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σ–π Energy Separation in Modern Electronic Theory for Ground States of Conjugated Systems[†]

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I. Introduction

In 1930 Hückel[1] published his seminal paper on the nature of the double bond and addressed the problem of restricted rotation in the C═C bond. He distinguished then between two types of orbitals: those symmetric with respect to a reflection in the molecular plane termed σ and those antisymmetric with respect to the same plane termed π.[1,2] This σ–π separation enabled Hückel to facilitate the treatment of conjugated systems in terms of π electrons moving in the effective field of σ electrons. His method, known now as the Hückel molecular orbital (MO) method, did not treat the σ electrons explicitly, though it assumed their presence and influence implicitly. Perhaps the greatest discovery of the method at that time was the crystallization of the notion of π bonding and its characterization as a bond which flanks the molecular plane through passing a node in the wave function. This was a stroke of genius which has ever since shaped the way we think about electronic structure.

With this notion of π orbitals and σ–π separation, Hückel turned to tackle the benzene problem. Chemical substitution experiments and X-ray diffraction results indicated that the molecule has equivalent positions and possibly a 6-fold symmetry.[3] Chemical experiments showed that the molecule also has a special stability which led to its preference of substitution over addition reactions, and hence, reactivity was allowed in the rim of the molecule while the aromatic nucleus remained intact. The contemporary theories of electronic structure of that time were unable to describe benzene in a satisfactory manner. The Hückel method gave a beautifully simple solution of the dilemma. In a single structure of D_{6h} symmetry, the σ–π separation technique gave six π electrons completely delocalized over the hexagonal σ frame. The delocalized π system was shown to have a closed shell and to be more stable than three isolated π bonds. Further applications by Hückel enabled him to generalize his observations and to formulate the $4n + 2$ rule for the entire class of aromatic compounds.[3,4] Later this rule, along with the notion of antiaromaticity, formed one of the most powerful paradigms in chemistry.

The approximate nature of the σ–π separation is well recognized. Nevertheless, its utility and connection to experimental facts are so significant that it remained with us, despite attempts to replace it by other "more appropriate" models (e.g., bent bonds).

[†] Dedicated to Peter G. Lykos and Lionel Salem for their pioneering contributions to σ–π separability and π-electron systems.
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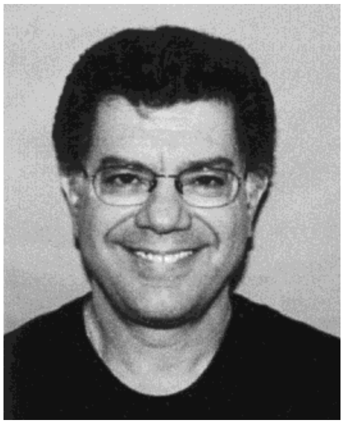
Karl Jug was born in Essen, Germany, in 1939. He studied physics in Frankfurt/Main, where he received his Diploma in Physics in 1964 and his Dr. phil. nat. in Physical Chemistry in 1965. His research work, under the direction of Hermann Hartmann, was on quantum chemical modeling of the spectra of inorganic and organic compounds. From 1965 to 1967, he was Head of Staff of Theoretica Chimica Acta in Frankfurt/M., before he moved to the IIT in Chicago to work with Peter Lykos. He was Assistant Professor in 1969 and Associate Professor in 1971 at St. Louis University. He returned to Germany in 1975 to take up a position as Professor of Theoretical Chemistry at the University of Hannover. His research interests have focused on the development of semiempirical methods and the theoretical basis of chemical concepts (charge, bonding, diradicals, aromaticity). In applied work, he has been concerned with thermal and photochemical reactions of organic compounds, the structures and reactivities of organic and inorganic compounds and clusters, the cluster simulation of solid-state surfaces, and heterogeneous catalysis.

Philippe C. Hiberty was born in 1948 in Paris. He studied Theoretical Chemistry at the University of Paris-Sud in Orsay. He prepared the French equivalent of an M.Sc. degree under the supervision of Professor W. J. Hehre; then he completed his Ph.D. degree under the supervision of Professor L. Salem in Orsay and got a research position at the Centre National de la Recherche Scientifique (CNRS). In 1979 he started his postdoctoral research with Professor J. Brauman at Stanford University and then with Professor H. F. Schaefer III at Berkeley. He went back to Orsay to join the Laboratoire de Chimie Théorique, where he started developing a research program based on valence bond theory. His main contribution to the latter field is the proposal of a new method, called “Breathing Orbital Valence Bond”, that is aimed at giving the valence bond method the accuracy it lacked. He became Directeur de Recherche in 1986, and in addition to his research position in the Laboratoire de Chimie Théorique, he now teaches organic chemistry at the Ecole Polytechnique. He started a long-term collaboration with Sason Shaik as early as 1984. His research interests are, among others, in the application of quantum chemistry and valence bond theory to the fundamental concepts of organic chemistry.



Sason Shaik was born in 1948 in Iraq. His family emigrated to Israel in the Exodus of the Iraqi Jewry. Has received his B.Sc. and M.Sc. degrees in Chemistry from Bar-Ilan University. His M.Sc Thesis, under the supervision of Professor M. Albeck, involved experimental investigations of electrophilic mechanisms of organotellurium reagents. In 1974 he went to the United States as a Fulbright Scholar (1974–1979), where he earned his Ph.D. degree in Quantum Chemistry working with Professor N. D. Epiotis at the University of Washington. In 1978 Sason Shaik started his Postdoctoral research with Professor R. Hoffmann at Cornell University. He has felt fortunate ever since to have had these two great mentors in theory and to have experienced a taste of experimental chemistry. In 1980 he started his first academic position as a Lecturer at Ben-Gurion University, where he became Professor in 1988. He still misses these formative years where his only duty was to teach and carry out research with wonderful colleagues such as Addy Pross and Philippe Hiberty. In 1992 he received a call and moved to The Hebrew University, where he is currently the director of The Lise Meitner-Minerva Center for Computational Quantum Chemistry. Among the awards he received are the Lise-Meitner-Alexander von Humboldt Senior Award in 1996–1999 and the 2001 Israel Chemical Society Prize. His research interests are in the use of quantum chemistry to develop paradigms which can pattern data and lead to the generation and solution of new chemical problems. He loves valence bond theory.

It is hard to imagine contemporary chemistry without the notions of π bonding, π electrons, and $\sigma-\pi$ separation. In fact, π bonds and π orbitals are associated with physical observables and chemical behavior. A huge edifice of π-MO characterization has been constructed by application of photoelectron spectroscopy (PES) and by its interpretation with Hückel MO theory.[5] Rotation barriers of conjugated systems are associated with breaking of π bonds. The reactivity of doubly bonded molecules reveals the existence of a bonding component which is reactive and best described in terms of a π bond, the weakest part of the double bond. UV−vis electronic absorption of conjugated molecules is well understood in terms of $\pi-\pi^*$ transitions. Conductivity of conjugated molecules is associated with the mobility of π electrons. The diamagnetic exaltation in benzene and other aromatics is best understood in terms of the behavior of π electrons in the magnetic field. Clearly, the notion of $\sigma-\pi$ separation is well entrenched in chemistry and physics and it seems to be here to stay. Nevertheless, one may feel that the notion of $\sigma-\pi$ energy partition is the mere outcome of a simplified theory. It is, therefore, important and even more essential to redefine the problem and devise methods of $\sigma-\pi$ partition at the level of modern all-electron theory.

This is the focus of the present work which reviews modern methods of $\sigma-\pi$ separation. We shall discuss here our methods[6,7] devised for semiempirical and ab initio all-electron calculations at the self-consistent field (SCF) MO levels, correlated MO levels, and valence bond (VB) levels. The $\sigma-\pi$ separation methods will be demonstrated for a variety of problems, e.g., determination of in-situ π bond energies, the role of π vs σ electrons in determining the geometry of conjugated molecules, the classification of substituents in terms of their individual effects on σ and π energies, etc. A companion review[8] draws on the $\sigma-\pi$ separation techniques and discusses the manifestation of π distortivity. While the emphasis here is on modern methods, we shall also trace the development of the $\sigma-\pi$ separation methods in Hückel methods, topological methods, and the Dewar PI-method.

II. Traditional View

In the early days of quantum chemistry, the separation of a part of the total number of electrons was a sheer necessity because it was impossible to treat a many-electron system like benzene explicitly with the available computational techniques. Calculations had to rely on analytical solutions, in contrast to numerical solutions as they are used nowadays. A special restriction that was imposed for this reason was the limitation to the outermost valence electrons. A special group of compounds seemed most appropriate for this treatment, unsaturated hydrocarbons with π electrons. In this sense, the pioneering work of Hückel[9−11] was designed to tackle a many-electron problem by considering the π electrons explicitly while incorporating the rest in an effective Hamiltonian. As is well-known, the Hückel method makes no reference to an explicit Hamiltonian and even the electronic interaction of the π electrons was not explicitly considered. In fact, for the calculation of the π-electron spectra of hydrocarbons, only a single bonding parameter β, the resonance integral, was needed because only the energy differences between ground and excited Π states had to be calculated. β is the two-center integral of the one-electron effective Hamiltonian H over π atomic orbitals at adjacent carbon atoms C and C′. It can, therefore, also be written as $H_{CC'}$. The total energy of the states was taken as the sum of the Hückel molecular orbital (HMO) energies

$$E_{\text{HMO}} = \sum_i^{\text{occ}} \epsilon_i \tag{1}$$

The atomic parameter α, also called the Coulomb integral, is the corresponding one-center integral H_{CC} of the effective one-electron Hamiltonian and serves as atomic reference energy. It was only needed if the total energy of the ground state was to be calculated and numbers assigned. α could be adjusted to the ionization potential of benzene.[12] The molecular orbital (MO) energies of benzene were $\alpha + 2\beta$ for the lowest doubly occupied orbital and $\alpha + \beta$ for the two degenerate higher-lying doubly occupied orbitals. The π-electron ground-state energy of benzene on the Hückel level was calculated as the sum of the occupied orbital energies

$$E_{\text{benzene}} = 6\alpha + 8\beta \tag{2}$$

The π MOs were delocalized over the whole C_6 framework. A reference system with localized π bonds was ethylene. Three noninteracting ethylenes were used to represent the localized situation of Kekulé structures of benzene.

$$3E_{\text{ethylene}} = 6\alpha + 6\beta \tag{3}$$

The difference between eqs 2 and 3 was called the delocalization energy

$$E_{\text{del}} = 3E_{\text{ethylene}} - E_{\text{benzene}} \tag{4}$$

In this way, a stabilizing delocalization energy of -2β was obtained. This led to the conclusion that delocalization of π electrons was a stabilizing factor which in turn is responsible for the D_{6h} structure of benzene. Since it was believed that in benzene there is a resonance interaction between two Kekulé structures,[13] the delocalization energy was also called resonance energy. This term originally derived from valence bond (VB) theory[13] carried over to MO theory.[14−16] It was also interesting to use the Hückel method in connection with the concept of a bond order[15] for the determination of bond lengths via a linear bond order−bond length relationship.[5,16] Another way of looking at the problem is described by Salem.[17] The so-called empirical resonance energy is defined as the difference between the absolute values of the observed heat of formation and the empirical heat of formation calculated for a single Kekulé structure. This quantity then represents an additional stabilization of conjugated molecules due to some interaction between the conjugated double bonds not taken into account by one Kekulé structure.

At the time when all-valence or even all-electron calculations for benzene and other larger conjugated systems were not feasible, it was widely believed that the MO energies of the π electrons were high above the energy levels of σ electrons. This argument was taken to support the separation of π electrons as those with the highest MO energies.

Beyond the Hückel method and with explicit inclusion of electron repulsion, a more rigorous approach to the $\sigma-\pi$ separability was given by Lykos and Parr.[18] The following conditions were formulated. (1) The total wave function Ψ (1,2,...,n) of an n-electron system may be written in the form

$$\Psi = A'\Psi_\sigma\Psi_\pi \tag{5}$$

where A' antisymmetrizes the product of the wave function Ψ_σ (1,2...,n_σ) for the σ electrons and the wave function Ψ_π (1,2...,n_π) for the π electrons with respect to exchange of σ and π electrons. Ψ_σ and Ψ_π are antisymmetrized products of σ and π orbitals, respectively. (2) The functions Ψ_σ and Ψ_π are simultaneously normalized to unity

$$1 = \int |\Psi_\sigma|^2\, d\tau = \int |\Psi_\pi|^2\, d\tau \tag{6}$$

(3) The functions Ψ_σ, Ψ_π and Ψ are well behaved. In particular, the functions Ψ_σ and Ψ_π, respectively, may be expanded in terms of orthonormal Slater determinants $D_{\sigma k}$ and $D_{\pi l}$ built from some orthonormal set of one-electron functions ψ_1, ψ_2 ... (mo-

lecular spin orbitals)

$$\Psi_\sigma = A_1 D_{\sigma 1} + A_2 D_{\sigma 2} + ...$$
$$\Psi_\pi = B_1 D_{\pi 1} + B_2 D_{\pi 2} + ...$$
$$\sum_k |A_k|^2 = \sum_l |B_l|^2 = 1 \qquad (7)$$

where no spin orbital ψ_i^π enters $D_{\sigma k}$ and no spin orbital ψ_i^σ enters $D_{\pi l}$.

From the normalization condition in eq 7, it follows that Ψ is also normalized. Lykos and Parr had already stated that an exact molecular wave function will, in general, not satisfy the $\sigma-\pi$ separability conditions. Of course, a full CI calculation will not satisfy eq 7 either. However, a π configuration interaction will satisfy eq 7.

It is quite remarkable that in this paper[18] there were two alternative ways presented to invoke the $\sigma-\pi$ separability. Let us write the total Hamiltonian in such a way that it is the sum of σ contributions, π contributions, and $\sigma-\pi$ interactions

$$H = H_\sigma^{(0)} + H_\pi^{(0)} + H_{\sigma\pi}$$

with

$$H_\sigma^{(0)} = H_\sigma^{\text{core}} + \sum_{\kappa<\lambda}^{n_\sigma} \frac{1}{r_{\kappa\lambda}}$$

$$H_\pi^{(0)} = H_\pi^{\text{core}} + \sum_{\mu<\nu}^{n_\pi} \frac{1}{r_{\mu\nu}}$$

$$H_{\sigma\pi} = \sum_\kappa^{n_\sigma} \sum_\mu^{n_\pi} \frac{1}{r_{\kappa\mu}} \qquad (8)$$

H^{core} is the core Hamiltonian consisting of the kinetic energy and the electrostatic attraction of the σ or π electrons in the field of the nuclei.

One can now combine the $\sigma-\pi$ interaction either with the pure π part

$$H = H_\sigma^{(0)} + H_\pi$$

with

$$H_\pi = H_\pi^{(0)} + H_{\sigma\pi} \qquad (9a)$$

or with the pure σ part

$$H = H_\sigma + H_\pi^{(0)}$$

with

$$H_\sigma = H_\sigma^{(0)} + H_{\sigma\pi} \qquad (9b)$$

Lykos and Parr[18a] pointed out that in a generalized self-consistent field (SCF) procedure of σ and π electrons, these two types of electrons have to be treated equivalently. Just as the π electrons may be regarded as moving in the field of a core of bare nuclei plus σ electrons, so the σ electrons may be regarded as moving in the field of a peel of bare nuclei plus π electrons. Nevertheless, the $\sigma-\pi$ separation according to eq 9a became the method of choice. This choice was suggestive because in this way the "inner" σ electrons would provide a natural screening effect of the nuclear charge for the "outer" π electrons and lead to an effective π-electron Hamiltonian with a reduced, effective nuclear charge. The electronic energy E_{el} then takes the form

$$E_{\text{el}} = \int \Psi^*(H_\sigma^{(0)} + H_\pi)\Psi \, d\tau = \int \Psi_\sigma{}^* H_\sigma^{(0)} \Psi_\sigma \, d\tau_\sigma + \int \Psi_\pi^* H_\pi^{(0)} \Psi_\pi \, d\tau_\pi + \int \Psi_\pi^* G_\sigma \Psi_\pi \, d\tau_\pi \qquad (10)$$

where $G_\sigma = J_\sigma - K_\sigma$ is the difference between the corresponding Coulomb and exchange operators. $H_\pi^{(0)} + G_\sigma$ is then considered as the effective π-electron Hamiltonian for the π-electron wave function Ψ_π. Lykos[19] gave a lucid account of the history and the details. Finally, the total energy of a system described with wave function eq 5 must be formulated as the sum of electronic energy and nuclear repulsion energy E_{NN}. An energy separation according to eq 9a could then have the following form

$$E_{\text{total}} = E_{\text{el}} + E_{\text{NN}}$$
$$= E_\sigma + E_\pi$$

with

$$E_\sigma = E_\sigma^{\text{core}} + E_{\sigma\sigma} + E_{\text{NN}}$$
$$E_\pi = E_\pi^{\text{core}} + E_{\pi\pi} + E_{\sigma\pi} \qquad (11)$$

The electronic energy terms refer to the operators in eqs 8 and 9a. The electronic repulsion terms $E_{\sigma\sigma}$, $E_{\pi\pi}$, and $E_{\sigma\pi}$ consist of Coulomb and exchange contributions. As we shall show in section VI, the equivalence of partitioning schemes in eqs 9a and 9b as suggested by Lykos and Parr can lead to an alternative definition of E_σ and E_π via eq 13. The link between the old Hückel method and the $\sigma-\pi$ separation based on the SCF theory was made subsequently. McWeeny[20] suggested a reformulation of the Hückel method on the basis of SCF theory. He identified Hückel parameters α and β with parameters of a Löwdin-orthogonalized basis[21] in SCF theory. A deduction of parameters in such a basis was given by Fischer-Hjalmars,[22,23] who tried to justify the additivity of the MO energies as total energy of a system. This was achieved by combining the Hückel π-electron energy reformulated on the SCF level and the nuclear repulsion simplified by a formula of Del Re and Parr.[24]

$$E_{\text{NN}} = \sum_{\mu<\nu} n_\mu n_\nu \gamma_{\mu\nu} \qquad (12)$$

n_ν is the number of electrons corresponding to an effective core charge Z_μ and $\gamma_{\mu\nu}$ are the electronic repulsion integral as an approximation for the electrostatic repulsion $1/R_{\mu\nu}$ of nuclei μ and ν at distance $R_{\mu\nu}$. Parr[25] had already formulated the total electronic energy E_{el} as a sum over occupied MOs i in a closed-shell system.

$$E_{\mathrm{el}} = \sum_{i}^{\mathrm{OCC}} (\epsilon_i^{\mathrm{core}} + \epsilon_i) \tag{13}$$

Here $\epsilon_i^{\mathrm{core}}$ is the core attraction energy of MO i and ϵ_i is the eigenvalue of the SCF operator F. He pointed out that in the case of the identification of the Hückel effective Hamiltonian with the SCF operator F, the π-electron energy E_π could not be written simply as a sum of eigenvalues ϵ_i. Later, Harris[26] showed that the operator H_{el} which determines the total electronic energy and the operator F which determines the MOs are different in Hückel methods if the matrix elements are dependent on net charges. $\mathbf{F}$ and $\mathbf{H}_{\mathrm{el}}$ matrices should always be different if the Hückel method is interpreted on the basis of SCF theory. However, it was shown that the form of the matrix elements can still be the same and a distinction between H_{el} and F is possible only by a different parametrization of the matrix elements.[27] A relation between the Hartree–Fock (HF) energy of a closed-shell system and its corresponding orbital energies was derived by Robinson and Schaad.[28] These authors found that the HF energy approximately equals one-fourth of the sum of spin–orbital energies of an isoelectronic system with double the nuclear charges and one-half the bond lengths.

The σ–π separability was used in the Pariser–Parr–Pople (PPP) model Hamiltonian[29,30] to calculate π-electron energies. The theoretical basis and design of the PPP model Hamiltonian was recently reviewed.[31]

III. π-Electron Methods

In this section we present a brief review of π-electron methods, since they were not only the direct result of σ–π separation techniques but also used to investigate the stability of conjugated systems and to develop aromaticity criteria. σ energies were initially not explicitly considered at the Hückel level but were later empirically included in order to achieve improved accuracy. The same trend was seen also at the PPP level, where the detailed empirical assessment of σ-energy contributions supplemented the direct π-electron calculations. This helped to overcome inherent difficulties of pure π-electron methods. In principle, such supplemented π-electron methods can be used to study distortions in conjugated systems. In section VII we have included examples of such studies.

A. Hückel Methods

1. Methods without σ-Electron Consideration

In their general theory of the electronic structure of conjugated systems, Coulson and Longuet-Higgins[32] did not specifically refer to Hückel but proceeded along the same lines. They stated that theoretical treatments of unsaturated molecules begin by dividing the electrons in three groups: (a) those which are not concerned with bond formation—the inner electrons; (b) those which are engaged in the formation of σ bonds, i.e., localized bonds having maximum density along the line joining two adjacent atoms; and (c) the π electrons which are called mobile electrons. The part of the molecule in which they move is called a conjugated system.

The inner-shell electrons and the σ electrons were supposed to have their energies and distribution governed solely by the atomic orbitals or pair of orbitals in which they move. All effects depending on conjugation of the mobile π electrons such as resonance energies and variation in bond order were ascribed to the π electrons. Such a mobile bond order between atoms r und s was formulated as[33]

$$p_{rs} = \sum_{j}^{\mathrm{occ}} n_j c_{rj} c_{sj} \tag{14}$$

and was together with the charge on atom r

$$q_r = \sum_j n_j c_{rj}^2 \tag{15}$$

derived from the MO coefficients c_{rj} and the occupation numbers n_j, which in turn were determined by the secular equation

$$(\alpha_r - \epsilon)c_r + \sum_{s \neq r} \beta_{rs} c_s = 0 \tag{16}$$

Here α_r was set to $H_{rr} - H_{\mathrm{CC}}$, i.e., as the difference between the Coulomb integral H_{rr} for the atom r and the Coulomb integral H_{CC} of a carbon atom in benzene. β_{rs} was set equal to H_{rs}. H is the effective Hamiltonian operator for each π electron. It was already observed by Coulson and Longuet-Higgins that it might be possible to allow for the variation of H_{rr} with q_r in order to make a truly self-consistent field, but the authors concluded that in a general case this would be quite impossible. Shortly afterward, Wheland and Mann[34a] proposed a linear dependence of H_{rr} on the charge q_r. This empirical approach gives rise to an iterative procedure[34b] and became popular under the name ω-technique.[34c]

Coulson and Longuet-Higgins[32] suggested that the mobile charges may be used, for example, to locate the active centers for cationic and anionic attack and that the bond order, which measures the double-bond character of a bond, will indicate its reactivity as well as its length and force constant. In a subsequent paper,[35] applications were made to unsaturated hydrocarbons, such as benzene and naphthalene as well as polyenes. Further papers by the same authors were devoted to bond orders[36a] and force constants.[36b] The conclusions of the papers are that (a) the force constant of an unsaturated bond in a conjugated system will depend on its self-polarizability as well as on its mobile bond order, (b) a pair of unsaturated bonds in a conjugated system will in general interact, the interaction constant being proportional to the mutual polarizability of the bonds, but also involving their mobile bond orders.

In a final paper of the series,[36c] the interaction of two conjugated systems such as in diphenyl was considered. The conjugation energy of two conjugated systems across a connected bond is the difference between the energy of the total system and the sum of the energies of the separate systems. It was also called group resonance energy with reference to Pauling.[37] The important result from this theory was that the conjugation energies are always positive. Hence, the total energy decreases when the number of atomic orbitals available to the mobile electrons of a conjugated system is increased.

Shortly after his comprehensive work,[35,36] Coulson[38] discussed the question of bond lengths in conjugated molecules. He observed that the energy of the π electrons needs to be supplemented by a term representing the energy of the σ bonds, because this term too will depend on the compression or extension of the σ bond from its natural lengths. He stated that this latter term, called the compression energy of the σ bonds, is large and in the case of benzene is only slightly less than the resonance energy. Only the sum of π-electron energy and the compression energy gives us the total energy of the resonating part of the molecule as a function of all internuclear distances. A minimization of the total energy would lead to the optimized distances. Although he recognized the significance of the σ framework, he proceeded on the π-electron level due to computational difficulties. However, improvement on the π-electron level was achieved with a β dependence on the bond length, using a relation proposed by Lennard-Jones.[39] Independently, Longuet-Higgins proceeded on the π-electron level in a series of papers[40−42] devoted to a variety of problems such as basicities of aza-aromatic amines[41] and substitution in aromatic and heteroaromatic systems,[42] etc. None of these works question the basis of π-electron theory.

With the advent of all-valence calculations[43] in the 1960s, the σ electrons were explicitly included and the effects such as charge transfer and polarization could be explained by an interplay of σ and π electrons. Needless to say that the approach, which separated π and σ effects, had an enormous impact on the interpretation of molecular properties.

2. Methods with σ-Electron Consideration

A new approach to π-resonance energies based on the Hückel molecular orbital level was presented 20 years after the Coulson and Longuet-Higgins treatments by Hess and Schaad.[44−49] They started to study linear polyenes on the Hückel level,[44] where they found that the total π Hückel molecular orbital (HMO) energy calculated as the sum of contribution from carbon−carbon single bonds and double bonds increased linearly with the number m of single carbon−carbon bonds. This led to the following standardization where average bond energies for single and double bonds were used

$$E^{\pi}_{\text{total}} = mE^{\pi}_{\text{C}-\text{C}} + (m + 1)E^{\pi}_{\text{C}=\text{C}} \qquad (17)$$

Here $E^{\pi}_{\text{C}-\text{C}}$ and $E^{\pi}_{\text{C}=\text{C}}$ can be determined from slope and intercept of the straight line mentioned above.

Since they found a different straight line for branched polyenes, they decided to introduce eight different types of bonds, which are representative of different σ frameworks. In this sense, there is an indirect influence of the σ electrons included to some extent. To determine the eight average bond energies, they chose 40 acyclic polyenes and used a least-squares fitting procedure to determine six of the eight bond energies. The last two types of bonds, $H_2C{=}CH$ and $H_2C{=}C$, were assigned the arbitrary bond energy of 2β. The ability to calculate accurately in an additive manner the total π- electron energies of acyclic polyenes allowed the calculation of localized structures of cyclic polyenes where the values of the bond energies of the acyclic polyenes were used. For benzene, such a localized structure has an energy

$$E_{\text{loc}} = 3E_{\text{HC}=\text{CH}} + 3E_{\text{HC}-\text{CH}} = 7.61\beta \qquad (18)$$

The resonance energy RE is then defined as the energy difference between the HMO energy E_{HMO} and E_{loc}

$$\begin{aligned}\text{RE} &= E_{\text{loc}} - E_{\text{HMO}} \\ &= (7.61 - 8)\beta = -0.39\beta \end{aligned} \qquad (19)$$

For standardization, we use the negative of the RE in the original paper. Due to the acyclic polyene reference, this energy is much smaller than the corresponding stabilization energy -2β from eqs 2 and 3. RE was normalized by the number of π electrons.

$$\text{REPE} = \text{RE}/n \qquad (20)$$

REPE was used as an aromaticity criterion, with a better predictive power than the total resonance energy (RE).

B. Topological Methods

Since 1975, the graph theory of aromaticity has been developed independently by Aihara[50,51] and by Trinajstić and co-workers.[52,53] In both approaches the π-electron network of a conjugated system is described by a molecular graph. The authors explicitly refer to the HMO theory in its simplest form. A characteristic polynomial for a nonaromatic localized structure of a conjugated compound is defined in such a way that all contributions from cyclic structures in the π system are excluded from the coefficients of an HMO characteristic polynomial of the compound.[51] Earlier, Trinajstić et al.[54] developed the graph-theoretical method for determining the coefficients of the HMO characteristic polynomial for a conjugated hydrocarbon. The evaluation of this polynomial allows the definition of a topological resonance energy (TRE)

$$\text{TRE} = \sum_{j=1}^{N} g_j (x_j - x_j^{\text{ac}}) \qquad (21)$$

Here g_j is the occupation number of MO j and x_j and x_j^{ac} are the corresponding eigenvalues of the characteristic polynomial of cyclic system and the acyclic reference system, respectively. For hydrocarbons, the

π-electron energy E_π is given as in HMO theory as

$$E_\pi = N\alpha + \sum_{j=1}^{N} g_j x_j \beta \tag{22}$$

The theory[53] was described as being parameter-free in a sense that it avoids the use of empirical parameters for reference structure bond energies based on least-squares fitting of numerical data and that it does not need the distinction of eight bond references for hydrocarbon used in the Hess–Schaad scheme. The first papers[53,55] were on hydrocarbons and gave similar results to the Hess–Schaad resonance energy (HSRE) method.[44] The same, of course, is true for the papers by Aihara.[50,51,56,57] It is clear, however, that such a theory cannot be parameter-free if heteroatoms are involved. These concern the h_X and k_{C-X} parameters of HMO theory.[51]

Although the initial success of the method seemed quite impressive, the method as such was much debated a few years later.[58–61] Gutman[58] revealed difficulties with the occupation numbers g_j of eq 21. In the case of cyclobutadiene, only the choice of $g_1 = g_2 = 2$, $g_3 = g_4 = 0$ led to the antiaromatic character whereas the choice $g_1 = 2$, $g_2 = g_3 = 1$, $g_4 = 0$ according to Hund's rule led to an obscure value. The equality of the g_j values for the conjugated system and the reference system was questioned. Subsequently, Gutman and Mohar[59] found other artifacts of the TRE concept like the near equality of aromaticity of the vinyl compounds $R-CH=CH_2$ and the allyl radical $R-C(CH_2)_2$. In his response, Aihara[60] denied these difficulties. However, Heilbronner[61] showed that the graph-theoretically defined TRE is neither compatible with the quantum chemical HMO model on which it is supposed to rely nor with chemical experience. The limitations of TRE became obvious also in a study of oxocarbon dianions.[62] It was found that not only the $C_3O_3^{2-}$ ring system was aromatic, but also the C_3O_3 ring system. This finding is not compatible with the Hückel $4n + 2$ rule because the two systems differ by two electrons. Moreover, it was found that C_3O_3 is not even stable to fragmentation into three CO molecules.[63]

C. PPP Methods

In contrast to the Hückel method, the PPP method is based on a specified Hamiltonian for the π electrons. It treats the electronic interaction of these electrons explicitly[28–30] and uses an antisymmetrized wave function. The idea is again that the σ electrons provide a fixed framework for the π electrons. This method was chosen by Dewar and co-workers[64–66] to study the ground states of molecules. The motivation was to overcome the inherent difficulties of the Hückel method in the study of aromatic hydrocarbons.[64] The authors expressed the total bonding energy as the sum of the contributions $E_{\sigma b}$ from σ bonds and $E_{\pi b}$ from π bonds

$$E_b = E_{\sigma b} + E_{\pi b} \tag{23}$$

In the case of aromatic hydrocarbons, where the carbon–carbon bond lengths do not vary much, they wrote for the σ-bonding energy

$$E_{\sigma b} = N_C E_{CC} + N_H E_{CH} \tag{24}$$

Here E_{CC} is the bond energy of an aromatic carbon–carbon σ bond, E_{CH} is that of a carbon–hydrogen bond, and N_C and N_H are the number of CC and CH bonds, respectively. The π-bonding energy was written as

$$E_{\pi b} = E_\pi - nW_p + E_{cr} \tag{25}$$

Here E_π is the total energy of the n π electrons, $-W_p$ is the valence state ionization potential of the carbon atom, and E_{cr} is the repulsion energy of the positively charged carbon atoms of the core.

Different from the original PPP approach, in Dewar's method the electronic repulsion energy of the core was approximated by the electronic repulsion energy of the π electrons. The carbon cores were here assumed to possess effective core charges of $+1$ created by the removal of the π electrons only. The resonance integral β was approximated by a thermocycle that gave an empirical estimate of the π-bonding energy $E_{\pi b}$

$$E_{\pi b} = (E_{C-C} - E_{C=C}) + (C'' - C') \tag{26}$$

where E_{C-C} and $E_{C=C}$ are bond energies of a single and a double bond and C' and C'' are compression energies. The latter quantities were given by Morse functions

$$C' = E_{C-C}[1 - e^{-a'(r'-r)}]^2$$
$$C'' = E_{C=C}[1 - e^{-a''(r''-r)}]^2 \tag{27}$$

and the constants a', a'' determined by force constants of the bonds and the bond energies. Subsequently, the resonance energy of hydrocarbons was defined as

$$\mathrm{DRE} = \Delta H^C - \Delta H \tag{28}$$

Here ΔH is the heat of formation of a hydrocarbon

$$\Delta H = N_{CH}E_{CH} + N_{CC}E_{CC} + E_{\pi b} \tag{29}$$

and ΔH^C is the heat of formation of a classical structure

$$\Delta H^C = N_{CH}E_{CH} + N'E' + N''E'' \tag{30}$$

N' is the number of single C–C bonds of bond energy E', and N'' is the number of double bonds of energy E''. N_{CC} is the number of C–C bonds in a conjugated system with a common bond energy E_{CC}. $E_{\pi b}$ is the total π energy. The contributions of C–H bonds are canceled in eq 28.

Initially, the σ-bond energies were adjustable parameters to fit heats of formation for selected compounds. In the improved treatment of hydrocarbons, they were calculated directly as a function of the bond length. In this way a smaller value of 20 kcal/mol was obtained for the resonance energy of benzene. It was observed that the original Hückel method would give reasonable results for resonance energies of aromatic compounds, once the β parameter was fitted to the experimental resonance energy, but failed to differentiate between aromatic and nonaromatic compounds,[68] whereas the Dewar resonance energy (DRE) arrived at small positive values for nonaromatic and negative values for antiaromatic compounds. Of course, this problem is avoided both in the improved Hückel model by Hess and Schaad[44] and the topological resonance energy.[51,53]

IV. Importance of a Rigorous $\sigma-\pi$ Separation Methodology

It is apparent by now that the notions of π energy, π bonds, etc., are fundamental and merit a rigorous treatment in terms of modern all-electron theories. Let us mention two examples where such a treatment is surely needed. Thus, Pauling classified σ single bonds as covalent, ionic, or polar and argued that a polar A−B bond is always stronger than the average of A−A and B−B covalent bonds owing to some resonance energy arising from the covalent−ionic mixing in the A−B bond. Pauling based his electronegativity scale on such considerations. To extend Pauling's statement to π bonds requires a suitable method to study the nature and strength of a π bond independently of the underlying σ bond. Another example is the $\sigma-\pi$ interplay in the resistance of benzene and other aromatic species to distortion from their regular geometries. Since both σ bonds and π bonds obviously play a role, how can one know which driving force is exerted by each system of bonds? These are two of the many issues that require a meaningful $\sigma-\pi$ separation, as will be addressed in the following sections.

A. Estimation of π-Bonding Energies

There are presently two common ways of estimating π-bonding energies: through rotational barriers or through some sort of thermochemical cycle. The idea behind rotational barriers is that when an $H_mA{=}BH_n$ molecule is rotated by 90° to the biradical transition state, the π bond is broken while the σ bond remains intact. However, in addition to breaking the π bond, there are other geometric changes associated with the rotation (length of the σ bond, changes in A−H and B−H bond lengths, pyramidalization of A and B atoms), and thereby the measured rotation barrier reflects relaxation effects in addition to π bonding. In addition, the 90°-rotated species can have some hyperconjugation effects, especially when A or B is an atom with lone pairs such as N or P. As a result, not *all* π-type interactions will be turned off upon rotation. Last, this procedure cannot be applied to molecules containing A=O or A=S because there are no hydrogens to rotate.

The method of thermochemical cycles suffers from similar effects of geometric changes and, in addition, also requires some major approximations to be made somewhere in the cycle. In the following cycle used by Schmidt et al. (eq 31),[69] the problem lies with the biradical species in eq 31b.

$$\begin{aligned}
&\text{(a) } H_{m+1}A{-}BH_{n+1} \rightarrow H_mA^{\bullet}{-}BH_{n+1} + H^{\bullet} \quad D(A{-}H)\\
&\text{(b) } H_mA^{\bullet}{-}BH_{n+1} \rightarrow H_mA^{\bullet}{-}B^{\bullet}H_n + H^{\bullet} \quad D(B{-}H)\\
&\text{(c) } H_mA^{\bullet}\text{-}B^{\bullet}H_n \rightarrow H_mA{=}BH_n \quad -D_\pi\\
&\text{(d) } 2H \rightarrow H_2 \quad -D(H{-}H)\\
&\text{(e) } H_{m+1}A{-}BH_{n+1} \rightarrow H_mA{=}BH_n + H_2 \quad \Delta H^\circ\\
&\text{(f) } D_\pi = D(A{-}H) + D(B{-}H) - \Delta H^\circ - D(H{-}H)
\end{aligned} \tag{31}$$

Experimentally, this species does not exist and further it cannot be calculated by standard molecular orbital (MO) methods.[70] Therefore, the value of D(B−H) must be approximated in some way.

An indication of the problems associated with determining π-bond energies can be seen in the disagreement among values obtained with different methods. Schmidt et al.[69] found π-bond energies by both rotation barriers and the hydrogenation reaction for $H_mA{=}BH_n$ molecules where A, B = C, N, O, Si, P, and S. Estimates of π-bond energies obtained with the two methods differ by as much as 9 kcal/mol^{-1} in the case of HN=NH. Using isodesmic reactions, Schleyer and Kost[71] obtained π-bond energies for $H_mA{=}BH_n$ molecules where A = C and Si and B = C, N, O, Si, P, and S, which were generally larger than those of Schmidt et al.[69] by as much as 16 kcal/mol^{-1} for $H_2C{=}O$. Notable also is the disparity with the values of Kutzelnigg[72] which were obtained through evaluation of experimental thermodynamical data.

What is needed then is a method to estimate the strength of π bonds in situ, i.e., without altering the geometry of the molecule, and this requires a technique of some kind to calculate π-bonding energies and σ-bonding energies separately for a molecule of given geometry. We will see in the next section that it is possible to turn the π-bonding interaction on or off, leaving all other interactions unchanged, thus resolving the above dilemma.

B. Evidence for $\sigma-\pi$ Interplay in Distortivity of Delocalized Systems

The traditional view that states that π-bonding systems are more stable in a symmetrical geometry than in one with bond alternation (at least for aromatic or allylic systems) has to face a number of disturbing paradoxes. These paradoxes as well as other points are analyzed in detail in the companion review.[8] As such, we shall mention these very briefly.

The first paradox shows up when one tries to draw a (legitimate) link between some π systems and their isoelectronic counterparts among σ-electronic systems. In 1982, Dewar[73] noted that the transition state for an S_N2 reaction on carbon, for example, that between a chlorine anion and methyl chloride, displays a p AO on CH_3 that interacts with AOs of two chlorine atoms to form a three AO system entirely analogous to the three AO π system of allyl anion. In both cases, four electrons are accommodated in the resulting three-center MOs since one of them is bonding and the other is nonbonding. Dewar argued that the relationship between the reactants (e.g., $CH_3Cl + Cl^-$) and the transition state $[Cl\cdots CH_3\cdots Cl]^-$ is the same as that between 90°-rotated allyl anion, where there are only two-center bonds, and planar allyl anion, where there is a three-center π bond. Despite this analogy, the planar anion is much lower in energy than its 90°-rotated form while the intermediate in an S_N2 reaction is a transition state, i.e., a saddle point on the potential surface and not a minimum. In the same way, the H_6 cluster of hydrogen atoms, arranged in a regular hexagonal structure, is isoelectronic to the π system of benzene. However, it is unstable and dissociates to three separate H_2 molecules, which are analogous to a Kekulé structure of benzene. Restricting now our attention to π bonds, the N_6 molecule, hexaazabenzene, is unstable and dissociates to three N_2 molecules. Unless one assumes the very unlikely proposal that electronic delocalization is of different nature for σ than for π systems, and even for C−C vs N−N π bonds, the above paradoxes already make the traditional view very uncomfortable.

There are other disturbing facts. Pentalene, like benzene, can be described as a resonance between two Kekulé structures. Like benzene and unlike antiaromatic systems, its electronic structure is a closed shell. Its resonance energy, as calculated by the Hückel method, is even larger, -2.456β, than that of benzene. Yet its symmetrical D_{2h} structure is unstable and distorts to an alternating structure of Kekulé type. Other conjugated molecules that are unstable in a symmetrical geometry have significant resonance energy in Hückel theory.[74]

All these facts become coherent and lead to a unified picture of electronic delocalization if one simply admits that π systems, just like their isoelectronic counterparts, are distortive in nature and that it is the underlying σ frame of C−C and C−H bonds that imposes the regular geometry. Except that it contradicts the traditional view, this idea has after all nothing shocking since the σ frame is made of a set of identical bonds and can only tend to equalize bond lengths. Further evidence is provided by semiempirical methods that go beyond the simple Hückel level. The users of PPP methods apply analytical functions to mimic the force constants of the σ frame, thus realizing an empirical σ−π separation, and are familiar with the idea that π systems are distortive in all annulenes.[75] Even the simple Hückel method, when improved by using a distance-dependent β integral, leads to the same conclusion.[74,76,77] Thus, Heilbronner[74] distorted a benzene ring from D_{6h} to D_{3h}, ascribing a resonance integral of the type $\beta(1 + \delta)$ to the short bond, and $\beta(1 - \delta)$ to the long one. He found that the Hückel total π energy decreases as a function of δ and showed that the π system is stabilized by a distortion leading to an alternating structure of Kekulé type.

The same conclusions have been reaffirmed by Epiotis[78] and Shaik and Bar[79] and have been put in a wider context of delocalization in isoelectronic species, using totally different reasonings based on qualitative analyses. On the experimental side, Berry[80] noted that the IR frequency associated with the b_{2u} vibrational mode of benzene, 1309 cm^{-1}, is amazingly low as compared to the breathing mode and argued that the low frequency originates in the distortivity of π electrons.

From the discussion of the above topics, it is apparent why methods which enable rigorous σ−π separation are so necessary. For these reasons our groups embarked on developing techniques which are physically justifyable within all-electron methods.

V. Recent All-Electron Methods for σ–π Partition as Applied to the Distortivity of Benzene and Allyl

A. Integral Partition Method

For any molecule displaying π bonds, it is natural to consider the total bonding energy of a conjugated molecule as an additive combination of σ and π contributions. If we now apply a geometric distortion to the molecule, the variation ΔE of the total energy can be identified with the total variations of the bonding energy and decomposed into variations of σ- and π-bonding energies, as in eq 32

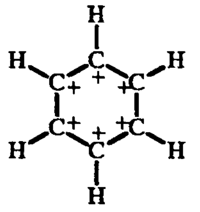
$$\Delta E = \Delta E_\sigma + \Delta E_\pi \qquad (32)$$

As shown in section II (eq 11), it is customary in semiempirical π-electron approximations to define the π system as a set of π electrons moving over a σ skeleton bearing effective positive charges on carbon, just like electrons in a hydrogen chain move over a set of nuclei each bearing a positive charge of +1 unit. As far as electronic energies are concerned, this definition can easily be extended to ab initio methods, e.g. Hartree−Fock. In this framework, the total (electronic + nuclear) energy reads (see eq 11)

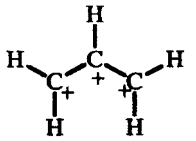
$$E = E_\pi^{\text{core}} + E_{\pi\pi} + E_{\sigma\pi} + E_\sigma^{\text{core}} + E_{\sigma\sigma} + E_{\text{NN}} \qquad (33)$$

Here E_π^{core} and E_σ^{core} are the corresponding sums over monoelectronic integrals of the π and σ MOs and represent the kinetic energy and electrostatic attraction of the π and σ electrons, respectively, in the field of the nuclei. $E_{\pi\pi}$, $E_{\sigma\pi}$, and $E_{\sigma\sigma}$ stand for the electron−electron repulsion of a type that is specified by the subscript. The last term E_{NN} accounts for nuclear repulsion.

Let us exemplify the method with two systems, benzene and allyl radical which are prototypical conjugated and delocalized species of the cyclic and open-chain varieties. The σ frame of a conjugated molecule is simply the cation that one gets after complete removal of all π electrons, leaving an effective charge on each carbon (or hetero) atom as represented below for benzene and allyl in **1** and **2**



1



2

Accordingly, the electronic energy of the σ frame reads as in eq 34

$$E_\sigma^{\mathrm{el}} = E_\sigma^{\mathrm{core}} + E_{\sigma\sigma} \tag{34}$$

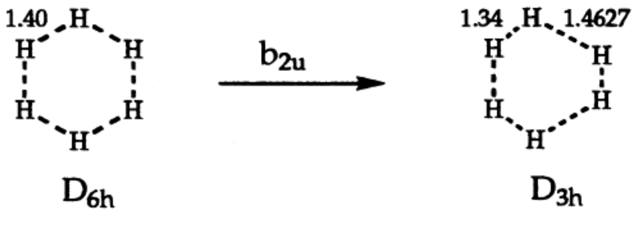
while the remaining electronic term of eq 33 is the electronic energy of the π system

$$E_\pi^{\mathrm{el}} = E_\pi^{\mathrm{core}} + E_{\pi\pi} + E_{\sigma\pi} \tag{35}$$

Physically, eq 35 expresses that the π electrons feel the attractive field of the bare nuclei, which is partly counterbalanced by electron−electron repulsion with all the σ-type electrons. Thus, this definition of the π-electronic energy is consistent with the concept of a set of π electrons moving in the field created by a σ skeleton like **1** or **2**, as discussed in section II (eq 11).

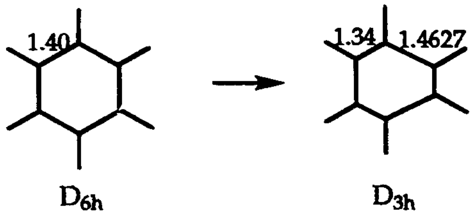
Unfortunately, pure electronic energies are of little practical interest by themselves as one is generally interested in total energies or bonding energies, which include the nuclear repulsion. From the problem at hand, the E_{NN} term causes some difficulties because it bears no obvious affinity to π or σ electrons, so that a direct separation of the *total* energy into additive σ and π components appears to be problematic. Section VI shows how this problem can be circumvented, in general, by an appropriate partition. However, here we present a way of evading the problem in the particular case of the b_{2u} and b_2 distortions of benzene and allyl, which are the bond alternating modes. In such cases, it will be shown that the variations of the π-bonding energy can be identified with the variations of π-*electronic* energy.

The idea is best illustrated by considering a set of six hydrogen atoms arranged in an hexagonal D_{6h} structure as in **3a**, e.g., with H−H bond lengths taken as similar to the C−C bonds of benzene, i.e., 1.40 Å. We are interested in distortions of b_{2u} type that alternately shorten and lengthen the bonds by about the same amout. If the distortion is carried out in such a way that the total repulsion between nuclei is kept constant, as in **3b**, then the variation of *electronic* energy is just the variation of the *total* energy which is itself the variation of bonding energy.

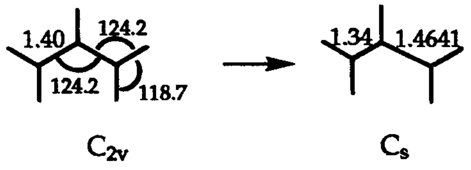


3a **3b**

The same idea carries over to the hydrocarbon case, where bare protons are replaced by carbons bearing (approximately) +1 effective charges. Here the distortion starts from the geometry displaying a regular structure with C−C bond lengths of 1.40 Å and leads to geometries typical of a Kekulé structure where the short bonds take the value 1.34 Å as in open polyenes. Concomitantly, the long bonds are determined so that the distortion preserves the total repulsion between formal positive charges just located at the position of the carbon atoms while the angles are kept unchanged. For benzene and allyl, this leads to the following distortions: **4a** → **4b** and **5a** → **5b** which are extremely close to b_{2u} and b_2 distortions.



4a **4b**



5a **5b**

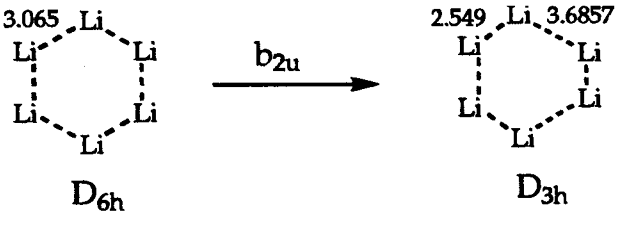
Using distortions of this special type, it becomes a simple task to calculate the distortion energy of the π system in various electronic states as a difference between electronic π energies. The latter are easily calculated through eq 35 if one deals with the SCF level. If one wants to take electron correlation within the π system into account, the distortion energy of the π system can then be estimated following eq 36

$$\Delta E_\pi = \Delta E_{\mathrm{GS}} - \Delta E_\sigma \tag{36}$$

where ΔE_{GS}, the distortion energy of the ground state, is calculated with inclusion of configuration interaction within the π space while ΔE_σ is calculated through eq 34.

Incidentally, the same kind of technique is applicable to separate core electronic energies from valence electronic energies, and this can be used as numerical test of the relevance of our σ−π separation. Consider a ring of six lithium atoms and a distortion that keeps E_{NN} constant, as in **6a** → **6b**. The valence electronic system is a set of six electrons moving over the field created by six positive charges of just one unit.

As the total repulsion between these point charges is kept constant along the distortion, the variation of bonding energy can be estimated from the variation of valence electronic energy. The latter can be calculated through eq 35 in which the subscripts σ



6a **6b**

Table 1. Distortion Energies (kcal/mol) for the Ground State, π System, and σ-Frame for Benzene and Allyl[a]

	ΔE_{GS}[b] (ground state)	ΔE_{π}[c] (ground state)	ΔE_{σ}[d] (ground state)	ΔE_{σ}[e] (bare σ frame)	ΔE_{HS}[f] (high spin)
		benzene			
SCF/6-31G	6.6	−9.7	16.3	14.1	14.5
π-CI/6-31G	7.2	−9.1	16.3		
		allyl			
SCF/6-31G				4.8	4.9
π-CI/6-31G	3.9	−0.9	4.8		
SCF/6-311G				4.7	4.8
π-CI/6-311G	3.8	−0.9	4.7		

[a] The geometric distortions follow **4a** → **4b** and **5a** → **5b**. [b] Variation of the total energy of the ground state. [c] Distortion energy of the π system as calculated from the ground state according to eq 35. [d] Distortion energy of the σ frame as calculated from the ground state according to eq 34. [e] Distortion energy of the bare σ frame. [f] Distortion energy of the high-spin state.

and π are replaced by core and valence, respectively. The distortion energy may also be calculated in the standard way, by comparing the total energies before and after distortion. At the RHF/6-31G* level, the distortion energy was obtained as 5.77 kcal/mol using straightforward calculations compared with 5.61 kcal/mol which is the variation of valence electronic energy using the integral partition. This excellent agreement between both values, with an error smaller than 3%, confirms the validity of the core−valence partition, which is formally analogous to the $\sigma-\pi$ partition above.

The $\sigma-\pi$ partition scheme under constant E_{NN} by means of eqs 34−36 has been used in a straightforward way to study the distortive properties of the π-electronic system in the ground states of benzene, allyl radical, and cyclobutadiene[81−86] and in a number of isoelectronic molecules bearing heteroatoms.[87,88] The typical results for allyl radical and benzene at different computational levels are shown in Table 1.

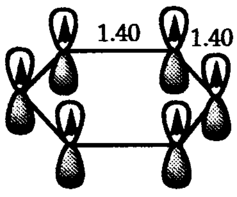
The table shows that the π-electron energy prefers to distort in both systems but is opposed by the σ frame. As may be witnessed from the original literature,[81] these conclusions do not depend on the choice of basis set. With all basis sets studied, the σ frame opposes the distortion while the π component favors it. This technique has, however, two inconveniences: (i) it cannot be applied to extended configuration interaction calculations involving excitations of $\sigma \rightarrow \pi$ type and (ii) it requires the manipulation of integrals that are not automatically provided by the standard ab initio programs. This is why we have deemed it necessary to devise more appealing and more intuitively self-evident ways to separate σ- from π-distortions energies. They all rest on the estimations of the distortion energy of the σ frame.

B. Bare σ-Frame Method

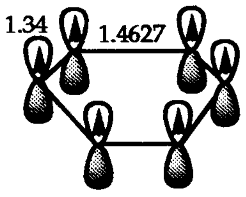
The easiest way to estimate the distortion energy of the σ frame of benzene or allyl is to effectively calculate these molecules devoid of π electrons, i.e., the $(C_6H_6)^{6+}$ and $(C_3H_5)^{3+}$ multications, in the specific geometries **4a**, **4b** and **5a**, **5b**. For the allylic system, this leads to distortion energies of the σ frame which are exactly similar (Table 1) to those calculated in neutral allyl using the integral partition described in section V.A.[81] For benzene, the agreement between both techniques is reasonable: the distortion energy of $(C_6H_6)^{6+}$ is found to be 14.1 kcal/mol using the bare σ-frame method vs 16.3 kcal/mol using the integral partition method.[81] All in all, this shows that the force constants of the σ bonds do not depend much on the presence or absence of the π electrons. For a higher accuracy, it is of course better to take the effect of π electrons on the σ frame into account, as in the two subsequent methods below.

C. High-Spin Method

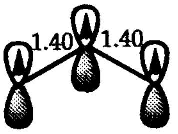
Another way to estimate the distortion energy of the σ frame in the presence of π electrons is to find a reference state in which the π-bonding interaction is “turned off”.



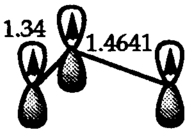
7a



7b



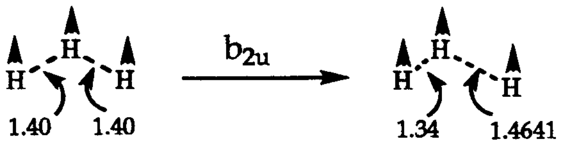
8a



8b

The π-septuplet and π-quadruplet states of benzene and allyl (**7a**, **7b** and **8a**, **8b**) are such states because their π electrons, which possess identical spins, do not form bonds and are energetically almost indifferent to distortion. This distortion alternately shortens and lengthens the distances of local triplet pairs. Now the bond length−bond energy dependence of the triplet state of ethylene is nearly linear in this range of bond lengths, and hence, the shortening and lengthening cause jointly a negligible net energetic effect.

The π insensitivity to the distortion in **7** or **8** becomes evident by calculating the distortion energy of quadruplet H_3 (**9a**, **9b**) which is isoelectronic to the π component of quadruplet allyl radical.



9a **9b**

This distortion is found to be marginally positive (0.5 kcal/mol) at the SCF/6-31G level. Since the overlap between hydrogen orbitals in **9** is larger than the corresponding π-type overlap in **8**, the π contribution to the distortion energy in quadruplet allyl will be even smaller than 0.5 kcal/mol. This intuitive order of magnitude can be made more quantitative by effectively calculating the distortion energy of the π component of the quadruplet allyl using the integral partition above (eq 35). The so-calculated value appears to be extremely small, 0.1 kcal/mol at the SCF/6-31G level.[81] The same type of calculation yields a distortion energy of 0.8 kcal/mol for the π component of the π septuplet of benzene.[81] It follows that the high-spin states of conjugated molecules have nearly the same distortion properties (within less than 1 kcal/mol) as the σ frames of the ground states, provided the distortion preserves the total nuclear repulsion between the carbon centers. The distortion energy of the π components of the ground state are then calculated, to a good approximation, as the difference between the total all-electron distortion energy of the ground state and the total distortion energy of the high-spin state (eq 37). This technique has the advantage of simplicity (no integrals to handle) and of being compatible with CI calculations of any desired level of accuracy.

$$\Delta E_{\pi} = \Delta E_{\mathrm{GS}} - \Delta E_{\mathrm{HS}} \tag{37}$$

It has been argued, however,[89] that the high-spin states experience some exchange repulsions which are not present in the ground states and that this could more or less influence the force constants of the σ bonds. To rule out this criticism, we have proposed the "quasiclassical state" method which is described below.

D. Quasiclassical State Method

1. Definition of Bonding Energies in Valence Bond Theory

The exact definition of bonding energy for two interacting fragments is the difference in total energy between the molecule at equilibrium geometry and at the separated fragments limit. This definition is, however, of no use for calculating π-bonding energies, since π bonds are always associated with an underlying σ bond. Valence bond (VB) theory offers a solution to the problem by allowing the formulation of a reference nonbonding electronic state, at equilibrium geometry, which permits a definition of the bonding energy of a given species, independently of the nuclear repulsion. This state is the spin-alternant determinant of an electronic system, which is referred to hereafter as the "quasiclassical" (QC) state, because its energy is concerned with the classical energy terms which sum up to zero. This quasiclassical energy has been used already by Kutzelnigg[90] to obtain a lucid picture of the physical origins of the chemical bond in the H_2 molecule. Malrieu[91−96] and others[97] emphasized the special status of the QC state (called there the spin-wave state or the Neel state). Malrieu used this state extensively in his VB treatment of conjugated hydrocarbons. This approach was further extended by Bernardi, Robb, and co-workers in their MM-VB method,[98−102] which combines a molecular mechanics force field description of the inactive atoms with a parametrized Heisenberg Hamiltonian valence bond description that represents the active electrons of a CASSCF calculation. This method has proved able to reproduce very well the ab initio results on covalent ground and excited states of quite large hydrocarbons.[99,103,104] Thus, the QC state can be used as a starting point for a $\sigma-\pi$ separation either in the MO or in the VB framework, and we will give examples of both treatments. Hereafter we wish to apply the QC state to elucidate the behavior of the bonding energy which is associated with the π electrons in benzene.

2. Quasiclassical State of H_2

Let us consider, first, briefly the H_2 molecule, with χ_a and χ_b being the atomic orbitals of the two hydrogen atoms, H_a and H_b. The corresponding QC state is defined then as the spin-alternant determinant in eq 38, where the two electrons in the spin orbitals, χ_a and χ_b, have opposite spins without being coupled into a singlet spin.

$$\Psi_{\mathrm{QC}} = |\bar{\chi}_a\chi_b| (\mathrm{or} |\chi_a\bar{\chi}_b|) \tag{38}$$

The quasiclassical feature of such a state is that its energy is nearly independent of the nuclear repulsion, so that its energy curve will be flat throughout the internuclear distance, from infinite distances to the region of equilibrium geometry.

This flatness of the QC energy curve eliminates altogether the problem of how to handle the E_{NN} term and allows a calculation of the bonding energy of H_2 to a good approximation. The bonding energy becomes then simply the difference between the energies of the ground state and the QC state, at any given internuclear distance. Moreover, the ground state (GS) can be taken at any desired level, RHF, CI, VB, etc., and provide thereby the bonding energy (E_{B}) and bond dissociation energy (D_{e}) appropriate to that level, as generalized in eq 39.

$$E_{\mathrm{B}} = E_{\mathrm{GS}} - E_{\mathrm{QC}} \quad (D_{\mathrm{e}} = -E_{\mathrm{B}}) \tag{39}$$

Technically, the energy of the QC state E_{GS} can be computed either by means of a VB ab initio method or more simply by using a guess function as input into standard ab initio programs (Gaussian, GAMESS, etc.).

Figure 1 shows the full CI curve (with the 6-31G basis set) for H_2. The dissociation energy at the full CI level is 97.4 kcal/mol, while the value defined by eq 39 relative to the QC state is 95.3 kcal/mol. Of course, this excellent agreement is rather fortuitous, since it rests on a coincidence of the QC curve with

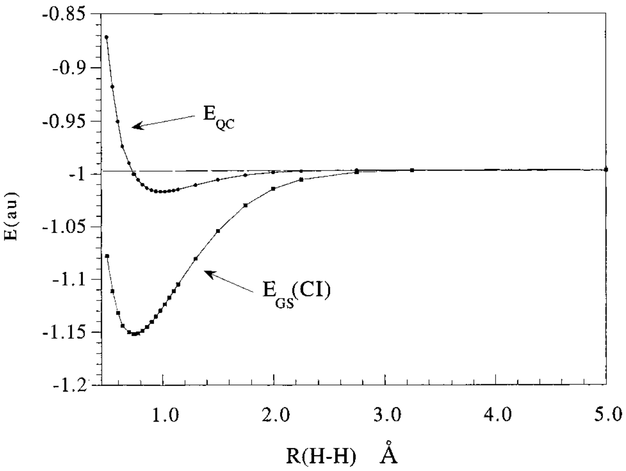
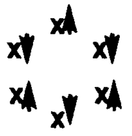


Figure 1. Quasiclassical (QC) and full CI energy curves for H_2 using the 6-31G basis set.

the asymptotic energy in Figure 1. Yet the bonding energy of the QC state remains small at any internuclear distance between equilibrium and infinite separation, so that the QC state appears as a convenient reference for defining bonding energies, at a good range of internuclear distances, for any computational level and with reasonable accuracy.

3. Quasiclassical State of X_6 Hexagons

To study the delocalization problem in a hexagonal six-electron-six-orbital species X_6, we must first establish a proper behavior of the QC state of these many-electron systems. The QC state is shown in **10**, and its wave function is given by eq 40, for a general case where core orbitals also exist. Thus, the AOs, χ, can be the 1s orbitals of H or the $2p_\pi$ orbitals of C, with the appropriate core orbitals whenever present. The ground state in **11** is the familiar delocalized state which is also traditionally represented as a resonance between two Kekulé structures.



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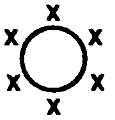

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$$\Psi_{QC} = |(\ldots\text{core}\ldots)\bar{\chi}_a\chi_b\bar{\chi}_c\chi_d\bar{\chi}_e\chi_f| \tag{40}$$

Along the b_{2u} mode the changes in the 1−3 triplet repulsion are expected to be mutually compensating. That this is indeed the case is apparent from Table 2. The first energy column shows the energy changes of the QC state upon b_{2u} distortion for H_6 made of six hydrogen atoms, initially arranged to match the positions of the six carbons in benzene. The QC state was calculated[7] with the 6-31G basis set, in various geometries ranging from the D_{6h} hexagon with R_{HH} equal to 1.39 Å all the way to a highly distorted D_{3h} hexagon with alternating bond lengths of 1.50 and 1.28 Å.

Table 2. Distortion Energies (kcal/mol) of Hydrogen Rings and Their Quasiclassical States for Various Bond Lengths (Å)

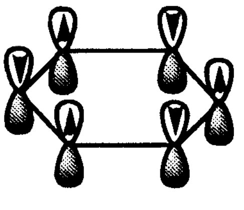
bond lengths	ΔE_{QC}	ΔE_{GS}[a]
(1.39/1.39)	0.0	0.0
(1.40/1.38)	−0.01	−0.11
(1.41/1.37)	−0.03	−0.42
(1.42/1.36)	−0.06	−0.95
(1.43/1.35)	−0.11	−1.67
(1.44/1.34)	−0.18	−2.59
(1.45/1.33)	−0.26	−3.71
(1.46/1.32)	−0.35	−5.00
(1.47/1.31)	−0.45	−6.47
(1.48/1.30)	−0.57	−8.10
(1.49/1.29)	−0.70	−9.88
(1.50/1.28)	−0.84	−11.80

[a] Calculated at the CISD level with size consistency correction.

It is seen from Table 2 that the energy curve ΔE_{QC} of the quasiclassical state is extremely flat, along the b_{2u} distortion, relative to the variation of the ground-state energy (ΔE_{GS}) of this system, which is calculated at the CISD level. It is apparent, therefore, that the energy difference between the ground state of H_6(1s) and its corresponding QC state along the b_{2u} distortion, i.e., $\Delta E_{GS} - \Delta E_{QC}$, will be reasonably close to the exact values of the actual distortion energy (ΔE_{GS}). It follows therefore that *the problem of delocalization can be studied safely along the b_{2u} mode, which is also the traditional localizing mode for hexagons.*

4. Application to π-Bonding in Benzene

Let us now consider the benzene molecule itself. The QC state is represented by a determinant in which the π system is made of pure π atomic orbitals exhibiting alternate α and β spins as in **12**.



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It represents an electronic state in which the π-bonding interaction is nearly set to zero. At the same time, the π electrons are present over the σ frame but do not exhibit any excess exchange repulsions. Therefore, the distortion energy of this QC state is very close to the distortion energy of the σ frame in the field of the π electrons when the molecule is in its ground state. As for the approximate π-binding energy E_B^π, it is given by eq 41 and is defined as the energy difference between the ground state and the QC state.

$$E_B^\pi = E_{GS} - E_{QC} \tag{41}$$

It is important to emphasize that the QC state approach for calculating the contribution of the π bonding to the distortion energy does not require *any σ–π partitioning* of integrals nor does it suffer from the E_{NN} problem. Therefore, eq 41 can be used to

Table 3. Distortion Energies ΔE (kcal/mol) of C_6H_6 along b_{2u} Distortion Modes R (Å)

	distortion		energy		
entry	$R(D_{6h})$	$R_1/R_2(D_{3h})$	ΔE_{QC}	ΔE_{GS}	ΔE_B^{π} [c]
1	1.39	(1.33/1.45)	+13.2	+7.5	−5.7
2	1.39	(1.28/1.50)	+45.3	+27.0	−18.3
3	1.45[a]	(1.39/1.51)	+9.5	+4.2	−5.3
4	1.45[a]	(1.36/1.54)	+21.6	+9.9	−11.7
5	1.40[b]	(1.34/1.4627)	+12.5	+7.1	−5.4

[a] This distance corresponds to the energy minimum of the QC state. [b] This entry corresponds to the distortion used in section V. [c] All values of ΔE_B^{π} are determined at the CISD(π) level with Davidson correction, using eqs 40−42.

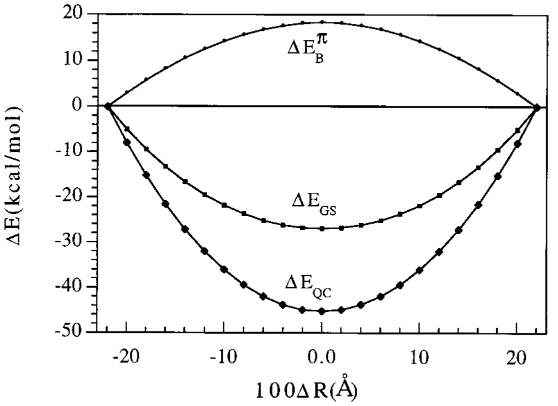


Figure 2. Energy changes due to the distortion of benzene from D_{6h} to D_{3h}. The CC bond lengths are 1.39 Å in the D_{6h} geometry, and the distortion keeps constant the sum of CC bond lengths. ΔR is the difference between the long and short CC bonds in the hexagon. All the energies are arbitrarily anchored at the zero of the energy scale. The ΔE_B^{π} corresponds to the bonding energy change (eq 42) of the π component. The other curves are the ground state (GS) and the QC state curves.

compute absolute values for the total π bonding energy as well as distortion energies for the π bonding system. In this latter case, *any type of distortion* can be envisaged and not only specific distortions as **4a** → **4b** above.

Some distortion energies for the ground state, the σ frame (QC state), and the π bonding system are displayed in Table 3 and in Figure 2.

These have been calculated as follows. In the first step, the resistance to distortion, ΔE_{GS}, of the D_{6h} ground state (with $R_{CC} = 1.39$ Å) is calculated at the level of CISD with Davidson correction for size-consistency among π electrons. The second step consists of calculating the resistance of the QC state to the same distortions as above. The QC state is calculated with the same σ orbitals as in the ground state at any point along the b_{2u} distortion. Finally, the distortion energy of the π system, ΔE_B^{π}, is the difference between the two latter quantities

$$\Delta E_B^{\pi} = \Delta E_{GS} - \Delta E_{QC} \tag{42}$$

The computational experiment has been applied[7] starting from several D_{6h} geometries of benzene (with $R_{CC} = 1.39$, 1.40 and 1.45 Å) and with distortions of various magnitudes (±0.06, ±0.09, and ±0.11 Å). Note that the distortions can now be such that the bond lengthenings are strictly equal to the shortenings, since the π energy in this method is free from the E_{NN} problem. The specific distortion **4a** → **4b** has also been included for comparison. It appears that in all cases the QC state of benzene, just like the high-spin state or the bare σ frame, resists a b_{2u} distortion more than the ground state and that the delocalized π-bonding system of benzene is distortive and prefers a D_{3h} structure. The agreement is not only qualitative but also quantitative, showing that the four methods of σ−π separation that have been described above (partition of integrals, bare σ frame, high-spin, and QC states) lead to comparable distortion energies for the π system of benzene.

5. Other Conjugated Systems

The quasiclassical method is general and can be applied to any even-membered ring or any conjugated system in which a spin-alternated determinant can be conceived, thus defining the π nonbonding state. However, for other conjugated systems, e.g. odd-membered rings, no spin-alternated determinant can be found. For example, in C_5H_5, the lowest determinant has two identical spins. In such cases, since there is no way to fully create a QC state, the reference determinant can be defined always as the lowest one. In odd-nonalternant systems, the lowest determinant will involve a triplet π-repulsion and the bonding and delocalization energy can be quantified with respect to that. If one insists on always having a QC reference, it is possible to define one even for odd-nonalternant systems by quantifying the triplet repulsion which is trivial, using triplet and singlet ethylene.

VI. Integral and Nuclear Repulsion Partition Method

As already mentioned in section IV.A, one of the initial problems with the σ−π partition was the role of the nuclear repulsion energy E_{NN}. In the partition scheme described in eqs 11 and 33−35, the nuclear repulsion energy was incorporated into the σ part of the total energy. To eliminate the influence of nuclear repulsion energy on the interpretation, the term E_{NN} was kept constant during the distortions.[81]

In this partition scheme distortions, which do not keep E_{NN} constant, are excluded. This was the reason why an alternative partitition scheme was introduced.[6]

$$E_{\sigma} = E_{\sigma}^{\text{core}} + E_{\sigma\sigma} + \frac{1}{2}E_{\sigma\pi} + E_{NN}^{\sigma}$$

$$E_{\pi} = E_{\pi}^{\text{core}} + E_{\pi\pi} + \frac{1}{2}E_{\sigma\pi} + E_{NN}^{\pi}$$

with

$$E_{NN} = E_{NN}^{\sigma} + E_{NN}^{\pi} \tag{43}$$

This means that the electronic interaction energy $E_{\sigma\pi}$ between σ and π electrons and the nuclear repulsion energy E_{NN} are no longer parts only of the π energy and the σ energy, respectively, but are partitioned in a similar way. The partitioning of $E_{\sigma\pi}$ into two equal parts assigned to the σ energy and π energy is supported by eq 13. If the total electronic energy E_{el} is written as a sum of one-electron contributions, it leads exactly to the partition in eq 43.

$$\begin{aligned} E_{\text{el}} &= \sum_i^{\text{occ}} (\epsilon_i^{\text{core}} + \epsilon_i) \\ &= \sum_i^{\text{occ}} (2\epsilon_i^{\text{core}} + \sum_j^{\text{occ}} G_{ij}) \\ &= \sum_i^{\text{occ}\sigma} (2\epsilon_i^{\text{core}} + \sum_j^{\text{occ}\sigma} G_{ij} + \sum_j^{\text{occ}\pi} G_{ij}) + \\ &\qquad \sum_i^{\text{occ}\pi} (2\epsilon_i^{\text{core}} + \sum_j^{\text{occ}\pi} G_{ij} + \sum_j^{\text{occ}\sigma} G_{ij}) \\ &= E_\sigma^{\text{core}} + E_{\sigma\sigma} + \frac{1}{2} E_{\sigma\pi} + E_\pi^{\text{core}} + E_{\pi\pi} + \frac{1}{2} E_{\pi\sigma} \quad (44) \end{aligned}$$

It is, therefore, reasonable to partition the nuclear repulsion in a similar way. For this procedure one can imagine that each negative charge of an electron has a corresponding positive charge in a neutral molecule. The nuclear charge of an atom A can, therefore, be written as

$$Z_{\text{A}} = n_{\text{A}}^{\sigma} + n_{\text{A}}^{\pi} \quad (45)$$

Such an assignment can be easily made if the number n_σ of σ electrons and n_π of π electrons in the neutral system is known via an SCF calculation. Now the nuclear repulsion is partitioned as

$$\begin{aligned} E_{\text{NN}} &= \sum_{\text{A}} \sum_{\text{B}<\text{A}} \frac{Z_{\text{A}} Z_{\text{B}}}{R_{\text{AB}}} \\ &= \sum_{\text{A}} \sum_{\text{B}\leq\text{A}} \frac{(n_{\text{A}}^{\sigma} + n_{\text{A}}^{\pi})(n_{\text{B}}^{\sigma} + n_{\text{B}}^{\pi})}{R_{\text{AB}}} \\ &= E_{\text{NN}}^{\sigma\sigma} + \frac{1}{2} E_{\text{NN}}^{\sigma\pi} + E_{\text{NN}}^{\pi\pi} + \frac{1}{2} E_{\text{NN}}^{\sigma\pi} \\ &= E_{\text{NN}}^{\sigma} + E_{\text{NN}}^{\pi} \quad (46) \end{aligned}$$

Here $E_{\text{NN}}^{\sigma\sigma}$ and $E_{\text{NN}}^{\pi\pi}$ are the parts of E_{NN} referring to σ electrons and π electrons, respectively. $E_{\text{NN}}^{\sigma\pi}$ is the part related to both σ and π electrons. This form of the nuclear repulsion remains unchanged if cations or anions of a molecule are considered. In such a case, only the electronic energy E_{el} will change.

This separation has the advantage that it allows arbitrary distortions of the molecule to be considered. The nuclear repulsion energy E_{NN} does not have to be kept constant. With this scheme of partitioning and the definition of a resonance coordinate[6] which interpolates the situation between the equilibrium structure of benzene and the two Kekulé structures, it can be shown that the energy curve for the σ energy E_σ has a positive curvature upon distortion from the equilibrium whereas the energy curve for E_π has a negative curvature (Figure 3). This means that the σ-energy component resists distortion, whereas the π-energy component favors distortion. In this sense, the σ framework tends to bond equalization and the π framework tends to localization. Since the curvature for the σ framework is larger, the bond equalization is favored. It was further proved for a series of six-membered azines with one to six nitrogen atoms that the qualitative conclusion drawn for benzene about the behavior of the σ and π framework is the same (Figure 4). Only the relative slopes of the σ- and π-energy curves are different. For hexaazine, the curvature of the E_σ and E_π curves were almost the same. A distortion of N_6 from D_{6h} to D_{3h} is favored because the curvature of the E_π curve is the larger one.

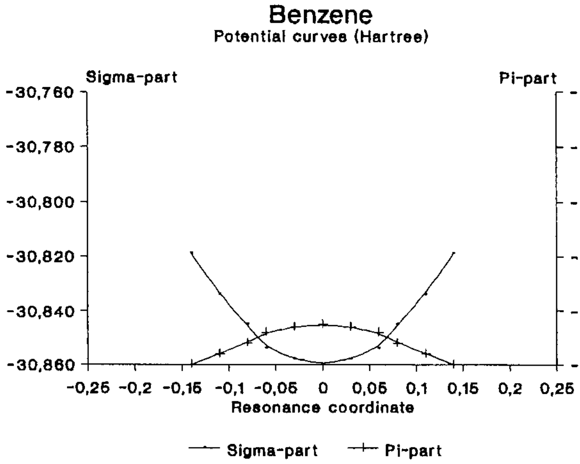


Figure 3. Dependence of σ and π parts of the total energy of benzene on the resonance coordinate.

The same behavior was found also for heterocyclic five-membered rings, although no symmetry of distortion can be observed in these cases. In the case of cyclobutadiene (Figure 5), the curvature of E_σ was clearly smaller than that of E_π, leading to the rectangular arrangement. A small CI calculation did not change the picture. In contrast, cyclobutadiene dication restricted to a planar form showed positive curvature for both E_σ and E_π, indicating a double resistance to distortion from equal bond lengths, so that a square would be the most favorable planar structure. Of course, the equilibrium structure of $C_4H_4^{2+}$ is puckered. It could be shown that the principal features for the σ- and π-energy curves are conserved also for butadiene. This means that not only in ring systems but also in open-chain π systems there is a tendency of the π framework to localize, in line with the findings on allyl described in the previous section.

VII. Other Approaches of σ–π Separation

A. Supporting View

Soon after the appearance of the new view[83,84] about the driving force for the D_{6h} structure of benzene, Hückel theory was reexamined by Kataoka and Nakajima.[105] They concluded that the traditional view, in which the π-electron delocalization energy

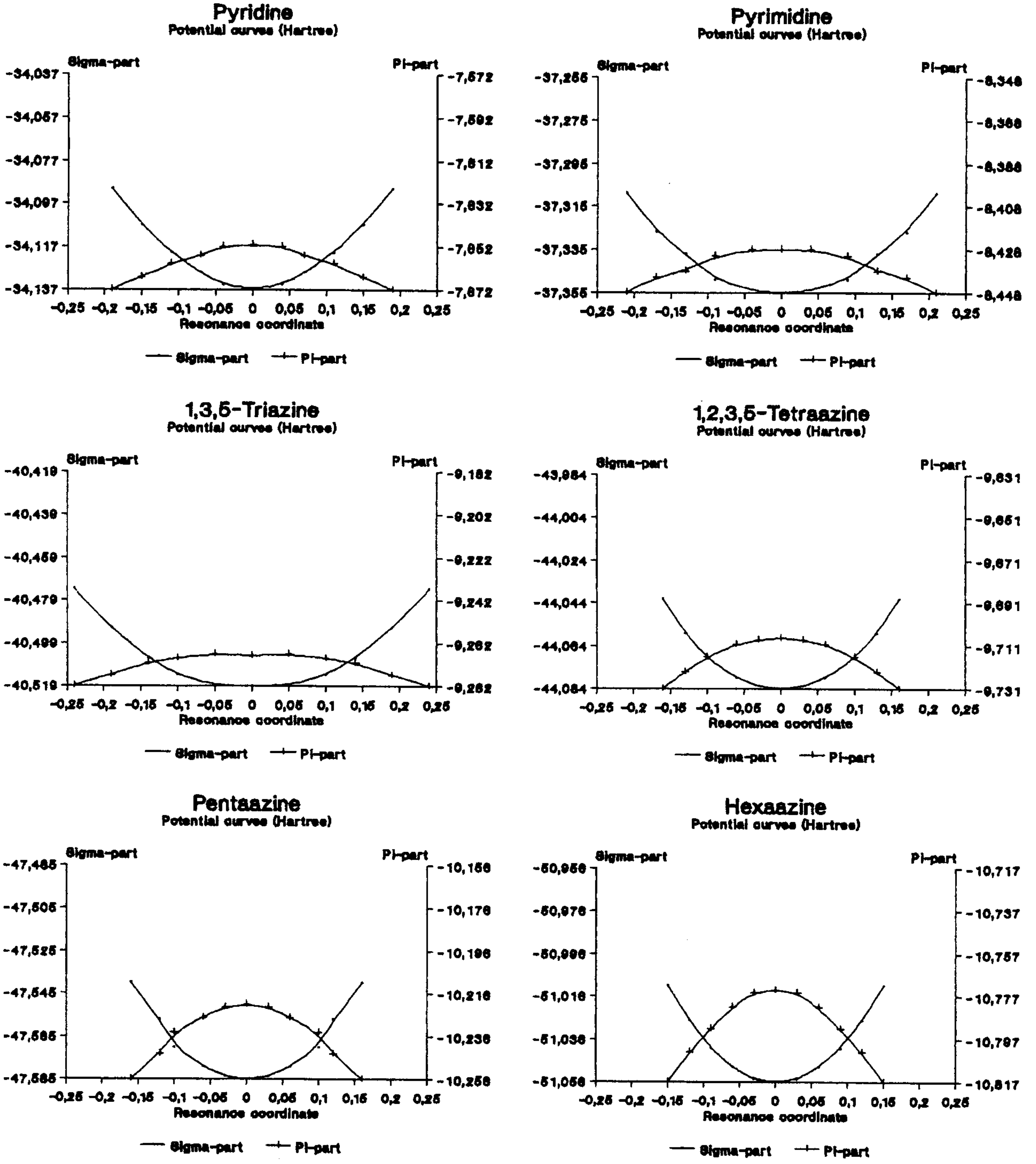


Figure 4. Dependence of σ and π parts of the total energy of different azines on the resonance coordinate.

(DE) is useful as a theoretical index to the empirical resonance energy (RE), would be erroneous under the circumstances that the symmetrical hexagonal structure of benzene is driven by the σ framework alone and the π electrons favor a distorted and localized structure. They then derived a formula for RE with a distance-dependent β parameter. They could show that the proportionality between RE and DE exists only under the assumption of a constant β. They criticized the Hess–Schaad justification[46] of the HSRE at the Hückel level, because their results would show erroneously that the σ-compression energy favors a distorted and localized structure. Later they worked out these ideas in more detail[106] with the inclusion of σ energies. They concluded that in benzenoid hydrocarbons the main contribution to the RE is not the π-electron DE but the compression energy of the σ bond. Heilbronner[74] discussed the question of the symmetry structure of molecules at the Hückel level. He showed that even at this level a variable β parameter can lead to a localized structure of benzene. His conclusion that the E_π curve has a negative curvature at the equilibrium structure of benzene and that this is offset by a positive dominating curvature of E_σ is in line with more refined analyses.[6,7] Cooper et al.[107] used VB theory and reported that the π electrons in benzene are virtually localized and that the characteristic properties of the system arise from the switching in the mode of spin coupling. However, it appears that they

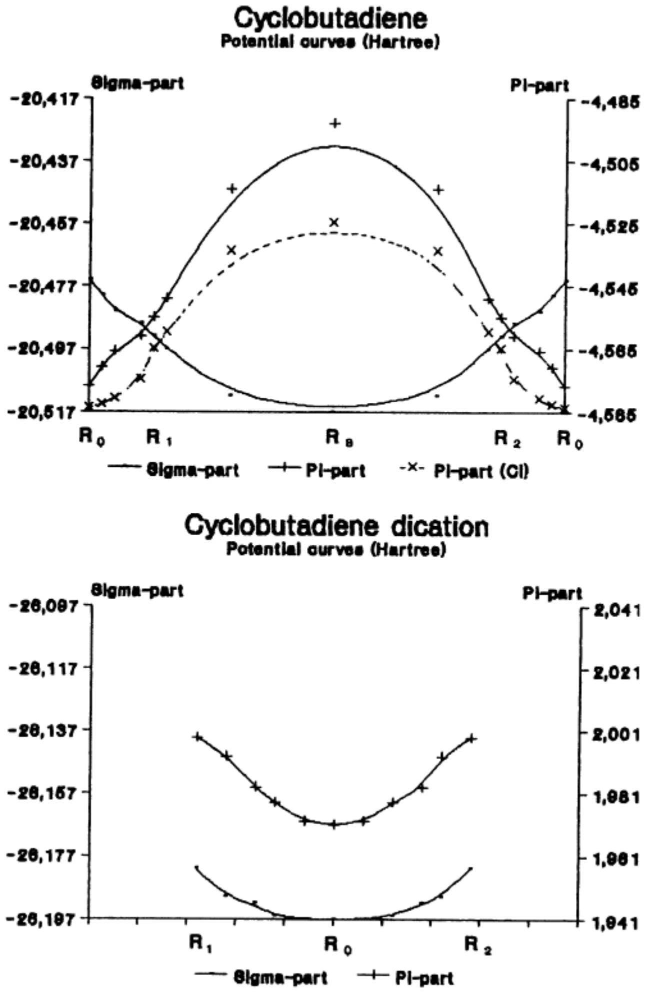


Figure 5. Dependence of σ and π parts of the total energy of cyclobutadiene and cyclobutadiene dication.

have only found that benzene can be accurately described by two Kekulé structures of equal weight.

Janoschek[108] criticized the assumption that π-electron delocalization is the reason for the D_{6h} structure of benzene. He used two arguments to invalidate this view. He compared the total π-overlap population of benzene (D_{6h}) and fictitious cyclohexatriene (D_{3h}) and found these to be equal with a value of 0.87. However, the CC σ-overlap population of 1.946 favors D_{6h} over for D_{3h}, where the overlap population is only 1.914. In addition, he used the Walsh diagram to compare the change of MO energies along the distortion from D_{6h} to D_{3h}. It was found that the three highest occupied MO (HOMO) levels behave in the following way. There is no change in the energy of the third HOMO $a_{2u}(\pi)$, whereas the $e_{2g}(\sigma)$ level is raised and the $e_{1g}(\pi)$ level is lowered upon benzene distortion. Since the raising of the σ level is more pronounced than the lowering of the π level, it was concluded that benzene resists distortion to cyclohexatriene due to the resistance of the σ framework.

A similar line of argument was pursued by Ou and Chu.[109] The mono-, bis-, and trisannelated benzocyclobutenes show the Mills–Nixon effect[110] which gives rise to alternation of CC bond distances in benzene. Interest in such studies was revived by the synthesis of tris(benzocyclobutadieno)benzene,[111] where the inner benzene ring showed a pronounced cyclohexatriene structure. Theoretical studies on such systems, where the benzene ring is fused to a small ring,[112–115] showed rehybridization of the fused carbon centers. This rehybridization of the benzene ring is expected to cause a CC bond alternation. Ou and Chu studied the mono-, bis-, and trisannelated benzocyclobutenes and compared their properties with those of the di-, tetra-, and hexasubstituted benzenes. They found increased bond alternation with increasing number of annelated rings accompanied by an increase of the s character of hybrid orbitals on the carbon atoms involved in the annelation. In contrast, the s character for the hybrid orbitals of the methyl-substituted site was constant. The authors used the sum of the three occupied π MO levels as an approximation to the total π-electron energy. They found that the π energy increases more slowly with increasing annelation than with increasing substitution. In consequence, stability of the annelated systems was increased compared to the corresponding methyl-substituted systems. Since annelation led to bond alternation, they concluded that the π electrons favor an alternating benzene ring and disfavor the highly symmetric structure.

Jenneskens et al.[116] analyzed this problem via the Dewar π-electron method[64–68] described in section III.C. Dewar's heat of formation of eq 29 is reformulated as

$$E_{\text{tot}} = E_\pi + E_\sigma + nE_{\text{CH}} \tag{47}$$

using the dependence of E_π and E_σ along a distortive reaction coordinate of b_{2u} symmetry. It was found that E_π is lowered upon distortion, whereas E_σ is raised and is the dominant force behind the D_{6h} structure.

Finally, Gobbi and Frenking[117] analyzed the allyl cation, radical, and anion. They stated that their results show that π-electron delocalization is a stabilizing factor operative in the symmetric (C_{2v}) and bond alternating (C_s) forms of the planar compounds. Delocalization resists the rotation of the methylene groups but not necessarily bond alternation. Subsequently, they analyzed the distortion energy for the three allyl systems. They partitioned the total energy in three parts

$$E_{\text{tot}} = E_\sigma + E_\pi + E_{\text{NN}} \tag{48}$$

Here E_σ and E_π correspond to eqs 34 and 35. When the total nuclear repulsion energy E_{NN} was kept constant, they found in all three cases that E_σ is raised and E_π is lowered upon distortion. The σ framework was found to be responsible for the C_{2v} symmetry of these structures. In a more comprehensive study of this question, Gobbi et al.[118] commented on the role of σ and π stabilization in benzene, allyl cation, and allyl anion. Their analysis was based on the first and second derivatives of the SCF canonical orbital energies ϵ_i with respect to normal coordinates Q. Since those energy derivatives show the behavior of the σ and π orbitals with respect to the deformation along each normal coordinate, the results indicate whether the orbital is stable or unstable toward deformation. They found that the second derivative of the HOMO π of the allyl cation with respect to the b_2-asymmetric CC stretching mode has a negative value. This means that the π-orbital energy is unstable along this asymmetric distortion. In contrast, the energy derivative of the second HOMO (σ) has a large positive value. Therefore, the σ-orbital energy is stable along the asymmetric stretching mode. The corresponding orbitals in the allyl anion show the same behavior. The nonbonding HOMO (π) has a positive value in this case. However, the other bonding π orbital has a large negative value, thus dominating and favoring distortion in the π system. The overall effect of all σ orbitals is, however, to resist this distortion. The same situation was observed for benzene.

Kollmar[119] introduced vertical and adiabatic resonance energies on the ab initio level. He proposed constructing the nonresonating π orbitals of a reference state according to three methods: (a) localized π MOs ascribed to the double bonds of the reference state are transferred from an SCF calculation of ethylene; (b) the basis function coefficients of the strictly localized π MOs of the reference state are obtained as the square roots of the corresponding diagonal elements of the bond order matrix of the conjugated system, (c) localization of the delocalized MOs and truncation. He could show that the energy of the reference state of benzene decreases upon bond alternation and that a minimum is reached. He emphasized relaxation of the σ orbital for the reference state. In the spirit of Kollmar, a method for a delocalization energy was developed where the interaction elements between σ and π blocks of the Fock matrix were removed and strictly localized π orbitals obtained.[120] It could be shown that the structural optimization of such a localized reference state leads to a cyclohexatriene-like structure for benzene and allows the calculation of an adiabatic delocalization energy. However, it was gratifying to see that regardless of whether the π electrons are strictly localized or calculated with the usual SCF procedure, the slope of the π-energy curves is negative upon distortion from the benzene equilibrium structure. Of course, the delocalization of the π electrons obtained from the usual SCF procedure is only partially reduced upon distortion. Mo et al.[121] used a VB SCF technique for their study of resonance energies. They studied vertical and adiabatic resonance energies of allyl cation, radical, and anion. They found that the weight of the short double–long single bond increases while that of the short single–long double resonance structure decreases when an allyl system distorts from a regular (C_{2v}) geometry to a bond alternant (C_s) geometry, quite in line with expectation. They explain the rotation barriers of the compounds in terms of changes in the delocalization.

Schütt and Böhm[122–124] investigated the consequences of correlation on the geometrical structure of conjugated systems. They used a Hückel model with fixed β to study the relation between bond alternation and charge fluctuation. Charge fluctuation originates from the admixture of ionic configurations to the covalent SCF configuration of benzene and other conjugated systems. They found, not unexpectedly, that correlation in the π system supports bond alternation. This trend is, however, compensated by mutual π–σ coupling which stabilizes the nonalternant structure. Unfortunately, the authors do not use the terms localization and delocalization in the usual sense. They refer to atomic localization which is related to the ionic contributions of the wave function.

Following the Longuet-Higgins–Salem[76] approach, Buck[125] studied the tendency of aromatic monocyclic compounds to bond alternation with increasing ring size. He used the Hückel model with variable β for the π electrons and a Morse potential for the σ electrons. His distortion energies show that the σ system resists distortion and the π system favors distortions from D_{nh} to $D_{(n/2)h}$ symmetry in C_nH_n annulenes with $n = 6, 8, 10, 12, 14, 16$. The symmetry of the HOMO and LUMO is used to predict whether the $C_{30}H_{30}$ bond alternation due to the π electrons should occur. It was subsequently shown[126] that this method can also be applied to the characterization of antiaromatic polycycles.

B. Opposing View

The opposition to the challenge of the traditional view has been limited to a few studies in which several points in the procedure and new interpretation of the role of σ and π electrons have been criticized. Baird[127] criticized the conclusions of Hiberty and Shaik,[82,83] because in his opinion these conclusions depend critically on a questionable assumption concerning the bond distances for the alternating structure. He expected that their conclusions will be reversed if more appropriate values will be used and that the traditional view—that the symmetrical structure is due to the π electrons—will be recovered. In their rebuttal, Hiberty and Shaik[128] argued that any one distortion mode is sufficient to prove instability of a structure toward a localizing distortion which lowers the energy of a localized structure. The objection by Baird has been laid to rest by partition of electron–electron and nuclear repulsion[6] described in section VI, where no restriction on the pathway is involved, and the results were qualitatively the same as in the earlier papers,[81,82] namely, decrease of E_π upon b_{2u} distortion.

Aihara[129] took up the objection by Baird to examine arguments from both sides. He used the Dewar–de Llano PPP method combined with a bond order–bond length relationship[67,68] to analyze the electronic structure of benzene and related structures. The energy of the σ frame was estimated by means of a Morse function with parameters established by Dewar and de Llano. Aihara then introduced four ring structures: an alternating polyene-like structure (A), a symmetric polyene-like structure (B), a distorted aromatic benzene (C), and a symmetric aromatic benzene (D). In structures A and B the π electrons were strictly localized in three olefinic $-CH{=}CH-$ units. He found that the transition from D to C is accompanied by an increase of the σ energy by 4.71 kcal/mol and a slight decrease of the π energy of -0.63 kcal/mol. The transition of D to B can be described by the vertical resonance energy and from D to A as the adiabatic resonance energy.[119] The vertical resonance energy of 28.92 kcal/mol is caused in this model only by the π electrons, whereas the adiabatic resonance energy of 20.03 kcal/mol can be attributed both to the σ electrons (4.71 kcal/mol) and to the π electrons (15.72 kcal/mol). Although his results for the transition from D to C confirm the new view, Aihara remarked that the π energy for symmetric and distorted benzene is essentially the same, because the increase in π energy due to bond-length alternation almost cancels the decrease in π energy due to diminished aromaticity. He concluded that it is true that the π frame of benzene would have a faint propensity to distort without the buttressing effect of the σ frame but that this does not contradict Baird's conclusion that the main symmetrizing force in benzene originates from the π frame.

Shortly afterward, Glendening et al.[130] examined the influence of π delocalization on the geometry of benzene at the ab initio SCF level of theory. They found that benzene favors a bond alternating geometry when canonical π MOs are replaced by three localized ethylenic orbitals. They concluded that delocalization of the π electrons is in part responsible for the equilibrium symmetric structure, in accord with classical resonance theory. However, it was shown already in the original work[81] and subsequently[120] that there is no contradiction between the traditional view concerning the resonance energy and the new view that the tendency of the π system is to distort benzene. The partitioning scheme[6] described in section VI was again used to study the behavior σ and π components of the energy in benzene upon distortion. Here the π-energy curves for both the delocalized and the strictly localized π systems were calculated along a distortion coordinate. The energy of the delocalized π system was always lower than that of the strictly localized π system, thus defining a positive vertical resonance energy. This corresponds to Aihara's vertical resonance energy for the two pairs of structures A−C and B−D. However, both π-energy curves E_π^{del} and E_π^{loc} decreased upon distortion, thus indicating the general tendency of π electrons to prefer alternating structures, even in cases where the resonance energy is large. Although the situation seemed to reach a consensus at that time, contributions by Ichikawa and Kagawa[131−133] revived the discussion. Their starting point is the following energy partition

$$E = E_\sigma + E_\pi$$

$$E_\sigma = E_\sigma^{\text{core}} + E_{\sigma\sigma} + \frac{1}{2}E_{\sigma\pi} + E_{\text{NN}}$$

$$E_\pi = E_\pi^{\text{core}} + E_{\pi\pi} + \frac{1}{2}E_{\sigma\pi} \qquad (49)$$

Of course, this partitioning is not equivalent to the partitioning of either eq 11 or eq 43. It is unbalanced and cannot be supported by reasonable physical arguments. The authors claimed that in π-electron theories such as the Hückel method or the PPP method the π electrons are considered to move in the average field created by the σ electrons as well as the nuclear charges. They thought that it may be most appropriate to include E_{NN} in the σ energy. However, this is not compatible with the partition of the σ−π electronic repulsion energy into two equal parts for the σ and π energy, respectively. It has been explained in section V that there is a correspondence between repulsion between the negative electrons and the repulsion between the positive nuclei. Partitioning of $E_{\sigma\pi}$ requires partitioning of E_{NN}. It is not very surprising that the allocation of $^1/_2E_{\sigma\pi}$ to the π energy as compared to eq 11 changes the value of the π energy and modifies its behavior along a distortion coordinate. On the basis of the above partition scheme of eq 49, the authors[131] argue that stabilization or destabilization of the π system is highly dependent on the reaction coordinate. Thus, even though they find a π-electron energy decrease along the b_{2u} distortion coordinate, they prefer to emphasize the π-electron energy increase along a minimum energy pathway. As mentioned already, it is sufficient to find a single bond alternating mode that lowers the π energy to deduce that the π component is unstable toward a localizing distortion.[128] In fact, as shown by Hiberty et al.,[128] even the highly distortive H_6 (D_{6h}) species may appear "stable" if one applies an arbitrary distortion which is a strong mixture of b_{2u} and a_{1g} mode. Such a conclusion for H_6 would, of course, be erroneous, and the finding of an energy increase of the π energy along a_{1g} by Ichikawa et al.[131] is, therefore, irrelevant. Ichikawa et al. further proposed the constrained Hartree−Fock method[132] to obtain the total energy and its components as functions of the predetermined electronic structure. In a subsequent paper,[133] they concede that it may now be difficult to obtain a consensus on what π energy is. Nevertheless, by constraining the wave function to a partially or fully localized π system, they obtain vertical resonance energies much like those obtained before.[119,120] Since the emphasis of Ichikawa et al. is restricted to fixed molecular geometries, their theory of constrained Hartree−Fock equations reflects what is already known about vertical resonance energies.

In another study an analysis of the changes experienced by the valence localized MOs of benzene, cyclobutadiene, and 1,3,5-hexatriene was presented.[134] These authors use the electronic energy partitioning of eq 13 which was also used in eq 43, but without the corresponding partition of the nuclear repulsion. They compared these electronic energies $\epsilon_i^{\text{core}} + \epsilon_i$ for the highest-lying MOs of σ- and π-type for undistorted and distorted benzene structures. They found an increase both in the π-electron energy and the σ-electron energy upon distortion. The latter increase was much more pronounced. However, the sum of the π MO energies ϵ_i was reduced upon distortion. It is clear that the neglect of the nuclear repulsion is in part responsible for these results. In addition, the authors[134] used the following criterion for the degree of delocalization[135] of an orbital

$$\text{NOC} = [\sum_A \sum_r^A c_r^2]^{-1} \qquad (50)$$

NOC is a measure for the effective number of centers spanned by the orbital. From their calculations it can be concluded that the delocalization of the π electrons in benzene is reduced upon distortion to a Kekulé structure. Despite these conflicting results, they conclude that the π electrons in benzene can be said to prefer a symmetric geometry.

VIII. Other Applications of σ–π Partition

A. Classification of Substituents

In the initial study of the behavior of E_σ and E_π with the partitioning scheme of eq 43, a resonance coordinate was defined[6]

$$r = \sum_{i}^{\text{atoms}} |\Delta \vec{r}_i| = \sum_{i}^{\text{atoms}} (\Delta x_i^2 + \Delta y_i^2 + \Delta z_i^2)^{1/2} \quad (51)$$

It is calculated as the sum of deviations from equilibrium bond lengths for all ring bonds.

The initial study was then extended to σ–π energy diagrams for substituted rings.[136] In this way, substituted benzene, substituted cyclobutadiene, and substituted trimethylenecyclopropane rings were studied. The question was how the curvature of the E_σ and E_π curves changes under substitution. The two important observations from sequences of substituents in benzene are that π donors have, on average, larger curvatures than π acceptors and that an increase in the σ-energy curvature is accompanied by an increase in the π-energy curvature. For cyclobutadiene substitution it was found that the dominance of the π-electron system is decreased with increasing positive or negative mesomeric effect of the substituent. This means that the more pronounced the donor or acceptor quality of the π system of the substituent is, the less antiaromatic is the substituted ring system. Similar studies were presented for the nonaromatic radialenes. These studies allowed the establishment of a classification scheme for aromatic, antiaromatic, and nonaromatic compounds by two sets of criteria: (1) the slopes of σ and π curves and their relative curvature and (2) the location in the r(L)–r(D) plane, where r(L) and r(D) designate the resonance coordinate of the localized and delocalized structure, respectively.

Some of these ideas could be generalized to a classification scheme for substituents[137] in terms of their donor (D) and acceptor (A) properties. Following the usual partition procedure, four groups were specified: (1) σ acceptor and π acceptor, (2) σ donor and π acceptor, (3) σ donor and π donor, and (4) σ acceptor and π donor. Substituted benzenes were considered, and each system was partitioned in two subsystems. Subsystem A consisted of the benzene ring and subsystem B of the substituents. The change of electronic charge in the carbon framework of the ring due to substitution was defined as

$$\Delta q_A = q_A - q_A^{\text{benzene}} \quad (52)$$

Here q_A is the population of electrons in the substituted system and q_A^{benzene} the reference population of the carbon framework of the unsubstituted system. A population analysis resulted in the distortion depicted in Figure 6, which reflects the presence of the above four groups of substituents. Then the σ–π separation was applied to substituted benzenes and the following energy changes upon substitution were defined

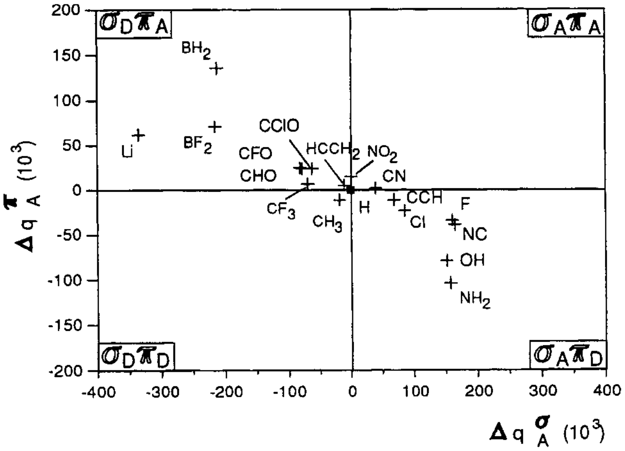


Figure 6. Changes of σ- and π-electron charges in the benzene ring due to substitution. (Copyright John Wiley & Sons.)

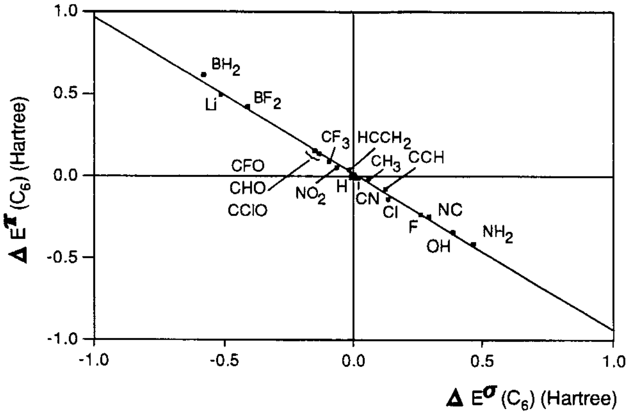


Figure 7. Changes of σ- and π-electron energy in the benzene ring due to substitution. (Copyright John Wiley & Sons.)

$$\Delta E_\sigma(\mathrm{C}_6) = E_\sigma(\mathrm{C}_6) - E_\sigma(\mathrm{C}_6^{\text{benzene}})$$

$$\Delta E_\pi(\mathrm{C}_6) = E_\pi(\mathrm{C}_6) - E_\pi(\mathrm{C}_6^{\text{benzene}}) \quad (53)$$

Here $E_\sigma(\mathrm{C}_6)$ and $E_\pi(\mathrm{C}_6)$ are the σ and π energies, respectively, of the ring system of the substituted benzenes. It was found that a decrease of ΔE_π was accompanied by an increase of ΔE_σ (Figure 7). This dependence was quasilinear. Moreover, positive ΔE_π values and negative ΔE_σ values compared to unsubstituted benzene were obtained for σ-donor–π-acceptor substituents. In contrast, negative ΔE_π values and positive ΔE_σ were found for σ-acceptor–π-donor substituents. Since the relationship was linear, it allowed a classification of substituents on a one-dimensional scale. It was gratifying to see that the relative location on such a linear scale did not change if the benzene ring was replaced by the nonaromatic buta-

Table 4. A=B π-Bonding Energies E^{π}_{B}(A=B) (kcal/mol)[a]

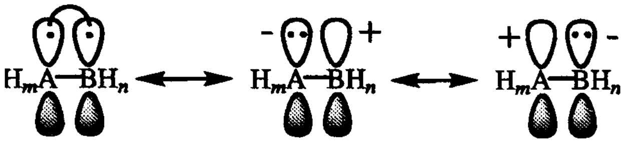
		C	N	O		Si	P	S
(a) C		65 (71)						
N	**1**	63 (81)	60					
O		77 (93)	62					
Si		38 (36)	36 (37)	50 (56)		25 (24)		
P	**2**	43 (49)	44	53	**3**	29 (30)	34	
S		52 (56)	42			50 (44)	40	
(b) C		72.0						
N	**1**	85.6 (81.4)	90.7					
O		105.0 (81.6)	98.2 (90.9)	91.1				
Si		47.1 (53.6)	58.4 (62.9)	79.0 (63.1)		35.1		
P	**2**	52.6 (56.1)	57.2 (65.5)	65.9 (65.7)	**3**	41.9 (37.7)	40.2	
S		60.7 (59.0)	59.9 (68.3)	64.1 (68.5)		57.7 (40.5)	47.5 (43.1)	45.9

[a] (a) Values according to Schmidt et al.[69] and due to Schleyer and Kost.[71] (b) BOVB bond energies calculated by Galbraith et al.[144] with arithmetic average of homonuclear π-bond energies in parentheses.

diene or the antiaromatic cyclobutadiene. This means the classification of substituents is widely independent of the backbone system. The scheme was extendable to borazine and double substitution.

B. Determination of in Situ π-Bonding Energies

In this subsection we shall demonstrate the versatility of the $\sigma-\pi$ separation method based on the QC state by using it as a reference state in a VB calculation of in situ π-bonding energies. The

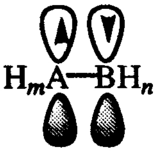


13a **13b** **13c**

H_mA=BH_n 2-electron π bonds can most simply be described as a resonance mixture of the three structures shown in **13**: the covalent Heitler–London (HL) structure, **13a**, hereafter referred to as Φ_{HL}, and the ionic structures **13b** and **13c** designated $\Phi_{A^-B^+}$ and $\Phi_{A^+B^-}$. The total wave function for the π bond then becomes

$$\Psi(H_mA{=}H_n) = c_1\Phi_{HL} + c_2\Phi_{A^-B^+} + c_3\Phi_{A^+B^-} \quad (54)$$

The HL structure itself is a combination of two determinants both exhibiting alternated spins. Either of them, e.g., **14**, can be taken as the QC state for the π A=B bond and will be referred to as Ψ_{QC} in the following.



14

The computation of the ground state $\Psi(H_mA{=}BH_n)$ or Ψ_{GS} for short can be done at any level, from HF to π CI. However, to obtain information on the role of π-bond ionicity, the BOVB method[138−142] was chosen. This method produces generally good dissociation energies due to the inclusion of left−right correlation as well as that part of dynamic electron correlation that is associated with the formation of the bond. Another advantage of working in the VB framework is that it allows the construction of specific states displaying π bonds for the O=O, S=S, and S=O molecules which are normally cylindrically symmetric triplets in their ground states.

The VB wave functions and the corresponding π-bond energies E^{π}_{B} were computed using TURTLE,[143] which is a general nonorthogonal CI program that simultaneously optimizes the VB coefficients (c_1 to c_3 in eq 54) as well as the orbitals. According to the QC state method above, the in situ π-bonding energy of the A=B π bond is calculated by use of eq 41 as the difference between the energy of the ground state and that of the QC state which is taken as the π-nonbonding reference state.

What trends might one expect for π A=B bonds according to the nature of A and B? One may first predict that upon moving from left to right of the Periodic Table, the bond strength should increase because the effective nuclear charge increases and the atomic radius decreases. For σ bonds, this trend is observed from Li−Li to C−C but breaks down for N−N to F−F. This irregular behavior of the σ bonds is the consequence of a weakening effect which is exerted on the σ bond by the lone pairs adjacent to it. This effect termed the lone pair bond weakening effect (LPBWE)[144−147] is due to repulsions between lone pairs of the bonded atoms and their electron pairs. Indeed, when the effects of LPBWE were removed, Sanderson[144] observed the expected bond energy increase from Li to F. In the case of π bonds, LPBWE is not expected due to the orthogonality between the lone pairs and the π-bond pair.

Table 4 displays the A=B π-bond energies as calculated through rotational barriers or through thermochemical cycles (a) and in situ calculated π-bond energies as calculated through the QC state method (b). As the breaking of π bonds is associated, with the QC state method, with no relaxation effects within the σ bond, our π-bond energy values are consistently higher than the π-bond energies of Schmidt et al.[69] and Schleyer and Kost[71] but in line with the intrisic π-bond strengths of Jacobsen and

Ziegler,[148] who applied to C_2H_4 and $SiCH_4$ a method bearing analogies to our procedure.

The A═B π bonds in Table 4 are gathered into three groups, 1−3, depending on whether both A and B belong to the first row of the Periodic Table (group 1), or A and B belong to different rows (group 2), or both A and B belong to the second row (group 3). Within each group, the expected tendency is observed among the in situ calculated π-bond energies: the C═C π bond is weaker than N═N, which is itself weaker than O═O (not much, but this is probably an indirect manifestation of the LPBWE that lengthens the underlying O−O σ bond). Similar trends are observed in the second row. For heteronuclear A═B bonds, moving both atoms from left to right in the Periodic Table also leads to a strengthening of the π bond. That is, π N═O is stronger than π C═N, etc. More generally, *all* the π-bond strengths do increase as expected along a descending diagonal of each group in Table 4b. On the other hand, no clear tendencies are exhibited in Table 4a, which collects the standard values for π-bond energies, according to Schmidt et al.[69] and Schleyer and Kost.[71] According to standard values, the π C═C bond is now *stronger* than π N═N, while π Si═Si is found on the contrary to be *weaker* than π P═P, and more generally the A═B π-bond energy either increases or decreases along a descending diagonal in Table 4a, displaying rather erratic tendencies.

Another tendency that might be expected for π bonds is a superiority of heteronuclear A═B π-bond strengths relative to the average of homonuclear A═A and B═B π-bond strengths. This property, which is observed for σ single bonds, has been stated as a rule by Pauling[149] and formed the basis of his widely used electronegativitiy scale. However, Pauling originally considered only single bonds. He specified that these relations “do not apply to substances containing double or triple bonds”.[149] Since the in situ procedure enables to consider the π bonds as separate entities, it is interesting to seek whether they are subject to the same relationships as single σ bonds.

A comparison of the BOVB calculated E_B^π for heteronuclear π bonds vs the corresponding arithmetic mean values of homonuclear bonds (Table 4b) shows that in some cases E_B^π (A═B) is larger than the average of E_B^π (A═A) and E_B^π (A═B), in accordance with the postulate of Pauling while in other cases it is not.[150] Closer examination of the E_B^π values (Table 4b) reveals that all A═B molecules from groups 1 and 3 in the table obey Pauling's statement while those in group 2 do not [C═S and O═Si are exceptions[151]]. As stated above, Pauling's rule was developed for σ bonds which are free to optimize their lengths and overlaps. However, π bonds are buttressed and their lengths constrained by the σ frame. The π bonds are therefore not optimal. When the two components of the A═B bond are from the same row of the Periodic Table, this buttressing effect is present to a similar extent in both homonuclear bonds and carries over also into the average. However, when A and B are from different rows, the σ constraint is sufficiently different from one row to the other to cause unequal contributions to the average and E_B^π values which are smaller than the average. Be it as it may, the set of in situ calculated π-bonding energies[151] forms a coherent series of values that obey regular tendencies that can be given logical explanations, unlike the commonly accepted values for π bonding energies arising from rotational barriers of thermochemical cycles.

IX. Concluding Remarks

Naturally arising from the symmetry properties of canonical orbitals, the notion of π orbitals and $\sigma-\pi$ separation has largely contributed to popularize MO theory. Moreover, this notion has shaped much of our understanding of chemistry and has led to fundamental concepts such as conjugation, aromaticity, antiaromaticity, and ring currents. Although it has sometimes been claimed (and refuted) that double or triple bonds are actually banana bonds, it is clear that the $\sigma-\pi$ model is universally accepted. In this model, the properties of conjugated systems are governed by two distinct set of bonds, σ and π. The σ bonds of a conjugated molecule are about the same as those of saturated systems and behave as a set of local two-electron bonds. On the other hand, because each π atomic orbital can overlap with more than one neighbor, π systems exhibit electronic delocalization which is at the origin of many of their special properties. The achievements of Hückel theory created the impression that consideration of π MOs alone is sufficient to understand the behavior of conjugated systems. However, many properties of conjugated molecules are governed by an interplay of π and σ energies. One example is the origin of the symmetric geometry of molecules such as benzene which cannot be understood by consideration of π electrons alone. Another problem is the determination of in situ π energies which require a physically sound reference state for the σ frame. Clearly, these problems and a host of others can be treated directly with the advent of rigorous $\sigma-\pi$ energy partition methods of modern electronic theories.

The present review describes several methods.The first three methods (sections V.A−C) involve partition of the energy terms into σ and π varieties along geometric coordinates. The difficulty of partitioning the nuclear repulsion term can be bypassed by limiting the partition to geometric changes that involve constant nuclear repulsion between the atoms which participate in the π bonding. Alternatively, the symmetrical partitioning proposed in the fourth method (section VI) also allows the dissection of the nuclear repulsion terms, using the equality of nuclear charge and the total number of electrons (eq 45). As such, the method based on eq 46 is more versatile and can be used to explore significant portions of the potential energy surface for a given problem.

The last method (section V.D) employs a reference state called the quasiclassical (QC) state which represents the σ frame and avoids thereby the task of dissecting terms. The QC approach is versatile and can be used at any computational level, including density functional theory.[152] The method can also be applied to nonplanar situations as well as to any geometric variation without limitation. It is based on the definition of the nonbonding state for the π system that goes back to the early roots of quantum chemistry. The QC state is, therefore, conceptually lucid and technically easy to use and may, therefore, constitute a general method for applications which require $\sigma-\pi$ separation.

An important test of the various methods is the consistency of their conclusions in a given set of problems. The set of problems used here is the $\sigma-\pi$ interplay in origins of the symmetric geometries of delocalized species such as benzene, allyl radical, etc. This is a stringent enough test because the interplay is very delicate. In this sense, all the methods lead to the same conclusion that the σ frame acts as a symmetrizing factor driving the molecule toward uniform geometries whereas the π-electron component drives the molecules to bond-alternated geometries where short and localized π bonds can be achieved. It is the σ frame that wins the delicate balance in species such as benzene and the allyl radical, while in other species (like open chain polyenes and antiaromatic species) it is the π component that wins out. The uniformity of the conclusions obtained in this delicate test indicates the rigor of the $\sigma-\pi$ notion. Thus, Hückel's original idea is endowed with a rigorous basis.

The $\sigma-\pi$ separation methods were applied also to two other problems. One is the determination of in situ π-bond energies, and the other is the classification of substituents. These two applications demonstrate the versatility of the methods and the insight that can be gained from their application.

Nonplanar situations arise in fullerenes where a description of π electrons in three dimensions is necessary. Haddon[153] argued that orbital orthogonality is the key to the $\sigma-\pi$ separability, and he presents a recipe on how to conserve orbital orthogonality in three dimensions. Hirsch et al.[154] showed that a new electron counting rule, different from the Hückel $4n + 2$ rule, can be used to describe the spherical aromaticity of fullerenes of I_h symmetry. This interesting work may provide a stimulus to take a closer look into the $\sigma-\pi$ separation of fullerenes.

Indeed, as the review shows, there is now an arsenal of modern $\sigma-\pi$ separation methods which are logical and can be used in many future applications.

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