ELECTRONS IN CHEMICAL REACTIONS

FIRST PRINCIPLES

Lionel Salem

Electrons in Chemical Reactions: First Principles

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Preface

Research is discovery, but also full understanding. In this respect this book is a research book, since in many sections I have attempted to go further and deeper than the usual interpretation or explanation as it now stands in the chemical literature.

Some readers will find that I have been short on references. Indeed, I have purposely taken a historical perspective and tried to restrict the 1970s references to a share that was proportional to their actual contribution to advancing our understanding rather than to their volume. Hence there are a relatively large number of references from the 1950s and 1960s and even the 1930s and 1940s.

I am grateful to Professors Gerald Segal, James McIver, Weston Borden, Nguyen Trong Anh, Josef Michl, Ken Houk, Olivier Kahn, and Alberte Pullman for their constructive comments on the successive chapters of the book. Monique Grisez and Françoise Pariset have also been of outstanding assistance.

Finally, this book reflects a theoretician's viewpoint and is a theoretician's translation of the experimental chemist's language. It owes its existence to *all* the scientists who in the last half century have made theoretical chemistry a living subject.

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Introduction: Resonance in Chemistry

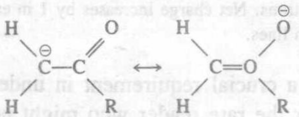
Resonance, introduced by Pauling and Wheland,[1] is the conceptual heart of chemistry. The notion that a molecule "hesitates" between different structures, borrows its characteristics from all of these and finally adopts a structure that is somewhat intermediate between them, is central to understanding electronic behavior.*

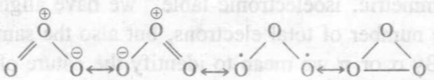
Resonance may involve alternative patterns for the distribution of double and single bonds, as in the famous case of benzene:

It may involve competition between convalent and ionic character, as in hydrogen chloride or in a phosphonium ylide:

$$\mathrm{H{-}Cl} \leftrightarrow \overset{\oplus}{\mathrm{H}}\overset{\ominus}{\mathrm{Cl}} \qquad \mathrm{R_2}\overset{\ominus}{\mathrm{C}} - \overset{\oplus}{\mathrm{P}}\mathrm{R_3} \leftrightarrow \mathrm{R_2C{=}PR_3}$$

It may illustrate the manner in which a net charge is actually distributed over several atoms, as in the enolate anion, in which case redistribution of unsaturation also occurs. Multiple possibilities may exist in the presence of unpaired electrons such as in ozone, where an unpaired diradical structure and zwitterionic structures are simultaneously available:





(see Section 3.5).

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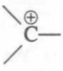
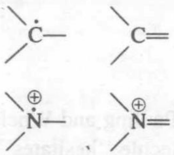
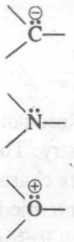
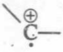
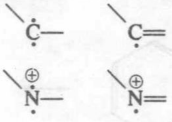
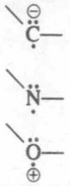
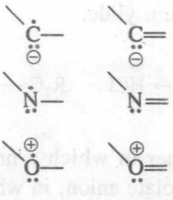
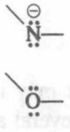
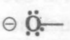
*For a lucid account of the history of structural uncertainty in organic chemistry, see Ref. 2.

TABLE I-1

Isosymmetric Isoelectronic Table for Simple Groups[a]

	π		
σ	0	1	2
0			
1			
2			
3			

[a] The number of electrons refers to the *labile electrons* at the atom (each σ bond adds nonlabile σ electrons in the immediate vicinity of the central atom). Dots *above* the atom refer to π electrons, dots *below* the atom refer to σ electrons. Net charge increases by 1 in each column from left to right and from second to third and fourth lines.

Electron counting is a crucial requirement in understanding the chemical behavior of molecules. For the rare reader who might not yet be familiar with this process, we give the electron count for some fundamental entities (Table I-1).

In this "isosymmetric, isoelectronic table" we have aligned groups that have not only the same number of total electrons, but also the same number of *both* σ and π electrons. By σ or π we mean to identify the nature of the atomic, hybrid, or molecular orbital occupied by each electron and its *symmetry*—σ, symmetric, or π antisymmetric—relative to the local plane of the bonds surrounding the atom (for an atom with a single bond to it, we proceed by continuity). It is clear that these symmetries serve

1. To distinguish electronic structures that have the same global count.
2. To refine the isoelectronic concept since chemical analogies will certainly be greater between two groups centered on different atoms and involving the same total number of electrons—but with *same* σ and π numbers—than between two groups with the same central atom but with *different* σ and π numbers.
3. Eventually, to develop rules for reactions between groups, based on the changes in σ and π counts during the reaction.

In Sections 1.2 and 1.3 the reader will find how resonance structures can be translated into a more quantitative language. In Chapter 3 a detailed study of the interplay of molecular orbital theory, valence–bond theory and resonance theory is given for a number of intermediates.

References

1. L. Pauling and G. W. Wheland, *J. Chem. Phys.* **1**, 362 (1933); L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, NY, 1960), p. 220.
2. C. A. Russell, *The History of Valence* (Leicester University Press, Leicester, UK, 1971), pp. 296 sqq.

1
Methods and Methodology

In the last half century (1930–1980) chemists have hardly modified their conceptual thinking on electrons in molecules. Either the electrons are regarded as being paired in bonds, according to the principles introduced by G. N. Lewis, or they are considered to exist as delocalized entities covering the entire molecule. In the first case the appropriate description of the electron pair is a *valence-bond* wave function, and in the second case each electron is described by a *molecular orbital* wave function. The actual numerical methods for calculating energies and chemical properties are far more numerous in the molecular orbital realm, although interest in valence-bond methods is increasing.

1.1 Wave Functions and Electronic States

Practically all studies of organic and inorganic reactions to date have been conducted within the framework of the Born-Oppenheimer approximation.[1] It is recognized that electrons are much lighter than nuclei (by a factor of at least 1836, the mass of the proton) and thereby move much faster. In the time it takes the electrons of a molecule to explore the entire space around all the nuclei, these have essentially remained at standstill. It is then common practice, except in sophisticated studies of nuclear-electronic coupling in the reactions of light molecules, to calculate all the electronic properties of molecules as if the nuclei were fixed. Hence, for *each* molecular geometry, the nuclei are given fixed positions, for which electronic wave functions and electronic stationary states are calculated. There will be a ground electronic state, with energy E_0 (or simply E) and excited electronic states, with energies E_1, E_2, E_3, and so on.

These electronic energies are obtained from the fixed nucleus wave equation

$$(V_{nn} + V_{ne} + V_{ee} + T_e)\,\Psi = E\Psi \tag{1-1}$$

where V_{nn}, V_{ne}, and V_{ee} describe the coulombic interactions between nuclei, between nuclei and electrons, and between electrons, respectively, and T_e represents the kinetic energy of the electrons.

If we now repeat the same operation for a different fixed-nucleus configuration, we get a new set of energies E'_0, E'_1, and so forth. For a given state, the set of energies E, E', E'', and so on form a *potential surface* (Fig. 1-1). Since each point on the surface corresponds to a different nuclear configuration, this surface actually describes the variation of molecular energy as a function of nuclear coordinates.

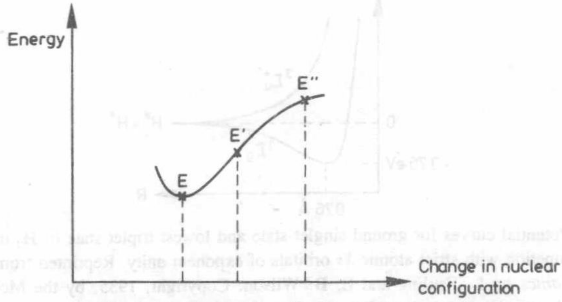


FIGURE 1-1. Potential surface for an electronic state.

The potential surface can then be understood as describing the potential energy to which the nuclei are subjected. In a dynamic manner the molecule can be regarded as moving *on* this surface.

1.2 Valence-Bond Wave Function for Two Electrons in a Covalent Bond

Heitler and London[2] introduced for the hydrogen molecule a function

$$\Psi^{\text{cov}} = \frac{1}{\sqrt{2 + 2S^2}} [\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)] \times \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2) \quad (1\text{-}2)$$

that has yet to be surpassed in its simplicity. It expresses the fact that when electron 1 is on atomic orbital ϕ_A, electron 2 is on atomic orbital ϕ_B, and conversely. In equation (1-2) S is the overlap integral

$$S = \int \phi_A\phi_B \, d\tau \quad (1\text{-}3)$$

between the two atomic orbitals ϕ_A and ϕ_B. The spin part of the wave function (α_1, upspin for electron 1; β_2, downspin for electron 2) shows the electrons to be paired in a singlet state. If the two electrons were present in the same bond but unpaired with parallel spins, the wave function would be that of the excited triplet state:

$$^3\Psi = \frac{1}{\sqrt{2 - 2S^2}} [\phi_A(1)\phi_B(2) - \phi_B(1)\phi_A(2)] \times \frac{1}{\sqrt{2}} (\alpha_1\beta_2 + \beta_1\alpha_2) \quad (1\text{-}4)$$

The corresponding potential curves drawn as a function of the internuclear distance R are shown in Fig. 1-2.

The wave function for the ground singlet state has the following characteristics, which are typical of simple valence-bond functions: (1) the bonding is covalent, with the electrons either sharing the bond region or each occupying alone, at a given time, the region of an atom; (2) the electrons are relatively well ''correlated,''

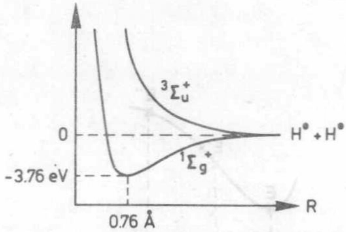


FIGURE 1-2. Potential curves for ground singlet state and lowest triplet state of H_2 using the Heitler-London wave function with strict atomic 1*s* orbitals of exponent unity. Reprinted from ***Introduction to Quantum Mechanics*** by L. Pauling and E. B. Wilson. Copyright, 1935, by the McGraw-Hill Book Company. Used with the permission of the McGraw-Hill Book Company.

keeping away from each other; and (3) the two electrons do not come together (except in the interatomic region) to profit simultaneously from the attraction of one of the nuclei. However, a consequential strength is the proper behavior of the function at large interatomic distances, where the molecule dissociates into two atoms.

The triplet wave function shares these features with the exception that the electrons avoid being in the bond region together; the probability that they will appear there is even less than in the case where the two atoms are simply brought alongside with all interactions turned off.

1.3 Mixing of Functions: A Quantitative Description of Resonance

In the same manner that the hydrogen molecule can be described as a resonance mixture of covalent and ionic structures

$$\mathrm{H{-}H} \leftrightarrow \overset{\oplus}{\mathrm{H}}\ \overset{\ominus}{\mathrm{H}} \leftrightarrow \overset{\ominus}{\mathrm{H}}\ \overset{\oplus}{\mathrm{H}} \qquad (1\text{-}5)$$

the valence-bond wave function can be improved by adding an ionic term

$$\Psi^{\text{ionic}} = \frac{1}{\sqrt{2 + 2S^2}}\,[\phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2)] \times \frac{1}{\sqrt{2}}\,(\alpha_1\beta_2 - \beta_1\alpha_2) \qquad (1\text{-}6)$$

to the previous covalent term (1-2). The mixing coefficient in

$$\Psi = \Psi^{\text{cov}} + \lambda\Psi^{\text{ionic}} \qquad (1\text{-}7)$$

will be determined variationally, so as to optimize the total electronic energy. Although the two component wave functions (1-2) and (1-6) are far from orthogonal,[3] it is convenient to use the mixing coefficient to express the percentages of covalent and ionic character in the bond (in the present case 93 and 7% at equilibrium).

For more complicated systems, with a series of resonance structures I, II, III, and so on, the wave function will be chosen as a linear combination of the corresponding functions Ψ_{I}, Ψ_{II}, Ψ_{III}, and so forth:

$$\Psi = \sum a_n \Psi_n \tag{1-8}$$

where Ψ_n is the wave function for a "canonical" valence-bond structure.* The function for a single structure is often quite complicated. It is an antisymmetrized product of atomic orbitals and spin orbitals,[4] which can be reduced to a combination of Slater determinants. Some examples are given in Table 1-1 for the simplest groups of atoms: two, three, or four. The resonance structures are shown alongside, where the notation $|\phi_A\bar{\phi}_B\phi_C|$ is the abbreviation for the determinant

$$|\phi_A\bar{\phi}_B\phi_C| \equiv \begin{vmatrix} \phi_A(1)\alpha(1) & \phi_B(1)\beta(1) & \phi_C(1)\alpha(1) \\ \phi_A(2)\alpha(2) & \phi_B(2)\beta(2) & \phi_C(2)\alpha(2) \\ \phi_A(3)\alpha(3) & \phi_B(3)\beta(3) & \phi_C(3)\alpha(3) \end{vmatrix} \tag{1-9}$$

In the resonance structures dotted lines indicate triplet "bonding" between parallel spins, whereas $\overset{\uparrow}{\mathrm{A}}$, $\overset{\rightarrow}{\mathrm{A}}$, and $\overset{\downarrow}{\mathrm{A}}$ indicate an atom with $S_z = ½$, $S_z = 0$, and $S_z = -½$ electron, respectively.

In the case of *ionic resonance*, where charge can move back and forth between two centers, there are clearly two possible combinations of the corresponding functions:

$$\overset{\ominus\oplus}{\mathrm{AB}} \leftrightarrow \overset{\oplus\ominus}{\mathrm{AB}} \begin{cases} \phi_A(1)\phi_A(2) \pm \phi_B(1)\phi_B(2) \quad \text{(spatial)} \qquad \text{or} \\ |\phi_A\bar{\phi}_A| \pm |\phi_B\bar{\phi}_B| \end{cases} \tag{1-10}$$

For H_2, in equation (1-6), we took the positive combination, which alone had the correct spatial symmetry to mix with the covalent Heitler-London function. The energy of the combined function (1-7) is calculated by the variational technique; the secular equations yield two roots, the lower one of which is the improved ground state and the higher one, a high-lying ${}^1\Sigma_g^+$ ionic state whose first approximation is the positive combination (1-10). The negative combination (1-10) is the wave function for another ionic state of high energy, the lowest excited singlet state (${}^1\Sigma_u^+$) of hydrogen. Thus it is generally useful to distinguish between "in-phase" resonance (positive combination) and "out-of-phase" resonance (negative combination) by appropriate signs written above the arrows:

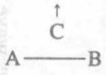
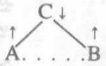
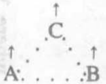
$$\overset{\oplus\ominus}{\mathrm{AB}} \overset{(+)}{\leftrightarrow} \overset{\ominus\oplus}{\mathrm{AB}} \qquad \overset{\oplus\ominus}{\mathrm{AB}} \overset{(-)}{\leftrightarrow} \overset{\ominus\oplus}{\mathrm{AB}} \tag{1-11}$$

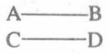
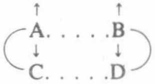
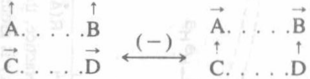
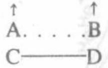
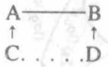
---

*For a given system of atomic orbitals, the number of linearly independent wave functions is restricted to the so-called Rumer diagrams in which no lines intersect ("canonical" set).[4]

TABLE 1-1

Valence-Bond Wave Functions for Two, Three, and Four Atoms[a]

A B (two centers, two electrons)			
One singlet	$\lvert\phi_A\bar{\phi}_B\rvert + \lvert\phi_B\bar{\phi}_A\rvert$	[identical with (1-2)]	A——B
One triplet	$\lvert\phi_A\bar{\phi}_B\rvert - \lvert\phi_B\bar{\phi}_A\rvert$	[identical with (1-4)]	$\vec{A}\,.\,.\,.\,.\,.\,\vec{B}$
A B C (three centers, three electrons)			
Two doublets	$\lvert(\phi_A\bar{\phi}_B + \phi_B\bar{\phi}_A)\phi_C\rvert$		
	$\lvert 2\,\phi_A\phi_B\bar{\phi}_C + (\phi_A\bar{\phi}_B - \phi_B\bar{\phi}_A)\phi_C\rvert$		
One quartet	$\lvert\phi_A\phi_B\phi_C\rvert$		

A B C D (four centers, four electrons)		
Two singlets	$\lvert(\phi_A\bar{\phi}_B + \phi_B\bar{\phi}_A)(\phi_C\bar{\phi}_D + \phi_D\bar{\phi}_C)\rvert$	
	$\lvert\phi_A\phi_B\bar{\phi}_C\bar{\phi}_D + {}_B\bar{\phi}_C\bar{\phi}_D\bar{\phi}_A\bar{\phi}_B - \frac{1}{2}(\phi_A\bar{\phi}_B - \phi_B\bar{\phi}_A)(\phi_C\bar{\phi}_D - \phi_D\bar{\phi}_C)\rvert$	
Three triplets (we write the $S_z = 1$ components)	$\lvert\phi_A\phi_B(\phi_C\bar{\phi}_D - \phi_D\bar{\phi}_C) - \phi_C\phi_D(\phi_A\bar{\phi}_B - \phi_B\bar{\phi}_A)\rvert$	
	$\lvert\phi_A\phi_B(\phi_C\bar{\phi}_D + \phi_D\bar{\phi}_C)\rvert$	
	$\lvert\phi_C\phi_D(\phi_A\bar{\phi}_B + \phi_B\bar{\phi}_A)\rvert$	
One quintet	$\lvert\phi_A\phi_B\phi_C\phi_D\rvert$	

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[a] Dotted lines indicate "triplet coupling" and full lines, "singlet coupling" between electron pairs.