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Optimal Double-Configuration Study of the Lowest Excited Π States of H_2

II. $\sigma - \pi$ Separation

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The $\sigma - \pi$ separation of energies and one-electron properties of the four lowestlying Π states of the hydrogen molecule considered in the preceding paper [1] is presented. The calculations are based on separate exponent optimization for all four states. The values of the σ electron properties of the four states are much closer than those of the π electrons. The degree of uniformity of the π electron property values increases when a lesser level of approximation based on a single-state ($^1\Pi_u$) exponent set is used. The assumption of equal parameter values for different states in semiempirical π electron methods is valid only on this level. Conclusions based on this assumption cannot lead us to a representative description of the antibonding character of molecular states.

Die $\sigma - \pi$-Separierung von Energien und Einelektroneneigenschaften der vier niedrigsten Π Zustände des Wasserstoffmoleküls, die in der vorhergehenden Arbeit [1] betrachtet worden sind, wird angegeben. Die Rechnungen basieren auf getrennter Exponentenoptimisierung für alle vier Zustände. Die σ-Elektroneneigenschaften der vier Zustände sind untereinander ähnlicher als die der π-Elektronen. Auch diese werden sich ähnlicher auf einer niedrigeren Approximationsstufe, die auf einem einzigen ($^1\Pi_u$) Exponentensatz basiert. Nur auf dieser Stufe kann die Annahme gleicher Parameterwerte für verschiedene Zustände in semiempirischen π-Methoden gerechtfertigt werden. Folgerungen aus dieser Annahme können uns nicht zu einer repräsentativen Beschreibung des antibindenden Charakters von Molekülzuständen führen.

Séparation $\sigma - \pi$ des énergies et des propriétés monoélectroniques pour les quatre plus bas états Π de la molécule d'hydrogène envisagés dans l'article précédent. Les calculs sont fondés sur une optimisation séparée des exposants pour les quatre états. Les valeurs des propriétés des électrons σ des quatre états sont plus voisines que celles des électrons π. Le degré d'uniformité des propriétés des électrons π augmente lorsque l'on emploie un degré d'approximation inférieur fondé sur un ensemble d'exposants d'un seul état ($^1\Pi_u$). L'hypothèse d'une identité des valeurs des paramètres pour les différents états dans les méthodes à électrons π semi-empiriques n'est validée qu'à ce niveau. Les conclusions fondées sur cette hypothèse ne peuvent nous conduire à une description représentative du caractère antiliant des états moléculaires.

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1. Introduction

The purpose of this paper is to investigate the basis of approximate molecular orbital theories where groups of electrons are separated from other groups. The most popular separation is the one of σ and π electrons, particularly in hydrocarbons. The conditions for a $\sigma - \pi$ separation were formulated by Lykos and Parr [2]. The Π states of H_2 are the simplest case where such a separation can be studied. In the following two sections we shall discuss the $\sigma - \pi$ separation of energies and one-electron properties and the consequences for approximate molecular orbital theories. In essence, we cannot support the assumption of equal parameter values for different states in semiempirical MO methods as valid in molecules.

2. $\sigma - \pi$ Separation

Figs. 1–2 contain kinetic (T_σ, T_π) and total electronic (E_σ, E_π) energy of the σ electron and the π electron and their interaction ($E_{\sigma\pi}$) for the four Π states with the optimal exponents listed in Table 1 of the preceding paper [1] on the ODC level.

Comparing the σ and π energies of the four Π states with each other, yields the following important result. The σ part E_σ of the total electronic energy shows almost no fluctuation over the whole range of internuclear distances. This is true

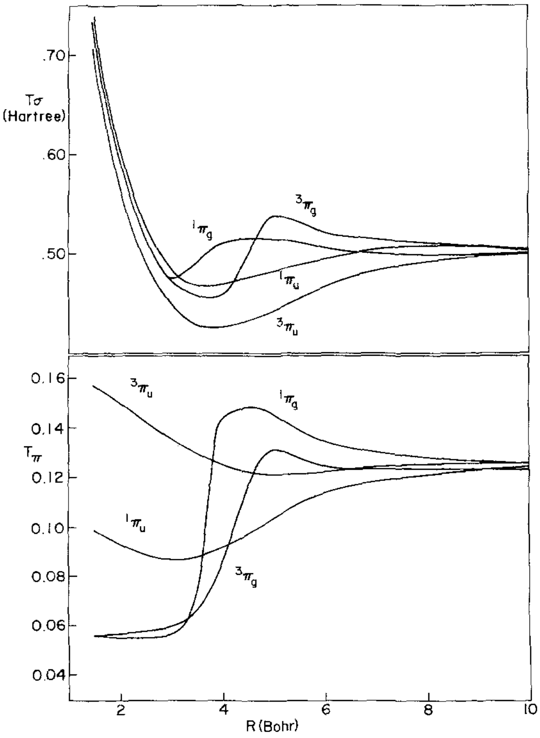

Fig. 1. σ and π part of kinetic energy

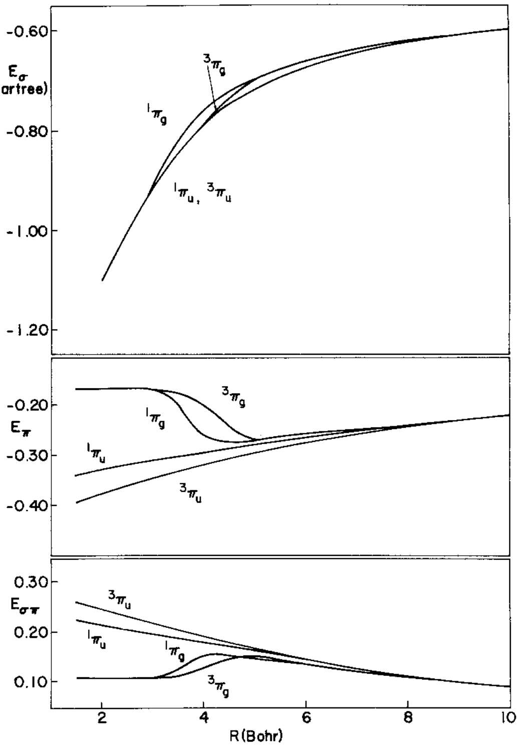

Fig. 2. σ and π part of electronic energy and $\sigma - \pi$ interaction energy

to lesser degree for T_σ. The energy differences between the four states arise from E_π and $E_{\sigma\pi}$. E_π is increasing in the order $^3\Pi_u$, $^1\Pi_u$, $^3\Pi_g$ or $^1\Pi_g$ for all distances on the HF level and for distances smaller than 8 Bohr on the ODC level where the asymtotic limits have not been reached closely. $E_{\sigma\pi}$ shows the opposite trend. With the optimal exponents for each state the differences between the Π_u and Π_g states are rather large, whereas the values of the $^3\Pi_u$ and Π_g states are fairly close to the $^1\Pi_u$ values if the energies for all four states are calculated with the $^1\Pi_u$ exponents. In particular, the Π_g states gain total energy decrease upon exponent optimization by a decrease in electronic interaction $E_{\sigma\pi}$ which is somewhat reduced by the increase in core energy E_π. For HF and CI levels, we obtain similar results except for $E_{\sigma\pi}$. The electronic interaction is decreasing from HF to CI and finally ODC. The effect increases with internuclear distance. The proper dissociation of the states is based on a decrease in electronic interaction.

We present in Table 1 a subdivision of $E_{\sigma\pi}$ in intraconfigurational and interconfigurational parts. It is interesting to note that the intraconfigurational part shows almost no difference for all three levels, HF, CI and ODC. The interconfigurational part is always negative and tends to reduce the total electronic interaction. Again we find a tendency to uniformity if these energies are calculated for all four states with the $^1\Pi_u$ exponents.

To complete the picture of $\sigma - \pi$ separation, we also mention the results for one-electron properties. The density distribution of the σ electron perpendicular

Table 1. Subdivision of $E_{\sigma\pi}$

	$^1\Pi_u$		$^3\Pi_u$		$^1\Pi_g$		$^3\Pi_g$		
R	E_{intra}	E_{inter}	E_{intra}	E_{inter}	E_{intra}	E_{inter}	E_{intra}	E_{inter}	
2.0	0.21740	0.0	0.24872	0.0	0.11091	0.0	0.11159	0.0	HF
	0.21734	−0.00167	0.24819	−0.00213	0.11093	−0.00034	0.11160	−0.00020	CI
	0.21749	−0.00383	0.24816	−0.00294	0.11109	−0.00035	0.11181	−0.00036	ODC
4.0	0.20208	0.0	0.20929	0.0	0.20397	0.0	0.13597	0.0	
	0.20227	−0.01826	0.20927	−0.01371	0.20346	−0.04431	0.13642	−0.00775	
	0.20118	−0.01868	0.20861	−0.01421	0.20234	−0.04693	0.13734	−0.00931	
6.0	0.19773	0.0	0.18304	0.0	0.17851	0.0	0.17229	0.0	
	0.19409	−0.04133	0.18351	−0.03171	0.19395	−0.05012	0.18140	−0.03629	
	0.19686	−0.05193	0.18430	−0.03781	0.20186	−0.06579	0.18223	−0.04386	
8.0	0.18305	0.0	0.16996	0.0	0.19004	0.0	0.17113	0.0	
	0.18514	−0.06571	0.17043	−0.05168	0.18755	−0.06869	0.17017	−0.05120	
	0.18437	−0.07010	0.16988	−0.05587	0.18812	−0.07562	0.16966	−0.05553	
10.0	0.17365	0.0	0.15813	0.0	0.18221	0.0	0.16236	0.0	
	0.17705	−0.08084	0.15979	−0.06430	0.17764	−0.08200	0.15988	−0.06375	
	0.17666	−0.08212	0.15986	−0.06613	0.17731	−0.08377	0.15981	−0.06528	

Table 2. Density distribution ϱ^2 (Bohr^2) of σ and π electrons perpendicular to molecular axis

	$^1\Pi_u$		$^3\Pi_u$		$^1\Pi_g$		$^3\Pi_g$	
R	$(\varrho^2)_\sigma$	$(\varrho^2)_\pi$	$(\varrho^2)_\sigma$	$(\varrho^2)_\pi$	$(\varrho^2)_\sigma$	$(\varrho^2)_\pi$	$(\varrho^2)_\sigma$	$(\varrho^2)_\pi$
2.0	1.291	31.169	1.415	19.240	1.321	77.554	1.322	76.934
	1.292	31.166	1.416	19.238	1.321	77.563	1.322	76.940
	1.295	31.121	1.414	19.229	1.322	77.463	1.322	76.817
4.0	1.886	31.574	2.192	22.269	2.013	21.098	1.996	51.564
	1.874	31.204	2.181	22.084	1.894	24.567	1.978	52.491
	1.885	31.245	2.146	22.163	1.944	25.232	1.959	51.435
6.0	1.995	27.168	2.308	24.488	2.177	22.445	2.237	22.076
	1.960	26.396	2.257	23.983	1.985	23.687	2.045	24.528
	1.972	25.995	2.172	23.590	1.998	22.779	1.908	24.165
8.0	2.003	26.352	2.190	24.877	2.735	20.777	2.248	21.229
	1.979	24.823	2.162	23.580	2.001	23.269	2.140	24.052
	1.997	25.007	2.057	23.638	2.020	23.355	1.979	24.183
10.0	1.979	25.536	2.133	25.111	2.005	21.836	2.092	22.158
	1.972	24.134	2.130	23.779	1.991	23.726	2.068	24.152
	1.987	24.185	2.022	23.823	2.018	23.787	1.985	24.193

to the molecular axis $\langle\varrho^2\rangle_\sigma$ and along the molecular axis $\langle z_a^2\rangle_\sigma$ is fairly equal for all four states. Great differences arise for the distribution of the π electron. The wavefunction is more contracted for $^3\Pi_u$ than $^1\Pi_u$, whereas for the Π_g states the functions are much more expanded than for $^1\Pi_u$. This is valid for both $\langle\varrho^2\rangle_\pi$ and $\langle z_a^2\rangle_\pi$. Table 2 shows the representative results for ϱ^2. The differences between the four states are greatly reduced when the $^1\Pi_u$ state exponents are used for all four states. Similar results are obtained for z_a^2.

Qualitatively the same conclusions hold for the quantities $\left\langle \frac{1}{r_a} \right\rangle$ and $\left\langle \frac{\sin^2\theta}{r_a} \right\rangle$. The σ parts are equal and the differences in the π part between Π_g and Π_u states arise from expansion of the π orbital in the Π_g states accompanied by a decrease in the above expectation values.

3. Consequences for Approximate Molecular Orbital Methods

Approximate molecular orbital methods are dealing with groups of electrons, which have certain features in common and can be treated separately from the others. π-electrons, σ-electrons, lone pairs, non-bonding $1s$-electrons are such groups. Conditions for a separation of π-electrons from σ-electrons were formulated by Lykos and Parr [2]. They include (A) the wavefunction Φ is an antisymmetrized product of σ part Φ_σ and π part Φ_π, (B) all three functions Φ, Φ_σ, Φ_π are normalized, (C) Φ_σ and Φ_π can be represented by linear combinations of configurations which are built up by sets of mutually exclusive subsets of orbitals for σ and π electrons. The total energy can be separated in σ part, π part and $\sigma-\pi$ interaction

$$E_{\text{total}} = E_\sigma + E_\pi + E_{\sigma\pi}\,. \tag{3.1}$$

The latter part can be considered as the π electron energy $E'_\pi = E_\pi + E_{\sigma\pi}$. In cases where the σ function Φ_σ does not change under π-electron excitation for all Π-states under consideration, energy differences can conveniently be written as

$$\Delta E = E'_{\pi_1} - E'_{\pi_2} \tag{3.2}$$

On the ODC level, condition (A) does not hold, however, (3.2) may still be valid.

This is used as a justification of semiempirical methods in which experimental transition energies between Π-states have been used to determine the parameters of the method [3]. Let us briefly outline the implications for H_2. Fig. 2 shows that E_σ is constant for all four states and we can consider the σ part as frozen. The simplest type of approximation, the Hückel method, uses orbital energies as representative for ground and excited Π-states. In particular, in diatomic molecules the orbital energies ε are representing two states in the following way

$$\varepsilon_\pm = \alpha \pm \beta \tag{3.3}$$

and the state energy difference ΔE is

$$\Delta E = \varepsilon_- - \varepsilon_+ = -2\beta\,. \tag{3.4}$$

If we consider the effective underlying Hamiltonian as the SCF operator and the AO's as symmetrically orthogonalized [4], the π part of H_2 can indeed be written as

$$\begin{aligned} \varepsilon_{\pi_g} &= \alpha_{\pi_g} - \beta_{\pi_g} \\ \varepsilon_{\pi_u} &= \alpha_{\pi_u} + \beta_{\pi_u} \end{aligned} \tag{3.5}$$

where α and β have the usual meaning and ε is the SCF orbital energy. If we identify $\varepsilon_- = \varepsilon_{\pi_g}, \varepsilon_+ = \varepsilon_{\pi_u}$ and assume $\alpha_{\pi_g} = \alpha_{\pi_u} = \alpha$ and $\beta_{\pi_g} = \beta_{\pi_u} = \beta$ we obtain Eqs. (3.3) with the consequence that

$$\begin{aligned}\beta &= \tfrac{1}{2}(\varepsilon_{\pi_u} - \varepsilon_{\pi_g})\\ \alpha &= \tfrac{1}{2}(\varepsilon_{\pi_u} + \varepsilon_{\pi_g}),\end{aligned} \tag{3.6}$$

We have now to ask the question whether these α's and β's have any resemblance to the theoretically calculated $\alpha_{\pi_g}, \alpha_{\pi_u}, \beta_{\pi_g}, \beta_{\pi_u}$ values based on the atomic basis sets $\{2p, 3d\}$ and $\{1s, 2s, 2p\}$ and the coefficients and exponents given in the preceding paper [1]. In Hückel methods, β adjustment is done at the equilibrium positions of the molecule. Let us take for convenience $R = 2$ Bohr as such a distance. With the optimal $2p\pi$-exponents for the four states $\zeta_{^1\Pi_u} = 0.442$, $\zeta_{^3\Pi_u} = 0.561$, $\zeta_{^1\Pi_g} = 0.245$, $\zeta_{^3\Pi_g} = 0.245$ we would not expect resemblance of α_{π_g} and α_{π_u} or β_{π_g} and β_{π_u}. Table 3

Table 3. α and β parameter values (Hartree) at $R = 2$ Bohr

	$^1\Pi_u$	$^1\Pi_g$	Empirical from (3.6)
α	−0.0696	−0.0728	−0.0831
β	−0.0413	−0.0174	−0.0277
$\bar{\alpha}$	−0.108	−0.090	—
$\bar{\beta}$	−0.106	−0.088	—

Non-orthogonal parameters with bar.

shows α and β parameter values for $^1\Pi_u$ and $^1\Pi_g$ states calculated with optimal exponents for each state. We find $^1\Pi_g$ much less antibonding than $^1\Pi_u$ bonding contrary to the usual Hückel type assumptions. The orbital energy ε for the π_g orbital equals the $3d$ energy of the hydrogen atom, although it is mainly composed of highly expanded $2p\pi$ orbitals.

If we take the $^1\Pi_u$ state exponents as a basis for our calculation, the various α and β parameters will be more uniform. Most semiempirical methods take for granted that the atomic orbitals used for the ground state can be used with the same exponents for excited states also. The choice of the same parameters for ground and excited states is then a simple consequence. Yet, from our present study we expect that also in hydrocarbons the assumption of equal exponents for all possible Π states is unrealistic and might be completely misleading. Huzinaga [5] showed that different exponents should be used for bonding and antibonding orbitals in ethylene.

Let us also show the implications for the Pariser-Parr method [6] where β is calculated by the state energy difference.

$$\Delta E = E^{\text{total}}_{\Pi_g} - E^{\text{total}}_{\Pi_u} = -2\beta\,.$$

We would have to take the difference between the ODC level energies with the optimal exponents for Π_u and Π_g states as the empirical energy difference. Fig. 3

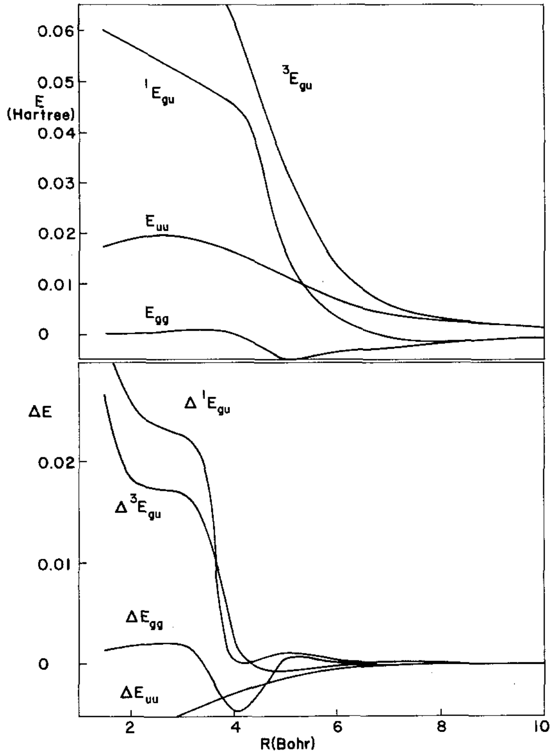

Fig. 3. ODC singlet-singlet $^1E_{gu}$, triplet-triplet $^3E_{gu}$ and singlet-triplet E_{uu}, E_{gg} transition energies and differences ΔE between $^1\Pi_u$ based and optimal values

shows these differences for all possible combinations. The β calculated in such a way is at best an average of the β's for Π_g and Π_u states. It cannot be interpreted as representative for either Π_u or Π_g. On the other hand, if we calculate all quantities with the same exponent set, the energy difference between two states is completely misrepresented. So the β's based on equal exponents for all states do not yield good excitation energies. The differences between optimal and $^1\Pi_u$ based excitation energies are also in Fig. 3.

We do not try to find further similarities with hydrocarbons, because H_2 is not a representative system. Further studies including $2s$-, $2p\sigma$- and $2p\pi$-interactions, might be done along the same lines for ethylene.

We feel that exponent optimization in a minimal basis set is necessary, because it is difficult to predict whether the atomic orbitals in a molecule are more contracted, as in $^3\Pi_u$ state, or more expanded, as in the $^1\Pi_u$ and Π_g states, than in the free atom. Large basis sets do not require such a careful exponent optimization. However, they involve a large number of parameters. We do not expect that parametrization schemes can be simplified to such a degree as Hückel or Pariser-Parr methods suggest.

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