion terms were neglected thus prohibiting the use of the theory for highly polar systems. All overlaps between interacting atomic orbitals ϕ_r and $\phi_{r'}$ were considered to be small with respect to unity ($S_{rr'} < 0.2$). This is especially valid for conjugated systems when the two molecules approach each other in roughly parallel planes (Scheme 2).



$$E_{\mathrm{int}} = -\sum_{rr'}(q_r + q_{r'})\eta_{rr'}S_{rr'} - 2\sum_{j}^{\mathrm{occ}}\sum_{k'}^{\mathrm{unocc}}\frac{\left(\sum_{rr'} c_{jr}c_{k'r'}\eta_{rr'}\right)^2}{E_{k'} - E_j} - 2\sum_{j'}^{\mathrm{occ}}\sum_{k}^{\mathrm{unocc}}\frac{\left(\sum_{rr'} c_{kr}c_{j'r'}\eta_{rr'}\right)^2}{E_k - E_{j'}} \qquad (1)$$

The expression (Eq. 1) is made of two terms with clear physical meaning:

1. A repulsive term proportional to the square of the overlap and to the sum of the π charge densities on the interacting atoms.[1] This repulsion arises because each conjugated molecule has a closed-shell structure in which all the bonding orbitals are full. The larger the π charge density on an atom, the larger the size of the exclusion shell into which other electrons are forbidden from penetrating.
2. An attractive term due essentially to the mixing of the occupied orbitals of one molecule with the unoccupied orbitals on the other. This term depends on the inverse of the energy difference between interacting molecular orbitals and is thus important for occupied and empty orbitals that are close in energy. This attraction takes place because conjugated molecules although being closed shells from the strict point of view of occupancy of bonding orbitals are also open shells since they possess a half-filled band of π levels.

This equation illustrates the dual nature of conjugated molecules: a closed shell but yet available low-lying antibonding orbitals. The great reactivity arises from the existence of half-filled bands of π electrons even though the valency shell of each carbon atom is full.

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[1] In this equation, $\eta_{rr'}$ is the resonance integral which is proportional to the overlap $S_{rr'}$, q_r is the charge density at atom r, E_j is the energy of the molecular orbital ψ_j

Lionel Salem also established the equation for the interaction energy when one molecule is excited. The interaction contains a term that is linear in the overlap in addition to terms that depend on S^2 and higher orders. For identical molecules the linear term dominates. "The stabilizing interaction depends essentially on the magnitude of the interaction between the molecular orbital ψ_j which loses the electron and its degenerate partner $\psi_{j'}$, and between the molecular orbital ψ_k which gains the electron and its partner $\psi_{k'}$. For different molecules the linear term disappears and the terms of higher order in S take precedent.

These equations were used subsequently to account for the thermal and photochemical dimerization of butadiene, the Diels–Alder addition between two acrolein molecules, where the asynchronous nature of the cycloaddition was demonstrated, and the endo mechanism. These equations provided a demonstration of the symmetry rules for the cycloaddition reactions, and could account for the photodimerization of tropone.

While this method allows a number of different reactions occurring between conjugated systems to be treated successfully, Lionel Salem pointed out some strengths and weaknesses of this theory. A major flaw, inherent to all molecular orbital theories, is the lack of correlation between the order of the orbitals and the order of the states. Other weaknesses are

1. The neglect of explicit intermolecular Coulomb interactions resulting in erroneous predictions of reaction paths, particularly when large net charges force a pathway different from that favored purely from the overlap viewpoint.
2. The neglect of explicit interaction with the σ electrons.
3. The use of a parameter k which links the resonance integral and the overlap (as is done in extended Hückel theory).

This theory was in the "air" at this time. Fukui [9, 10] had presented a perturbation treatment of the interaction between conjugated molecules but which neglected overlap explicitly. Closely related papers were published by Klopman [11, 12]. In these papers a perturbation treatment explicitly including the ionic terms was designed to treat hard and soft acids and bases (HSAB theory).

This type of approach had a major impact in popularizing the theoretical approach amongst a large group of people, especially experimentalists. The shape and energy of π orbitals could be obtained from EHT programs and even through simple Hückel programs. The physical meaning of the terms had a close relationship with concepts used by experimental chemists. While the Woodward–Hoffmann rules gave a Yes/No answer to what was allowed or forbidden, this approach gave a numerical estimate of the interaction between reagents and a rough idea of the reactions paths. It was certainly a great tool. In the case of Diels–Alder reactions, the asynchronicity was easy to demonstrate. In fact assuming full asynchronicity gave the major isomer for a large number of systems [13]. A generalization of the perturbational approach which explained nicely how any substituent could influence the diene and dienophine molecular orbital energies and coefficients was presented shortly after by Houk [14].

3 The present time

There is no longer explicit use of this theory to probe reaction paths because it is now possible to calculate reaction paths for rather large systems with quantitative methods. For instance, the transition states for a large number of cycloadditions were calculated with ab initio methods [15, 16]; however, it is not realistic and not useful to calculate paths for every reaction and perturbation theory still remains the best tool for explaining a large number of experimental results. The power of this tool is clearly illustrated in the books of Fleming [17] for organic chemistry, of Albright, Burdett and Whangbo [18] for a general approach to chemistry of Hoffmann [19] and of Iung and Canadell [20] for solid state chemistry.

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