

Some New Aspects of π -Electron Theory

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An approximate method is proposed for treating the non-orthogonality of atomic functions and correlation of π -electrons by means of perturbation theory and Pariser-Parr-Pople (PPP) method as a zero approximation. The formula derived for the ground state energy of π -systems is suitable to describe a number of effects, which the PPP theory, in principle, cannot account for. In particular, it is shown how such intermolecular phenomena like exchange repulsion and dispersion interaction can be accounted for in MO method.

The ground state energies of π -electron systems are calculated with and without an account of π -electron correlation. If for the atomic functions non-orthogonality is taken into consideration the experimental values of these energies can be described using a "spectroscopic" set of standard calculation parameters. Probably, within the framework of this method, it is possible to describe simultaneously and consistently the spectroscopic, thermochemical and kinetic data.

Für die Behandlung der Nicht-Orthogonalität von Atomfunktionen und die Korrelation der π -Elektronen wird eine Näherungsmethode vorgeschlagen, bei der die Pariser-Parr-Pople- (PPP)-Methode als nullte Näherung in einer Störungsrechnung verwendet wird. Die Formel für den Grundzustand von π -Systemen ist für die Beschreibung einiger Effekte geeignet, die in der PPP-Beschreibung nicht berücksichtigt werden. Insbesondere wird gezeigt, wie solche intermolekulare Phänomene wie Abstoßung infolge Austausch und Dispersions-Wechselwirkung bei der MO-Methode berücksichtigt werden können. Die Energie des Grundzustandes von π -Elektronensystemen wird mit und ohne Berücksichtigung der π -Elektronenkorrelation berechnet. Wenn für die Atomfunktionen die Nicht-Orthogonalität berücksichtigt wird, so können die experimentellen Werte dieser Energie mit Hilfe eines „spektroskopischen“ Satzes von Standardparametern erhalten werden. Vermutlich ist es möglich, im Rahmen dieser Methode, die spektroskopischen, thermochemischen und kinetischen Daten einheitlich und konsistent zu beschreiben.

On propose une méthode approchée pour traiter la non orthogonalité des fonctions atomiques et la corrélation des électrons π au moyen de la théorie des perturbations utilisant l'approximation de la méthode de Pariser-Parr-Pople comme ordre zéro. La formule obtenue pour l'énergie du fondamental permet de décrire un certain nombre d'effets dont la théorie PPP ne peut rendre compte. En particulier on montre comment certains phénomènes intermoléculaires comme la répulsion d'échange et la dispersion peuvent être pris en considération.

L'énergie de l'état fondamental des systèmes d'électrons π est calculée avec et sans corrélation. Si la non orthogonalité des fonctions d'onde atomiques est incluse, les valeurs expérimentales de ces énergies peuvent être décrites en utilisant un ensemble «spectroscopique» de paramètres standards. Dans le cadre de cette méthode il est probablement possible de décrire simultanément les propriétés spectroscopiques, thermochimiques et cinétiques.

Introduction

The approximation, using the minimal AO basis set for all valence electrons (i.e. including the valence electrons AO's only) but free from any other limitations is, probably, the natural limit to which semi-empirical methods of quantum chemistry could be extended. If it is so, then the potentialities of semi-empirical theories are far from being exhausted. We would like to make use of some of these

possibilities to improve the Pariser-Parr-Pople semi-empirical procedure (PPP), which has become already a standard method to treat the electronic structure of π -systems.

There are a number of physical effects which the PPP theory cannot explain by any selection of parameters.

1) So as to make the calculations of π -systems bonding energy agree with the experiment, such a value of the resonance parameter β should be used which significantly differs from the value used for describing their optical and electric properties [1, 2].

2) The interaction energy of two non-polar alternant π -systems, calculated by the PPP method, is always negative and vanishes whenever the exponentially decreasing intermolecular overlap integrals vanish [3]. Thus two important effects are lost, viz, a) The exponential repulsion at small and medium distances R , which is usually called as "exchange" repulsion, and b) London dispersion forces, corresponding to an attraction proportional to R^{-6} at large intermolecular distances.

The problem of the reactivity of organic molecules stimulated our interest in this topic. Usually, in quantum chemistry, this problem is treated by means of so-called reactivity indices. Perhaps, this treatment is no more perspective, and further development seems to consist in examining the elementary reaction act and the transition states by semi-empirical methods. Consequently, such methods should be adequate enough to describe intermolecular interactions.

Today, a large number of papers exist which analyse the PPP theory approximations. Our purpose is to unify these results in a form suitable for practical applications. Such an improved theory should be capable of describing theoretically the above mentioned effects in principle, irrespective of selection of parameters and at the same time should retain such undoubted merits of PPP theory as simplicity and universality.

Formulae and Notations

One-electron space functions will be labelled by latin indices ($\lambda_r, \varphi_i \dots$), and spin functions by greek indices ($\lambda_\mu, \varphi_\nu \dots$), with the convention that $\lambda_\mu \equiv \lambda_r \sigma \dots$, where the spin function σ can take two different values. Let the minimal basis set of $2p$ AO χ_r be given. It is at once convenient to go over to the orthogonal basis set of Löwdin orbitals

$$(\lambda_r) = (\chi_r)S^{-1/2},$$

where (...) denotes a row matrix, and S is the matrix of overlap integrals. Let us write the model π -electron Hamiltonian in the second quantization representation:

$$H = \sum_{r,s>r} V_{rs} + \sum_{\mu\nu} l_\mu^\dagger \lambda_{\mu\nu} l_\nu + \frac{1}{2} \sum_{\mu\nu\varrho\tau} l_\mu^\dagger l_\varrho^\dagger \lambda(\mu\nu|\varrho\tau) l_\tau l_\nu, \quad (1)$$

$$\lambda_{\mu\nu} = \int \bar{\lambda}_\mu(1) h(1) \lambda_\nu(1) d1,$$

$$\lambda(\mu\nu|\varrho\tau) = \iint \bar{\lambda}_\mu(1) \bar{\lambda}_\varrho(2) \frac{1}{r_{12}} \lambda_\nu(1) \lambda_\tau(2) d1 d2. \quad (2)$$

V_{rs} is the effective repulsion energy of the core nuclei r and s , h is the one electron core Hamiltonian, l_μ^\dagger and l_μ are the creation and annihilation operators of the spin-orbitals λ_μ .

Self-consistent MO's φ_i are obtained from the orbitals λ_r by means of an unitary transformation C with the coefficients $c_{\mu i}$:

$$(\varphi_i) = (\lambda_r)C. \quad (3)$$

In the (φ_μ) basis the Hamiltonian (1) becomes

$$H = \sum_{r,s>r} V_{rs} + \sum_{\mu\nu} f_\mu^+ {}^{\sigma}h_{\mu\nu} f_\nu + \frac{1}{2} \sum_{\mu\nu\varrho\tau} f_\mu^+ f_\nu^+ {}^{\sigma}(\mu\nu|\varrho\tau) f_\tau f_\nu. \quad (4)$$

The notations used for the matrix elements in (4) are similar to that used in (2); f_μ^+ and f_μ^- are the creation and annihilation operators of spin orbitals φ_μ .

The MO's φ_μ are the eigenfunctions of the one-electron operator $F^{(0)}$ with eigenvalues ε_μ :

$$F^{(0)} = \sum_{r,s>r} V_{rs} + \sum_{\mu} f_\mu^+ \varepsilon_\mu f_\mu. \quad (5)$$

Let us consider a two-electron operator $F^{(1)}$, diagonal in the configurational basis:

$$F^{(1)} = \sum_{r,s>r} V_{rs} + \sum_{\mu} f_\mu^+ {}^{\sigma}h_{\mu\mu} f_\mu + \frac{1}{2} \sum_{\mu\nu} f_\mu^+ f_\nu^+ [{}^{\sigma}(\mu\mu|\nu\nu) - {}^{\sigma}(\mu\nu|\nu\mu)] f_\nu f_\mu. \quad (6)$$

This is really the Hamiltonian of a single configuration approximation:

$$F^{(1)}|\Psi_M\rangle = \langle\Psi_M|H|\Psi_M\rangle|\Psi_M\rangle = E_M|\Psi_M\rangle$$

where $|\Psi_M\rangle$ is a Slater determinant built from spin orbitals φ_μ .

The solution of the π -electron problem in this approximation consists in finding φ_i , i.e. the self-consistent C matrix. Thus it is necessary to introduce the values of matrix elements (2) as parameters. It is sufficient to give the integrals of space functions λ_r only. According to Pople [4], we have

$$\begin{aligned} {}^{\lambda}h_{rr} &= W_r - \sum_{s \neq r} N_s(rr|ss) \equiv h_{rr}, \\ {}^{\lambda}h_{rs} &= \beta_{rs}, \\ {}^{\lambda}(rt|su) &= \delta_{rt}\delta_{su}(rr|ss), \\ V_{rs} &= N_r N_s(rr|ss). \end{aligned} \quad (7)$$

The matrix elements without the super indices relate to atomic basis set and are given parametrically. The energy of an isolated AO – the value W_r – is equal to

$$W_r = \int \bar{\chi}_r(1) [-\nabla^2 + U_r^+] \chi_r(1) d1,$$

where U_r^+ is the atomic core potential. The parameter β_{rs} vanishes for all non-neighbouring atoms. The integral quantity N_r gives the number of electrons which the r -atom contributes to the total π -system.

In most of the recent semiempirical calculations, the approximate Hamiltonian (6) is used instead of the exact Hamiltonian (4), and the matrix elements are approximated according to formulae (7). These are two independent approximations, and we shall examine them separately and introduce the necessary corrections within the framework of perturbation theory.

Non-Orthogonality of Atomic Functions

In calculating the matrix elements (2), usually the matrix $S^{-1/2}$ is expanded as a series [5]. An analysis [5, 3] shows that the second and third relations in (7) are accurate up to the order of S^3 , where S is the standard value of overlap integral (in a π -system $S \approx 0.25$). When ${}^{\lambda}h_{rr}$ is expanded as a series, we have

$${}^{\lambda}h_{rr} = h_{rr} + \sum_{s \neq r} U_{s,rr} - \sum_{s \neq r} h_{sr} S_{rs} + h_{rr} \sum_{s \neq r} S_{rs}^2 + \frac{1}{4} \sum_{s \neq r} S_{rs}^2 (h_{ss} - h_{rr}) + O(S^3).$$

Summation is carried out over all atoms s adjacent to r . The non-diagonal matrix elements of the core Hamiltonian in an atomic basis are denoted by h_{rs} and $U_{s,rr}$ is the penetration integral of order S^2 [5], and S_{rs} – the overlap integral.

If the system is not too polarised, the inequality $(h_{rr} - h_{ss})/h_{rr} < S$ holds. Also the following estimation is true: $h_{rs} - S_{rs}h_{rr} = \beta_{rs} + 0(S^3)$ [5].

Then

$${}^\lambda h_{rr} = h_{rr} + \sum_{s \neq r} (U_{s,rr} - S_{rs}\beta_{rs}) + 0(S^3).$$

The last sum of the order of S^2 is not accounted for in (7). According to (3), we have

$${}^\varphi h_{ii} = \sum_{rs} \bar{c}_{ri} c_{si} {}^\lambda h_{rs}.$$

Hence, the correction to ${}^\varphi h_{ii}$ is equal to

$$\Delta {}^\varphi h_{ii} = \sum_{r,s \neq r} \bar{c}_{ri} c_{ri} (U_{s,rr} - S_{rs}\beta_{rs}) + 0(S^3).$$

The correction to the total energy E_p of the configuration $|\Psi\rangle$, calculated by the Pople method, to the first order of perturbation theory [6] amounts to

$$E - E_p = \sum_{\mu} \langle \Psi | f_{\mu}^+ \Delta {}^\varphi h_{\mu\mu} f_{\mu} | \Psi \rangle$$

or taking the commutation relations for f^+ and f into account

$$E - E_p = \sum_{r,s > r} [(q_r U_{s,rr} + q_s U_{r,ss}) - (q_r + q_s) S_{rs} \beta_{rs}] + 0(S^3), \quad (8)$$

where $q_r = \sum_{\mu=1}^m \bar{c}_{r\mu} c_{r\mu}$ is the atomic charge of the $|\Psi\rangle$ configuration (summation over all the occupied spin-orbitals).

Let us add one more correction $\sum_{r,s > r} [V_{rs} - N_r N_s (rr|ss)]$, due to the error in the last equation of (7). By making use of the identity $U_{r,ss} = U_{r,ss}^+ + N_r (rr|ss)$, where U_r^+ is the atomic core potential, let us introduce the following notation

$$Q_{rs} = q_r U_{s,rr}^+ + q_s U_{r,ss}^+ + q_r q_s (rr|ss) + V_{rs} \quad (9)$$

for the total atomic electrostatic interactions, and

$$q_{rs} = (q_r - N_r) (q_s - N_s) (rr|ss)$$

for the electrostatic interactions of resultant atomic π -charges. After a few simple transformations, we have

$$E = E_p + \sum_{r,s > r} [Q_{rs} - (q_r + q_s) \beta_{rs} S_{rs}] - \sum_{r,s > r} q_{rs} + 0(S^3)$$

or using the expression of E_p [4]:

$$E = \sum_r q_r \left[W_r + \frac{1}{4} q_r (rr|rr) \right] + 2 \sum_{r,s > r} p_{rs} \beta_{rs} - \frac{1}{2} \sum_{r,s > r} p_{rs}^2 (rr|ss) \quad (10)$$

$$+ \sum_{r,s > r} [Q_{rs} - (q_r + q_s) \beta_{rs} S_{rs}] + 0(S^3),$$

where p_{rs} are bond orders. In the ground state of homoatomic alternant systems, where $q_r = N_r = 1$, and $q_{rs} = 0$,

$$E = E_p + \sum_{r,s>r} [Q_{rs} - 2\beta_{rs}S_{rs}] + 0(S^3). \quad (11)$$

Origin of the Activation Energy

Let us confine ourselves only to a discussion of non-polar systems, for which the ground state energy is given by the expression (11). The first term Q_{rs} in the sum corresponds to the Coulomb pair interaction of atoms when $q_r = N_r = 1$. It coincides with the Coulomb integral of the valence bond method. The second term corresponds to exchange repulsion. In practical calculation, we can assume that $\beta_{rs} = (\beta_0/S_0)S_{rs}$, where β_0 and S_0 relate, for example, to C-C bond in benzene. But it is very cumbersome to compute Q_{rs} . According to (9), Q_{rs} is a small difference of two large quantities, and it is very sensitive to the selection of the orbital exponents. Therefore, in such a situation, it is expedient to take recourse to empirical estimation. As Q_{rs} is proportional to S_{rs}^2 , let us write

$$E = E_p + \gamma \sum_{r,s>r} S_{rs}^2 + 0(S^3). \quad (12)$$

It follows from (11) that the factor γ is constant in different alternant systems; it can be found from the experiment. It will be shown further that $\gamma > 0$, so including of the non-orthogonality correction gives repulsion.

In standard calculations, where the geometry of the molecule is regarded as fixed, this correction vanishes when calculating the energy difference. For example, in treating the energy of the low lying optical transitions in alternant systems by the Pople method, the charges q_r are constant and equal to the unit in the first excited configuration as in the ground state. For such an excited state, the equalities (11) and (12) follow from the general formula (10) again, and the correction is excluded from the transition energy expression.

But, it is very significant when the processes are studied, in which the environment of atoms composing the system changes. Let us consider the interaction energy U of two π -systems A and A' when they approach each other. If the intramolecular interaction does not change, then

$$U = \Delta + \gamma \sum_{r,r'} S_{r,r'}^2 + 0(S_{r,r'}^3). \quad (13)$$

Summation is carried out over the atomic pairs r and r' from the different molecules. Δ is the interaction energy of the Pople approximation

$$\Delta = E_p^{AA'} - E_p^A - E_p^{A'}.$$

In fact, this is the resonance energy and it is easy to show that Δ is always less than or equal to zero [3]. Thus, in the Pople approximation, it is not possible to get a repulsion and explain the origin of activation barriers in bimolecular reactions. Formula (13), combining both attraction and repulsion, can, in principle, be used

for calculating the activation energy. Notice that in computing Δ , all intermolecular integrals $\beta_{rr'}$ have to be considered, while inside a molecule β_{rs} is assumed to be equal to zero for all non-adjacent atoms according to the Pople theory.

Now let us explain how we estimated the accuracy of (13). Let us suppose, that we succeeded in computing the S^3 -order corrections to the matrix elements (7) corresponding to the interactions inside each molecule. In treating the difference of energies U , such corrections are included with the factor $(p_{rs} - p_{rs}^0)$ (matrix elements of one-electron operators) or $(p_{rs}p_{tu} - p_{rs}^0p_{tu}^0)$ (two electron matrix elements), where the bond order p_{rs} has been calculated in a unified system AA' , and p_{rs}^0 - in isolated molecules A or A' . This can be argued in the same manner as we did to prove (8). But inside a molecule $p_{rs} = p_{rs}^0 + 0(S_{rr'}^2)$ [7]. Thus, the error due to intramolecular interaction is of the order $S_{rr'}^2 \cdot S^3$, but that due to intermolecular interaction is of the order $S_{rr'}^3$. When $S^3 \lesssim S_{rr'}$, we obtain the error estimation given in (13).

Correlation of π -Electrons

A complete solution to the many-electron problem for a model Hamiltonian (4) reduces to the configuration interaction problem. The computational difficulties involved are well known. But when the values of the parameters (7) are those characteristic of π -systems, then the ground state correlation energy is obtained with good accuracy already in the second order of perturbation theory.

The selection of zero approximation for the perturbation theory is not unique. One-particle Hartree-Fock operator $F^{(0)}$ (5) does not give a good convergence. Therefore, it is expedient to use a two-particle operator $F^{(1)}$ (6) [8, 9], which is diagonal in configurational basis, as a zero approximation. Here, the perturbation $V = H - F^{(1)}$ has no diagonal part, and the first order correction vanishes. In the second order the correlation energy of the ground state $|\Psi_0\rangle$ is equal to

$$E_{\text{cor}} = \sum_M \frac{\langle \Psi_0 | V | \Psi_M \rangle \langle \Psi_M | V | \Psi_0 \rangle}{E_0 - E_M} \quad (14)$$

and it is sufficient to confine the summation to double excited configurations $|\Psi_M\rangle$ only. As it will be shown in the next section, formula (14) gives more than 90% of correlation energy and the correlation energy of π -system amounts to about 10% of bond energy. Since $S \approx 0.25$, the correction of order S^2 due to non-orthogonality, and the correlation correction are close with respect to the order of magnitude. Hence, they have to be simultaneously accounted for.

Strictly speaking, to calculate E_{cor} , it would be proper to use in the denominator the energies calculated by formulae (10)–(12) in which non-orthogonality has been already accounted for. However, it is simpler to use the E_p energy calculated by the Pople method yielding in practice the same results, since the non-orthogonality correction is small when compared to E_p and has a tendency to compensate in calculation of the energy differences. In this last approximation, which we shall make use of, the correction due to non-orthogonality and correlation energy are independently determined.

Bonding Energies of π -Systems and Estimation of γ

We shall apply the formulae obtained to study the ground state bonding energies E_π of π -electron systems. Until recently, these values were not systematically calculated, probably due to the difficulties encountered in their experimental evaluation. The difficulty lies in determining the bonding energy E_σ of the σ -core, which has to be subtracted from the experimental atomisation energy E_a so as to find E_π :

$$E_\pi = E_a - E_\sigma. \quad (15)$$

It is very essential to have reliable values of equilibrium energies of C-C (ϵ_{CC}) and C-H (ϵ_{CH}) bonds formed by carbon in sp^2 state. Furthermore since the C-C bond length in π -systems is shorter than the equilibrium one, a necessary energy correction has to be introduced due to compression. So, the values of equilibrium length (r_0) and of force constant (f) are needed (or Morse constant, if compression energy is determined by Morse formula). Today, two sets are found in the literature for the values of these constants. The first one proposed by Dewar *et al.* [1, 10], is based on multiple interpolations, and gives

$$\begin{aligned} \epsilon_{CC} &= 97.0 \text{ Kcal/mol}, \\ \epsilon_{CH} &= 100.5 \text{ Kcal/mol}, \\ r_0 &= 1.49 \text{ \AA}, \\ f &= 6.03 \times 10^5 \text{ dyne/cm}. \end{aligned} \quad (16)$$

The second set, proposed by Lorquet [2], is based on a statistical treatment of experimental bond lengths and atomisation energies values for hydrocarbons

$$\begin{aligned} \epsilon_{CC} &= 92.2 \text{ Kcal/mol}, \\ \epsilon_{CH} &= 99.5 \text{ Kcal/mol}, \\ r_0 &= 1.52 \text{ \AA}, \\ f &= 4.90 \times 10^5 \text{ dyne/cm}. \end{aligned} \quad (17)$$

The differences in values of quantities as given by (16) and (17) lead to considerable disparity in the estimation of experimental π -energy by formula (15). However, comparing these estimates with calculated E_π values in the Pople approximation, both Dewar and Lorquet came to the same conclusion, namely, that it is not possible to reproduce the "experimental" values of π -energy if the usual spectroscopic parameters β and $(rr|ss)$ are used in the calculation. The experimental and calculated values coincided, when these authors took the value of standard resonance parameter in benzene to be $\beta_0 = -1.6 \div -1.7$ eV instead of the spectroscopic value $\beta_0 \approx -2.4$ eV.

In our calculation, we made use of the following parameter values given by Goodman [11, 12].

$$\begin{aligned} \beta(1.39 \text{ \AA}) &= -2.37 \text{ eV}, \\ \beta(1.34 \text{ \AA}) &= -2.78 \text{ eV}, \\ (11|11) &= 11.06 \text{ eV}, \\ (11|22)(1.39 \text{ \AA}) &= 6.86 \text{ eV}, \\ (11|22)(1.34 \text{ \AA}) &= 6.94 \text{ eV}, \end{aligned}$$

which reproduce well the spectra and ionisation potentials of π -systems. E_π energies were calculated with and without an account of correlation.

Correlation was taken into account according to (14). Whenever it was possible, we compared results with the "exact" calculation, i.e. with the exact eigenvalue of the ground state energy for the model π -electron Hamiltonian (4), obtained by the complete solution of the configuration problem.

The calculated values widely differ from the "experimental" values given by Dewar or Lorquet. Although, this disparity can be removed by a special selection of β , we proceede in an entirely different manner. Let us suppose that this disparity is due to some physical effect, not accounted for in the Pople method. Since correlation only increases the error, we have to investigate the role of non-orthogonality. According to (12) we shall regard that the differences in calculated and experimental values of π -energies are proportional to the sum of squares of the neighbouring atoms overlap integrals:

$$E_\pi^{\text{exp}} - E_\pi^{\text{cal}} = \gamma \sum_{r,s > r} S_{rs}^2.$$

The respective plots are shown in Fig. 1. Good straight lines are obtained which almost pass through the origin, and their slope gives the values of γ , which varies depending on the experimental estimates of E_π (according to Dewar or Lorquet).

Table. Comparison of experimental and calculated bonding energies (in Kcal/mol)

Molecule	Calculated values - E_π			Experimental values - E_π	
	Exact calculation	Correlation acc. to perturbation theory	Pople method	According to Dewar	According to Lorquet
Ethylene	89	90	81	45	57
Trans-butadiene	178	176	161	88	116
Benzene	304	303	284	146	197
Styrene		396	371	190	256
Naphthalene		518	488	245	336
Anthracene		730	688	342	474
Phenantrene		737	698	350	481
1,2-Benzanthracene			900	451	621
Naphtacene			887	450	620
Triphenylene			913	456	627
Chryzene			906	455	625

Remarks. The experimental E_π values were determined by formula (15). E_σ energy of the σ -core was calculated from data (16) and (17). Experimental values E_a of atomisation energy were taken from [13] and corrected to 0° K. The C-C bond lengths were assumed to be: for ethylene 1.34 Å; butadiene - 1.35 Å and 1.46 Å; styrene (in chain) - 1.35 Å and 1.46 Å; all aromatic molecules - 1.39 Å.

If correlation correction is added to the calculated E_π value, then the linear dependency is retained (γ -values, of course, change). This corroborates Sinanoğlu's statement [14] that correlation can be accounted for by a selection of empirical Hartree-Fock parameters values for the ground state.

The γ values so found seem to be plausible. If Coulomb interactions Q_{rs} are neglected, then according to formula (11) and accepting β_{rs} proportional to S_{rs} , we find $\gamma = 2\beta_0/S_0 \approx 18.4$ eV.

Estimates from Fig. 1, considerably lesser in values, can be regarded as a measure of the neutral atom Coulomb interaction contribution into the energy.

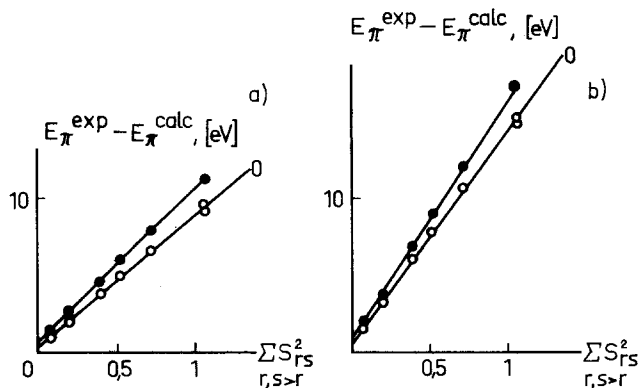


Fig. 1. Determination of the factor γ from thermochemical data. a) data according to Lorquet $\gamma = 8.51$ eV (without correlation), $\gamma = 9.89$ eV (with correlation). b) data according to Dewar $\gamma = 13.75$ eV (without correlation), $\gamma = 14.19$ eV (with correlation)

It should be remembered that as follows from (9)–(12) γ depends on the atomic π -charges q_r . Thus if treating the bonding energies of non-alternant or heteroatomic π -systems our procedure needs several corrections.

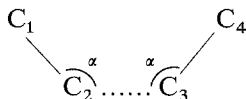
Dispersion Interactions

Dispersion forces are typical correlation effects. Hartree-Fock interaction energy (13) vanishes at such distances, where the one-electron interactions proportional to $S_{rr'}$ vanish. The π -electron contribution to dispersion energy can be defined as the change in correlation energy (14) in the unified system AA' with respect to the isolated molecules A and A' . It would be interesting to investigate the connection of such a description with the classic London theory.

The London theory is based on configurations built of one-electron functions, which are localised in the isolated molecules A and A' . On the other hand the MO's found for the unified system AA' are used in formula (14).

Let us consider a model example. It is of no physical sense but illustrates well the manner in which the two descriptions can be compared.

We treated the interaction of the π -systems of two ethylene molecules. The symmetry plane coincides with the plane of drawing. Angle $\alpha = 120^\circ$.



From the intermolecular resonance integrals only β_{23} was taken into account. The MO of the combined system, calculated by the Pople method, were converted into the partially localized equivalent orbitals:

$$\begin{aligned}\varphi_1 &= k\varphi_1^+ + \sqrt{1-k^2}\varphi_2^-, \\ \varphi_2 &= \sqrt{1-k^2}\varphi_1^- + k\varphi_2^+, \\ \varphi_3 &= k\varphi_1^- + \sqrt{1-k^2}\varphi_2^+, \\ \varphi_4 &= \sqrt{1-k^2}\varphi_1^+ + k\varphi_2^-, \end{aligned}$$

where $\varphi_1^\pm = \frac{1}{\sqrt{2}}(\lambda_1 \pm \lambda_2)$ and $\varphi_2^\pm = \frac{1}{\sqrt{2}}(\lambda_3 \pm \lambda_4)$ are the MO's of isolated ethylene molecules. When $k = 0.99$, we obtain "cis-butadiene", and when $k = 1$,

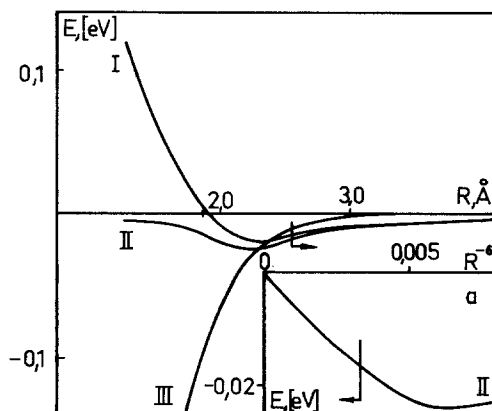


Fig. 2. Dispersion energy of two ethylene π -systems, as a function of the distance R . *I* the difference of the correlation energies of the combined system and isolated molecules. *II* the contribution of the local double excitations (London part of the correlation energy). *III* the stabilisation energy calculated in one-electron approximation

Fig. 2a. Curve *II* in R^{-6} coordinate. The arrow shows the region coinciding in the main Fig. 2 and in Fig. 2a

– two "ethylenes". If φ -orbitals are used, it is at once possible to separate from the sum (14) the London part at any distance R . These are the terms corresponding to the local double excitations $\varphi_1 \rightarrow \varphi_3$ $\varphi_2 \rightarrow \varphi_4$. Their contribution is shown by curve *II* in Fig. 2. Curve *I* is the difference ΔE_{cor} of the correlation energy of the combined system and isolated molecules; the contributions of all double excitations are taken into account in it. Curve *III* represents the stabilisation energy $\Delta = \Delta E_\pi = E_\pi^{AA'} - E_\pi^A - E_\pi^{A'}$ calculated according to Pople method, and is shown here for the sake of comparison. When $R \lesssim 2 \text{ \AA}$, the relative contribution of correlation in the interaction energy is small. When $R \gtrsim 2.5 \text{ \AA}$ and $\Delta \lesssim E_{\text{cor}}$, curve *I* practically coincides with the London curve *II*. In this region, interaction energy changes according to the R^{-6} law (Fig. 2a).

Even if symmetry is absent, a transition from the MO's of the unified system to the orbitals localised in interacting fragments is still possible. Let C be a $n \times n/2$

matrix of coefficients of the occupied MO's of the system AA' with n centers λ_r . Similarly B is a $n \times n/2$ matrix of MO coefficients of isolated molecules A and A' :

$$B = \left[\begin{array}{c|c} A & 0 \\ \hline 0 & A' \end{array} \right],$$

where the blocks A and A' belong to the respective molecules. We shall search for such a transformation U , that the quantity

$$Sp(\tilde{U}\tilde{C} - \tilde{B})(CU - B)$$

is a minimum when the additional unitarity condition $\tilde{U}U = I$ holds. The solution to this variational problem is

$$U = Y^{-1}\tilde{C}B,$$

where Y is hermitian matrix ($Y = \tilde{Y}$), and due to unitarity of U we have

$$Y^2 = \tilde{C}B\tilde{B}C. \quad (18)$$

The matrix $\tilde{C}B$, in general, is not hermitian. To find Y , let us diagonalize hermitian matrix $\tilde{C}B\tilde{B}C$ by means of unitary transformation T :

$$\tilde{T}\tilde{C}B\tilde{B}CT = \varrho$$

(ϱ is a diagonal matrix), and then operate the matrix $\varrho^{1/2}$ with inverse transformation

$$Y = T\varrho^{1/2}\tilde{T}.$$

The matrix Y so found satisfies the condition (18). The matrix of orbital coefficients $C' = CY^{-1}\tilde{C}B$ gives the best localised description of the unified system. This description, when R is great, becomes the London description. Vacant MO are also transformed exactly in the same way.

Notice that it is always expedient to pass to the localised description before applying the perturbation theory, because in that case the convergence is the best.

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