σ-π Separation: Excited H_2 as a Model System* **

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The low-lying Π states of H_2 consist of one core (σ) and one valence (π) electron and afford a direct evaluation of intershell σ-π interaction. After resolution of the electronic energy into σ only, π only, and σ-π parts, it is shown that an electronic change in this model system is due solely to a change in the π electrons. Simple Hückel theory is examined. If the molecular core is represented properly, regardless of the π wave function the calculated α and β parameters are in reasonable agreement with the "empirical" parameters. This agreement appears to be due to a fortuitous cancellation of energy contributions.

Die niedrig liegenden Π-Zustände des H_2 bestehen aus einem Rumpfelektron σ und einem Valenzelektron π und ermöglichen eine direkte Auswertung der σ-π-Wechselwirkung zwischen zwei Schalen. Nach der Zerlegung der elektronischen Energie in σ-, π- und σ-π-Anteile wird gezeigt, daß eine elektronische Veränderung in diesem Modellsystem nur auf eine Veränderung des π-Elektronenanteils zurückgeht. Die einfache Hückeltheorie wird untersucht. Wenn der Molekülrumpf geeignet dargestellt wird, so sind, unabhängig von der π-Wellenfunktion, die berechneten Parameter α und β in guter Übereinstimmung mit den empirischen Parametern. Diese Übereinstimmung scheint auf eine starke Auslöschung von Energieanteilen zurückzugehen.

Les états inférieurs π de H_2 consistent en un électron de coeur (σ) et un électron de valence (π) et fournissent une évaluation directe de l'interaction entre couches σ-π. Après expression de l'énergie électronique en parties σ, π et σ-π, on montre qu'une modification électronique de ce système modèle est due seulement à une modification des électrons π. La théorie de Hückel simple est examinée. Si le coeur moléculaire est convenablement représenté, quelle que soit la fonction d'onde π, les paramètres α at β calculés sont en accord raisonnable avec les paramètres empiriques. Cet accord apparaît comme le résultat d'une compensation fortuite de contributions énergétiques.

Introduction

Conventionally, the π-electron approximation allows one to consider that an electronic change in a molecule containing π electrons is related solely to a change in those electrons. But, as indicated by studies on excited states of various molecules, the σ core often undergoes a sizeable rearrangement upon excitation of the molecule. For example, upon excitation ethylene is no longer planar [1], acetylene no longer linear [2–4], and benzene no longer hexagonal [5, 6]. Hence the assumption that an electronic change is a function of the change in the π electrons only, in general, is not valid for quantitative studies.

The purpose of this paper is to examine the classical π-electron approximation in a systematic, quantitative manner. The low-lying Π states of the hydrogen molecule are the systems examined. Because the electronic configurations for these

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states consist of a single σ (core) molecular orbital and a single π (valence) molecular orbital, there is no intra-shell correlation and a direct evaluation of one σ electron interacting with one π electron is possible. In addition, there is only one geometrical variable, the internuclear distance between the two atoms.

The selected Π states of H_2 are molecular Rydberg systems. Since the core electron is highly localized about the nuclei while the valence electron is very loosely bound, the frozen core description is expectedly an accurate one [7]. Thus, the selected states represent idealized π systems and will be considered as analogs to conventional π systems. Furthermore, highly accurate calculations have been performed on these small systems [8]. Such calculations provide insight into the π-electron approximation and its use on more conventional conjugated systems where similar, comparably-accurate calculations are not yet available.

An hierarchy of two wave functions is employed in this work. The first wave function is the familiar single-configuration analytical LCAO-MO-SCF wave function generated by the method formulated by Roothaan [9–11]. The extended basis self-consistent field (SCF) calculations of this work are Hartree-Fock (HF) calculations. The second wave function is the double-configuration SCF wave function, hereafter called the optimal double configuration (ODC) wave function. Table 1 and Fig. 1 demonstrate lucidly the "goodness" of the HF and ODC calculations compared with the experimental results of Herzberg [12] and Namioka [13] for the $C\,^1\Pi_u$ state of H_2. Because this molecular system has weak electron-electron repulsion, correlation energy is small (0.12 eV [8] contrasted with 1.1 eV [14] for the ground state of H_2) and the single-configuration HF potential curve closely approximates the experimental curve near the minimum (R_e). Consequently, the spectroscopic constants derived from this curve are quite good. But at larger internuclear distances (R), the HF model is inappropriate because it considers electron correlation improperly and dissociation to a mixture of atomic and ionic states rather than to purely atomic states occurs. At large R the ODC model includes all electron correlation and proper dissociation occurs. At R_e about half of the correlation is included and the ODC spectroscopic constants show a corresponding improvement over the HF constants.

Table 1. *Spectroscopic constants for* $H_2(C\,^1\Pi_u)$

E(hartrees)	HF[a] -0.7139131	ODC[a] -0.7158284	Exp.[b] -0.71859[c]
R(bohrs)	1.934	1.948	1.952
ω_e(cm^{-1})	2548.0	2489.0	2443.0
B_e(cm^{-1})	31.9	31.5	31.4
$\omega_e x_e$(cm^{-1})	57.3	61.5	67.0
α_e(cm^{-1})	1.490	1.565	1.626

[a] Ref. [8].
[b] Ref. [12].
[c] Namioka [13] gives values of $\omega_e = 2448$ cm^{-1} and $E = -0.7183492$ hartrees at 1.952 bohrs. There is doubt as to the reliability of the older Herzberg value, -0.71859 hartrees.
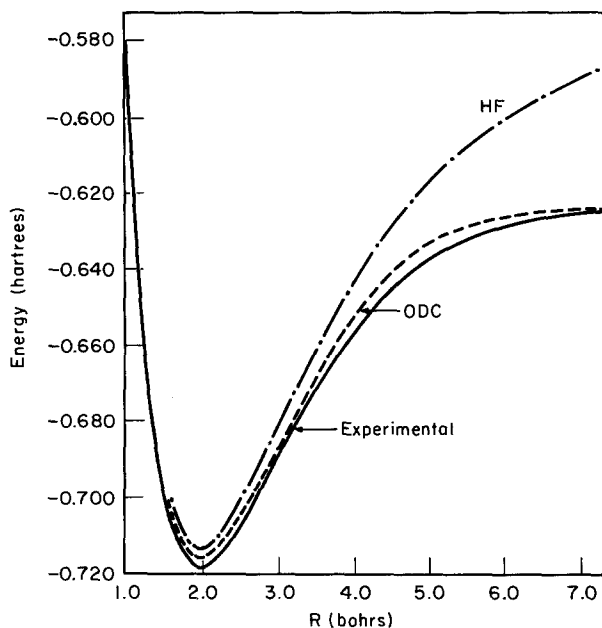
Fig. 1. Potential energy curves for the $C^1\Pi_u$ state of H_2 (Ref. [8])

These two wave functions can be resolved readily into σ only, π only, and σ-π parts. This is essential to the analysis of this paper. More complex wave functions [15–17] approach more closely the experimental results, but they can not be so resolved. In light of the purpose of this paper, these two wave functions are more than sufficiently accurate to provide the quantitative analysis intended.

The π-Electron Approximation

Lykos and Parr [18] put the π-electron approximation on firm theoretical ground when they defined the σ-π separability conditions:

A) The total n-electron wave function $\Psi(1, 2, ..., n)$ may be written as the antisymmetrized product of the σ wave function $\Sigma(1, 2, ..., n_\sigma)$ and the π wave function $\Pi(n_\sigma + 1, n_\sigma + 2, ..., n)$. The σ wave function is an anti-symmetrized function based on the coordinates of the n_σ σ electrons; the π wave function is an antisymmetrized function based on the coordinates of the n_π π electrons. Algebraically,

$$\Psi(1, 2, ..., n) = N_{\sigma\pi} \mathscr{A}\{(\Sigma)(\Pi)\},$$

where $\mathscr{A}$ is the antisymmetrization operator which antisymmetrizes the $(\Sigma)(\Pi)$ product with respect to exchange of the n_σ σ electrons with the n_π π electrons, $N_{\sigma\pi}$ is the normalization factor defined by

$$N_{\sigma\pi} = (n!/n_\sigma! n_\pi!)^{-\frac{1}{2}},$$

and $n = n_\sigma + n_\pi$.

B) Each function Σ, Π, and Ψ is normalized to unity.

C) The functions Σ and Π can be expanded in terms of orthonormal Slater determinants which are built from orthonormal sets of one-electron functions, no member of which enters both Σ and Π.

Consider the electronic Hamiltonian for an n-electron system

$$
\begin{aligned}
\mathscr{H}(1, 2, \ldots, n) = & \sum_i \left(T_i + \sum_\alpha V_{\alpha i} + \sum_{i > i'} V_{ii'} \right) \\
& + \sum_j \left(T_j + \sum_\alpha V_{\alpha j} + \sum_{j > j'} V_{jj'} \right) + \sum \sum V_{ij} ,
\end{aligned}
\tag{1}
$$

where the i and i' summations are over the σ electrons, the j and j' summations are over the π electrons, and the α summation is over the nuclei. T_i is the kinetic energy of the ith electron, $V_{\alpha i}$ is the potential energy of the ith electron in the field of the αth nucleus, and V_{ij} is the potential energy of the ith electron in the field of the jth electron. Eq. (1) can be rewritten

$$
\begin{aligned}
\mathscr{H}(1, 2, \ldots, n) = & \mathscr{H}_\sigma^0(1, 2, \ldots, n_\sigma) + \mathscr{H}_\pi^0(n_\sigma + 1, n_\sigma + 2, \ldots, n) \\
& + V_{\sigma\pi}(1, 2, \ldots, n_\sigma, n_\sigma + 1, \ldots, n).
\end{aligned}
$$

Consider now a molecular wave function which obeys the σ-π separability conditions and determine the expectation value of the electronic energy for the system:

$$
\begin{aligned}
E_{\text{elect}} = & \langle \Psi(1, \ldots, n) | \mathscr{H}(1, \ldots, n) | \Psi(1, \ldots, n) \rangle / \langle \Psi(1, \ldots, n) | \Psi(1, \ldots, n) \rangle \\
& = E_\sigma^0 + E_\pi^0 + E_{\sigma\pi},
\end{aligned}
\tag{2}
$$

where

$$
E_\sigma^0 = \langle \Sigma | \mathscr{H}_\sigma^0 | \Sigma \rangle / \langle \Sigma | \Sigma \rangle,
$$

$$
E_\pi^0 = \langle \Pi | \mathscr{H}_\pi^0 | \Pi \rangle / \langle \Pi | \Pi \rangle,
$$

and

$$
E_{\sigma\pi} = \langle \Psi | V_{\sigma\pi} | \Psi \rangle / \langle \Psi | \Psi \rangle.
$$

The latter two energy terms may be incorporated into E_π resulting in the equation $E_{\text{elect}} = E_\sigma^0 + E_\pi$.

As usually written, the π-electron approximation is defined as that approximation where the wave functions for different states of the system, Ψ and Ψ', satisfy the three separability conditions and have a common σ wave function. The energy of transition between these states, ΔE_{elect}, is then a function of the change in the π electrons only:

$$
\Delta E_{\text{elect}} = E_{\text{elect}}' - E_{\text{elect}} = (E_\sigma^0 + E_\pi') - (E_\sigma^0 + E_\pi) = E_\pi' - E_\pi.
$$

Parallel to the general development of an n-electron system, the energy of the two-electron systems is resolved into E_σ^0, E_π^0, and $E_{\sigma\pi}$ terms. The Hamiltonian for H_2 is written

$$
\begin{aligned}
\mathscr{H}(1, 2) = & (T_1 + V_{\alpha 1} + V_{\beta 1}) + (T_2 + V_{\alpha 2} + V_{\beta 2}) + V_{12} \\
& = \mathscr{H}_\sigma^0(1) + \mathscr{H}_\pi^0(2) + V_{\sigma\pi}(1, 2),
\end{aligned}
$$

where the electrons are labelled 1 and 2 and the nuclei, α and β. Since the energy expectation value is independent of spin, the spin part of the wave function is

factored off to yield the space-only single-configuration wave function

$$^{1,3}\Psi_{\text{HF}} = \{\sigma(1)\,\pi(2) \pm \sigma(2)\,\pi(1)\}/\sqrt{2}\,,$$

where the positive sign designates the singlet state and the minus sign, the triplet state. It is unnecessary to subscript the σ and π molecular orbitals (MO's) according to their parity until later, when referring to a particular Π state. The electronic energy is

$$^{1,3}E_{\text{HF}} = \langle\,^{1,3}\Psi(1,2)\,|\,\mathscr{H}(1,2)\,|\,^{1,3}\Psi(1,2)\rangle/\langle\,^{1,3}\Psi(1,2)\,|\,^{1,3}\Psi(1,2)\rangle$$

$$= \langle\sigma(1)\,\pi(2)\,|\,\mathscr{H}(1,2)\,|\,\sigma(1)\,\pi(2)\rangle \pm \langle\sigma(1)\,\pi(2)\,|\,\mathscr{H}(1,2)\,|\,\sigma(2)\,\pi(1)\rangle.$$

Expansion of the Hamiltonian and algebraic manipulation yield

$$^{1,3}E_{\text{HF}} = \langle\sigma(1)\,|\,\mathscr{H}_\sigma^0(1)\,|\,\sigma(1)\rangle + \langle\pi(2)\,|\,\mathscr{H}_\pi^0(2)\,|\,\pi(2)\rangle$$

$$+ \langle\sigma(1)\,\pi(2)\,|\,r_{12}^{-1}\,|\,\sigma(1)\,\pi(2)\rangle \pm \langle\sigma(1)\,\pi(2)\,|\,r_{12}^{-1}\,|\,\sigma(2)\,\pi(1)\rangle \qquad (3)$$

$$= H_\sigma + H_\pi + (J_{\sigma\pi} \pm K_{\sigma\pi}).$$

The one-electron terms are the energies of the σ electron and the π electron, respectively, in the field of the two nuclei. The two-electron terms are the coulombic and exchange contributions of the two electrons mutually in the field of one another. Comparison of Eqs. (2) and (3) gives the following equalities:

$$E_\sigma^0 = H_\sigma\,, \qquad E_\pi^0 = H_\pi\,, \qquad \text{and} \qquad E_{\sigma\pi} = J_{\sigma\pi} \pm K_{\sigma\pi}\,.$$

So far the only limitation to the wave function is that it be a single-configuration wave function. Lykos and Parr [18] show that functions Σ and Π may be expanded in terms of orthonormal Slater determinants. The total wave function, for example, becomes

$$\Psi = (A_1\Sigma_1 + A_2\Sigma_2)\cdot(B_1\Pi_1 + B_2\Pi_2)\,,$$

where no one-electron σ MO enters both Σ_1 and Σ_2 and no one-electron π MO enters both Π_1 and Π_2. If $A_2 = 0$, one has employed the method known as "configuration interaction within the π-electron approximation". That is, the Σ wave function (core) is frozen and Π is expanded in a series of Π_i configurations.

The ODC wave function also can be recast in terms of the π-electron approximation [1]. The ODC wave function is written

$$^{1,3}\Psi_{\text{ODC}} = A\{\sigma(1)\,\pi(2) \pm \sigma(2)\,\pi(1)\}/\sqrt{2}$$

$$+ B\{\sigma'(1)\,\pi'(2) \pm \sigma'(2)\,\pi'(1)\}/\sqrt{2}\,,$$

where as before the minus sign designates the triplet state, and A and B are the configuration mixing coefficients. The first configuration corresponds to a bonding state and the second, a repulsive state. The electronic energy is written

$$^{1,3}E_{\text{ODC}} = A^2(H_\sigma + H_\pi + J_{\sigma\pi} \pm K_{\sigma\pi})$$

$$+ B^2(H_{\sigma'} + H_{\pi'} + J_{\sigma'\pi'} \pm K_{\sigma'\pi'}) + 2AB\cdot E_{\text{coupling}}\,,$$

---

[1] Clearly, the earlier wave function with $A_2 \neq 0$ is not the same as the ODC wave function. That is, $(A_1\Sigma_1 + A_2\Sigma_2)\cdot(B_1\Pi_1 + B_2\Pi_2) \neq A\Sigma_1\Pi_1 + B\Sigma_2\Pi_2$.

Table 2. *Division of energy of* H_2 *molecule into* σ *and* π *parts*

Wave function	E_σ^0	E_π^0	$E_{\sigma\pi}^{\text{within a}}$	$E_{\sigma\pi}^{\text{between}}$
HF	H_σ	H_π	$J_{\sigma\pi} \pm K_{\sigma\pi}$	
ODC	$A^2 \cdot H_\sigma + B^2 \cdot H_{\sigma'}$	$A^2 \cdot H_\pi + B^2 \cdot H_{\pi'}$	$A^2(J_{\sigma\pi} \pm K_{\sigma\pi})$ $+ B^2(J_{\sigma'\pi'} \pm K_{\sigma'\pi'})$	$2AB \cdot E_{\text{coupling}}$

a $E_{\sigma\pi}^{\text{total}} = E_{\sigma\pi}^{\text{within}} + E_{\sigma\pi}^{\text{between}}$.

where the energy E_{coupling} is composed of exchange contributions arising from exchange of electrons between the two configurations. In the HF case, E_σ^0 and E_π^0 are just the H_σ and H_π, respectively. But in the ODC case, the E_σ^0 and E_π^0 are composed of one-electron energies from both configurations, each properly weighted. For easy comparison, the division of energy into σ only, π only, and σ-π interaction parts is found in Table 2.

The σ-π interaction for the HF wave function is intra-configurational. In the ODC wave function there is an intra-configurational σ-π interaction within the first configuration, one within the second configuration, and an inter-configurational σ-π interaction between the two configurations. That is, in the two-configuration wave function there occurs a σ-π interaction contribution distinct from (in addition to) that of the single configuration. Evaluation of $E_{\sigma\pi}$ contributions will be presented in the next section.

It is important to realize that the ODC wave function transcends the π-electron approximation. The orbitals are partitioned as before into σ and π classes, but the restriction that the total wave function be an antisymmetrized product is removed by the addition of a second configuration. The ability to divide the energy of the system into σ and π parts with both wave functions, the HF wave function obeying the π-electron approximation and the more accurate ODC wave function transcending the π-electron approximation, affords quantitative examination of the approximation.

Results and Discussion

Selected one-electron expectation values for σ and π MO's for HF and ODC wave functions have been presented for the $C\,^1\Pi_u$ state of H_2 [8]. Close agreement between HF and ODC σ MO expectation values was observed, but HF and ODC π MO expectation values differed considerably. Fig. 2 compares the core energy, E_σ^0, of the four Rydberg systems for the HF model. If E_σ^0 curves for the ODC model were included, they would be superimposed over those presented. Thus, the σ charge density is essentially unchanged regardless of the wave function model employed in determining the π charge density.

But the nearly identical curves of Fig. 2 are not unexpected. The σ electron is in the field of two bare nuclei and strongly influenced by them. The π electron is weakly attracted by the nuclei and does not strongly affect the σ electron. Comparison with the E_σ^0 value for the one-electron H_2^+ system shows that indeed the σ electron does not "feel" the outer-lying π electron. This is the case whether the

Table 3. *Transition energies (hartrees)*

R(bohrs)	Singlet states[a]				Triplet states[b]			
	Δ_π(HF)	Δ_π(ODC)	Δ(ODC)	Δ(Browne)[c]	Δ_π(HF)	Δ_π(ODC)	Δ(ODC)	Δ(Browne)[c]
2.00	0.0695	0.0689	0.0696	0.0742	0.0867	0.0874	0.0866	0.0935
4.00	0.0532	0.0169	0.0406	0.0432	0.0672	0.0408	0.0589	0.0635
6.00	0.0477	−0.0046	0.0042	0.0039	0.0515	0.0035	0.0135	0.0139
8.00	0.0374	−0.0484	−0.0010	−0.0012	0.0325	0.0018	0.0030	0.0031

[a] $\Delta = E_{\text{total}}(^1\Pi_g) - E_{\text{total}}(^1\Pi_u)$; $\Delta_\pi = E_\pi(^1\Pi_g) - E_\pi(^1\Pi_u)$.
[b] $\Delta = E_{\text{total}}(^3\Pi_g) - E_{\text{total}}(^3\Pi_u)$; $\Delta_\pi = E_\pi(^3\Pi_g) - E_\pi(^3\Pi_u)$.
[c] See Ref. [21] for the Π_u state energies and Ref. [22] for the Π_g state energies.

π electron is in a bonding MO (Π_u states) or an antibonding MO (Π_g states). Because the σ core is effectively insensitive to the π electron, the frozen core assumption of the π-electron approximation is obeyed for these systems.

However, the E_π^0 energies are dependent strongly upon the molecular state. Fig. 3 shows the E_π^0 energies as a function of R for the one-electron H_2^+ and two-electron H_2 systems. The E_π^0 curve for H_2^+ is the total electronic energy for the $^2\Pi_u$ state [19]. For this system there is only one π electron in the field of two bare nuclei and the E_π^0 curve is lowest in energy. For the H_2 systems there is one π electron in the field of two nuclei shielded by the inner σ electron. Correspondingly, the E_π^0 curves for H_2 are above that for H_2^+. Because the π electron is in a bonding MO for the Π_u states and an antibonding MO for the Π_g states, E_π^0 curves for the latter states are higher in energy. As expected, the triplet state curves are lower in energy than the singlet state curves of the same symmetry because additional energy is required to pair up two electrons in the singlet states[2].

The insensitivity of the core for both HF and ODC models has been demonstrated; an evaluation of the π-electron approximation in terms of transition energies and ionization potentials now follows. Table 3 contains the energy transitions between states of the same multiplicity for increasing R. Included in the table are HF Δ_π values, ODC Δ_π values, and two Δ values, determined from the ODC calculations and the calculations of Browne [21, 22] on these four states. The Δ_π values are within the frozen core approximation and only E_π differs upon excitation. The Δ values are energy transitions where no frozen core approximation is assumed. Although slight differences in the Δ values occur due to the differences in the specific calculations, they show similar behavior with increasing R.

The energies of Table 3 correspond to excitation of the π electron from a bonding to an antibonding MO. The results of the table indicate that ΔE_{elect} approximately equals $E_\pi' - E_\pi$ near the minimum of the potential curve (2.00 bohrs) for either HF or ODC wave function. As one moves toward larger R, the frozen core approximation collapses for the HF model. However, with the ODC model the

[2] Hartree-Fock wave functions were used in calculating the H_2 curves of Fig. 3. For the Π_u states, E_π^0 energies for the ODC model are very nearly those for the HF model. For the Π_g states, E_π^0 energies for the ODC model fall lower in energy than the corresponding HF E_π^0 energies [20]. These differences are due to the basis set which was optimized explicitly for the $^1\Pi_u$ state. If a fully-optimized basis set for the Π_g states were available, it is expected that differences between HF and ODC curves for these states would be slight.
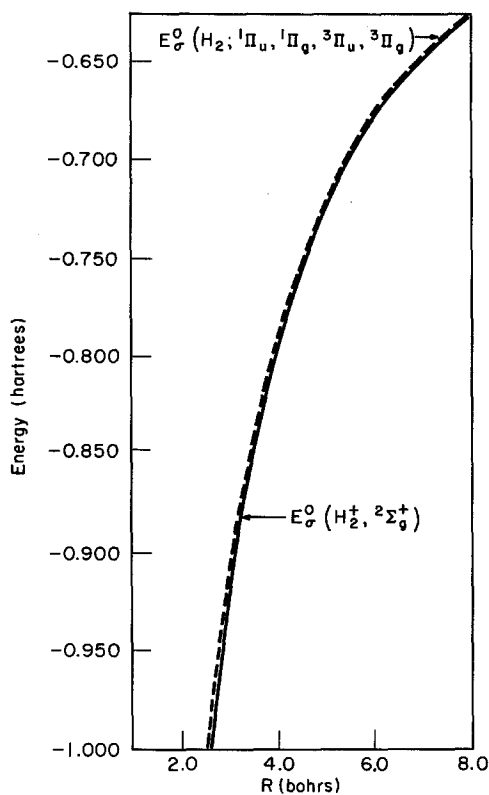
Fig. 2. One-electron energies for the four lowest-lying Π states of hydrogen molecule and the ground state of hydrogen molecule-ion

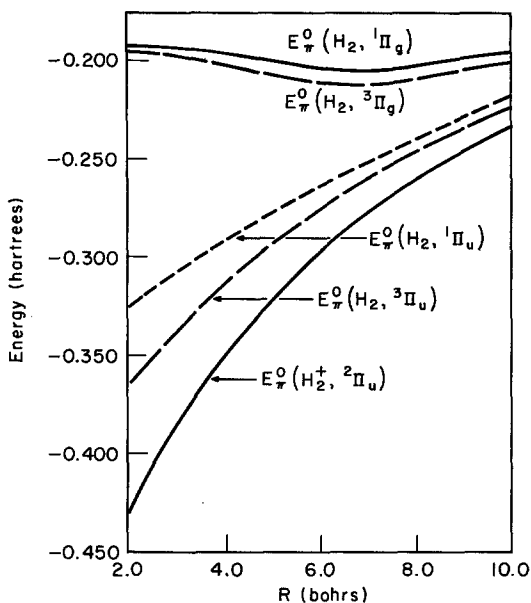Fig. 3. One-electron energies for the four lowest-lying Π states of hydrogen molecule and the $^2\Pi_u$ state of hydrogen molecule-ion

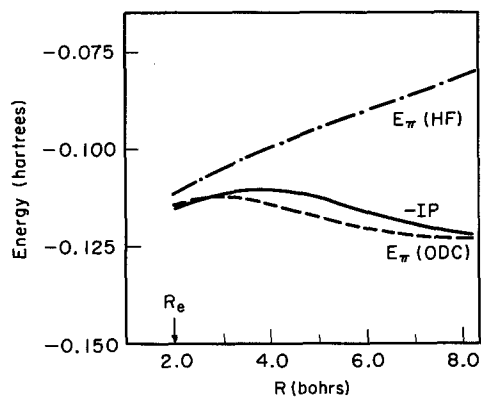Fig. 4. Ionization potentials for the C $^1\Pi_u$ state of hydrogen molecule

essential validity of the frozen core remains. The ODC Δ_π values give somewhat less satisfactory results from 4.00–6.00 bohrs because of large potential maxima occurring at this region of the potential curves for the Π_g states [8, 22, 23]. Thus one can conclude that, even though the HF model obeys the σ-π separability conditions and the frozen core conditions, the HF transition energies within the π-electron approximation lose their significance at large R. Whereas with the more flexible ODC model, which transcends the σ-π separability conditions, transition energies are quite reasonable within the frozen core approximation at all R.

The ionization potential (IP) necessary to remove completely the π electron from the unchanging core is just $-E_\pi$:

$$\text{IP} = E_{\text{H}_2^+} - E_{\text{H}_2} = E_\sigma^0 - (E_\sigma^0 + E_\pi) = -E_\pi.$$

Fig. 4 contains curves of $-$IP and E_π for the $^1\Pi_u$ state of H$_2$ over all R. The IP values are the differences between $E_{\text{total}}(\text{H}_2^+, {}^2\Sigma_g^+)$ and $E_{\text{total}}(\text{H}_2, {}^1\Pi_u)$. The very accurate energies of Kolos and Wolniewicz [15] for H$_2$ and Bates, Ledsham, and Stewart [19] for H$_2^+$ were used to determine the IP curves of Fig. 4. There are no calculations comparable to the Kolos and Wolniewicz ones for the potential curves of the other three H$_2$ states and these states are not included in the figure.

The HF and ODC calculations at R_e yield E_π results which are close to the $-$IP value. But upon moving toward large R, the HF curve runs counter to the $-$IP curve. In contrast, the ODC curve shows the essential features associated with the removal of the outer π electron at all R values. The answer to the collapse of the HF model lies in the repulsive interaction between σ and π electrons, viz. $E_{\sigma\pi}$. The analytical division of $E_{\sigma\pi}$ into intra-configurational and inter-configurational contributions was presented in Table 2; evaluation of these contributions is now presented.

Table 4 contains a breakdown of $E_{\sigma\pi}$ into $E_{\sigma\pi}^{\text{between}}$ and $E_{\sigma\pi}^{\text{within}}$ contributions for the ODC wave function and $E_{\sigma\pi}$ for the HF wave function, all as a function of R. Data are presented only for the $^1\Pi_u$ state; similar data occur for the other three states [20] and are not presented. It is understood that any conclusions drawn from analysis of Table 4 are in general valid for all four molecular states.

One expects $E_{\sigma\pi}$ to vanish as the molecule is pulled apart and the electrons are located on the separate nuclei. But $E_{\sigma\pi}(\text{HF})$ does not diminish rapidly enough with increasing R while $E_{\sigma\pi}(\text{ODC})$ does. Although $E_{\sigma\pi}^{\text{between}}$ for the ODC model actually increases slightly as R increases, this is not unexpected because the two configurations are mixed together more at large R than at small R. The inclusion of both intra-configurational and inter-configurational electron-electron repulsion is necessary for the proper behavior of $E_{\sigma\pi}^{\text{total}}$ as a function of R. Clearly, then, the collapse of the HF model within the π-electron approximation is due to the improper evaluation of $E_{\sigma\pi}$. In order to evaluate the molecule properly for increasing R, one should use a more flexible wave function.

The ability to resolve excited H$_2$ into separate parts for these wave functions affords examination of the separability problem as the "π bond" is stretched apart; but in π-electron systems the molecule is usually considered in non-dissociative processes. Why then examine separability with the single-configuration wave function which becomes incorrect when the internuclear distance is stretched well beyond R_e [24]? To the contrary, separability is worthy of examination as a function of R because of the sensitivity to change in geometry upon excitation of the molecule. If the LCAO–MO–SCF wave function cannot account for σ-π inter-

Table 4. σ-π interaction energies (hartrees)

R(bohrs)	$E_{\sigma\pi}^{\text{within}}$(HF)	$E_{\sigma\pi}^{\text{within}}$(ODC)	$E_{\sigma\pi}^{\text{between}}$(ODC)	$E_{\sigma\pi}^{\text{total}}$(ODC)
2.00	0.21405	0.17402	0.03948	0.21350
4.00	0.19218	0.13144	0.05031	0.18175
6.00	0.17404	0.08107	0.06092	0.14199
8.00	0.15896	0.04201	0.07051	0.11252
10.00	0.14755	0.01514	0.07812	0.09326

action properly at all geometries, results may lose their meaning. This suggests particular care in the use of such functions for conventional π-electron systems. Although the geometrical variable treated in this work is the bond distance, it is understood that one must excercise care also in selecting wave functions for larger molecules when changes in bond angles are to be considered.

Hückel Theory

Communication of the results concerning the π-electron approximation may be presented also in terms of simple Hückel theory[3]. Traditionally, workers using Hückel theory calibrate the method with experimental results; the particular calibration then allows examination of related molecular systems in the same or similar experimental situation. Despite many apparent successes of Hückel theory [28–30], the validity of transferring the calibrated parameters from one system to related systems is often largely a matter of faith, and attempts have been made to relate the theory to the underlying quantum mechanics[4]. The quantum mechanically well-defined wave functions and energy levels of these model π-electron systems permit the Hückel operator $\mathscr{H}^{\pi}_{\mathrm{eff}}$ to be defined explicitly and, subsequently, afford a quantitative test of simple Hückel theory.

Hückel theory states that the Hamiltonian is a sum of one-electron operators over the π electrons only,

$$\mathscr{H}^{\pi}_{\mathrm{eff}}(\text{total}) = \sum_i \mathscr{H}^{\pi}_{\mathrm{eff}}(i)$$

and

$$\mathscr{H}^{\pi}_{\mathrm{eff}}(i) \cdot \phi(i) = \varepsilon_{\pi} \cdot \phi(i);$$

that the Π wave function is a simple product of one-electron functions; and that the one-electron functions are LCAO functions [25].

For the Π states of H_2, application of the variation method yields the secular equation

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0,$$

where as in the simplest Hückel method one does not consider overlap between neighbors, and α and β are the familiar coulomb and resonance integrals, respectively. Solution of this equation yields the two energy levels $E = \alpha \pm \beta$. As both α and β are inherently negative quantities, the eigenvalue $E = \alpha + \beta$ is the lower one and it should be occupied by the single π electron.

The Hückel method does not explicitly define the $\mathscr{H}_{\mathrm{eff}}$ Hamiltonian and evaluation of α and β is done empirically. The total energy is usually assumed to be just the sum of the orbital energies $\left(E_{\mathrm{elect}} = \sum_i \varepsilon_{\pi_i}\right)$. For this one-electron π

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[3] Pariser-Parr-Pople and other similar semiempirical treatments will not be discussed here. Excellent reviews including references may be found in the literature [25–27].

[4] See Ref. [25] and the references therein.

system, the electronic energy is just the orbital energy:

$$E_{elect} = \varepsilon_\pi \text{ (or } \varepsilon_{\pi*})$$
$$= \langle 2^{-\frac{1}{2}}(2p_a \pm 2p_b)|\mathscr{H}^\pi_{eff}|2^{-\frac{1}{2}}(2p_a \pm 2p_b)\rangle$$
$$= \langle 2p_a|\mathscr{H}^\pi_{eff}|2p_a\rangle \pm \langle 2p_a|\mathscr{H}^\pi_{eff}|2p_b\rangle$$
$$= \alpha \pm \beta,$$

where π and $\pi*$ MO's are simple LCAO functions with overlap neglected. Assuming that the same basis set characterizes both states, α is constant and change in the energy of the system by a transition from the bonding to the antibonding level gives:

$$\Delta E_{elect} = E_{antibonding} - E_{bonding} = (\alpha - \beta) - (\alpha + \beta) = -2\beta.$$

Hence experimental excitation energies afford an evaluation of β. Once β is determined, α may be obtained by equating $-(\alpha + \beta)$ to the energy of ionizing the π electron.

Table 5 contains calibrated and calculated α and β values. The "empirical" transition energies are obtained from potential energy curves of the appropriate Π states and "empirical" ionization energies, from the same curves and that for the ground state of H$_2^+$.

For the Π states, the Hückel operator is defined

$$\mathscr{H}^\pi_{eff} = -1/2 V_1^2 + (-r_{a_1}^{-1} - r_{b_1}^{-1}) + V_{eff}(1) = T + U + V_{eff},$$

where T is the kinetic energy term, U is the nuclear attraction term, and V_{eff} is the electron repulsion term. V_{eff} is the averaged repulsion between the σ core and the π electron and is written explicitly

$$V_{eff} = \langle \sigma_g(2)|r_{12}^{-1}|\sigma_g(2)\rangle_2,$$

and then

$$\alpha = \langle 2p_a(1)|\mathscr{H}^\pi_{eff}(1)|2p_a(1)\rangle$$
$$= \langle 2p_a(1)|T(1)|2p_a(1)\rangle + \langle 2p_a(1)|U(1)|2p_a(1)\rangle$$
$$+ \langle 2p_a(1) 2p_a(1)|r_{12}^{-1}|\sigma_g(2)\sigma_g(2)\rangle,$$

and

$$\beta = \langle 2p_a(1)|T(1)|2p_b(1)\rangle + \langle 2p_a(1)|U(1)|2p_b(1)\rangle$$
$$+ \langle 2p_a(1) 2p_b(1)|r_{12}^{-1}|\sigma_g(2)\sigma_g(2)\rangle.$$

So far the functions $2p_a$ and $2p_b$ are free-atom $2p\pi$ AO's located on centers a and b, respectively, and only one set of α and β parameters arises. However, one should more realistically envision the molecular environment and consider distorted AO's. For example, consider the case where π and $\pi*$ MO's include overlap explicitly:

$$\pi = (2p_a + 2p_b)/\{2(1 + S_{ab})\}^{-\frac{1}{2}}$$

and

$$\pi* = (2p_a - 2p_b)/\{2(1 - S_{ab})\}^{-\frac{1}{2}}.$$

The α and β parameters including overlap differ according to ungerade (u) and gerade (g) parity as follows:

$$\alpha_u = \alpha/(1 + S_{ab}^u)\,, \qquad\qquad \beta_u = \beta/(1 + S_{ab}^u)\,,$$
$$\alpha_g = \alpha/(1 - S_{ab}^g)\,, \quad \text{and} \quad \beta_g = \beta/(1 - S_{ab}^g)\,.$$

Finally, the dependency of α and β upon multiplicity should be noted. Actually, then, for these model π systems there are four unique sets of α and β parameters, rather than just the traditional set calibrated via experiment.

Table 5 contains three different calculated α and β parameters, compared with the calibrated parameters. The three calculations will be denoted by I (best-molecule $2p\pi$ AO's and best-molecule core), II (free-atom $2p\pi$ AO's and best-molecule core), and III (free-atom $2p\pi$ AO's and free-atom core). Distorted or best-molecule $2p\pi$ AO's are the best AO's in the SCF sense, where the functions are determined in the average field of the molecular core. This molecular core is the best σ_g MO in the SCF sense, also. Free-atom AO's are described above, and the free-atom core is the simplest possible LCAO–MO function: $\sigma_g = 2^{-\frac{1}{2}}(1s_a + 1s_b)$ where $1s_a$ and $1s_b$ are free-atom AO's.

Columns I and II of Table 5 contain values which are not unreasonable when compared with the calibrated values. But the calculated α and β values have very nearly the same value while the calibrated values show α as roughly twice the magnitude of β. One wonders why α, a property of the atom, and β, a property of the bond, are nearly identical for the calculated results. In addition, representing the core with the minimal basis LCAO–MO function excluding overlap poses another question. Why are these parameters positive, opposite in sign to those obtained empirically? A resolution of the calculated parameters into one- and two-electron parts provides the answers.

Table 6 contains the various contributions to the calculated α's and β's of Table 5. The notation here is the same as before. A comparison of II and III of

Table 5. *Evaluation of Hückel α and β parameters*[a]

Calibrated from potential curves[b]		Calculated		
ODC	Browne[c]	I Best-molecule $2p\pi$ AO's and best-molecule core	II Free-atom $2p\pi$ AO's and best-molecule core	III Free-atom $2p\pi$ AO's and free-atom core
$^1\Pi_u$ State				
$\alpha = -2.13$	-2.03	-3.00	-3.05	0.548
$\beta = -0.95$	-1.01	-2.94	-3.08	0.181
$^3\Pi_u$ State				
$\alpha = -2.37$	-2.28	-3.19	-3.05	0.548
$\beta = -1.18$	-1.27	-3.27	-3.08	0.181

[a] Units for α and β are eV; all values are for $R = 2.00$ bohrs (i.e. about R_e).

[b] α and β values are obtained from $^1\Pi_u \rightarrow {}^1\Pi_g$ or $^3\Pi_u \rightarrow {}^3\Pi_g$ transition energies and from $^1\Pi_u$ and $^3\Pi_u$ ionization energies. See text for complete description.

[c] Data on Π_u states from Ref. [21] and on Π_g states from Ref. [22].

Table 6. *Resolution of Hückel α and β parameters* (eV)

Type of energy contribution	I Best-molecule $2p\pi$ AO's and best-molecule core		II Free-atom $2p\pi$ AO's and best-molecule core		III Free-atom $2p\pi$ AO's and free-atom core	
	α	β	α	β	α	β
$^1\Pi_u$ State						
Kinetic	1.35	1.11	3.40	2.75	3.40	2.75
Nuclear attraction	−5.92	−5.40	−12.89	−11.68	−12.89	−11.68
Coulombic repulsion	1.57	1.35	6.44	5.85	10.03	9.11
Total	−3.00	−2.94	−3.05	−3.08	0.54	0.18
$^3\Pi_u$ State						
Kinetic	1.93	1.71				
Nuclear attraction	−6.91	−6.62	same as above		same as above	
Coulombic repulsion	1.79	1.64				
Total	−3.19	−3.27				

Table 6 shows that the coulombic repulsion are too large if the core is represented by the minimal basis LCAO–MO rather than the SCF–LCAO–MO function. If overlap were included explicitly in the simple MO, the α and β values would be smaller; but both values would still be positive. However, if the core is represented by the SCF–LCAO–MO function, the best-molecule core, coulombic repulsions decrease and α and β take on reasonable, negative values. This is not unexpected because the latter representation is a more realistic one in that the core charge density is more tightly contracted about the molecular axis and then coulombic repulsions must diminish in magnitude.

Columns I and II of Table 6 show the dependence of α and β values upon the $2p\pi$ functions. In going from II to I, these functions become more diffuse and the π electron does not feel the nuclei as strongly. Although kinetic energy, nuclear attraction energy, and repulsion energy all change significantly with a change in the $2p\pi$ representation, the total sum varies little and α and β seem nearly insensitive to this change. A closer look at this situation shows that the kinetic and nuclear attraction energies become 40–60 % of their previous values in going from II to I. The repulsion energy, on the other hand, becomes about 25 % of its previous value. It would appear that the β values are too large versus α values because the negative nuclear attraction is too large. Support for this conclusion is present in the data for the triplet state; in this state the π electron penetrates closer to the nuclei (no Fermi hole) and both α and β are larger (more negative) than for the singlet state.

Although an explanation has been offered as to why β is approximately equal to α, a further point must be made. It appears that the abnormally short bond length of this model system is part of the answer. At this very short internuclear separation the kinetic energies and nuclear attraction energies are about the same for α and β, respectively, regardless of the fact that the π electron is associated with one nucleus in α and two nuclei in β. If the "π bond" were to get longer, surely β would get smaller in magnitude than α.

Conclusions

The idealized π systems of this paper were selected to fulfill the conditions of the π-electron approximation, particularly the tenet that the σ wave function remains unaltered by a change in the π wave function. In addition, the calculations readily afforded partitioning into σ and π classes.

It was shown (Fig. 2) that the core energy did not vary upon adjustment (reorganization) of the π MO accompanying a change in molecular state. Transition energy and ionization potential comparisons showed that the single-configuration wave function describes properly the molecular changes at R_e, within the frozen core approximation. Yet general conclusions on the π-electron approximation are limited to an extent by the specific molecular systems considered. The analog π systems of this work are Rydberg systems with a principal quantum number of 1 for the σ core and involve $1s - 2p\pi$ intershell effects. What about more conventional π systems which involve $2s - 2p\pi$ intershell effects? In spite of the core distinctions, general conclusions about the analog systems should be more or less applicable to conventional systems because σ-π interactions of the analog systems are not negligible and σ-π interactions of conventional systems should be larger in magnitude. Certainly the influence of the σ core on the π electrons (and vice versa) is larger in conventional systems than in Rydberg systems. That is to say, these idealized systems can be considered as a limiting case for peel and core interaction.

Since accurate LCAO–MO–SCF calculations have been performed on several "conventional" π-electron systems, the discussion will consider a few of them. The intent here is to compare results of this study with those reported on a broad spectrum of conventional systems.

The explicit definition of the Hückel one-electron π-electron operator $\mathscr{H}_{eff}$ and subsequent calculations of the Hückel coulomb and resonance integrals for these idealized π systems afford unambiguous conclusions. Reasonable calculated α and β values are obtained when the molecular core is taken into account properly. If the core is represented poorly, for example by a free-atom minimal basis LCAO–MO, α and β are opposite in sign to experimentally derived values (Table 5). Although calculated α and β values vary with a change in the type of π MO, the variation is small in going all the way from minimal basis free-atom to large basis best-molecule $2p\pi$ MO's (Table 5). It would appear, then, that linear combinations of SCF AO's should be adequate for qualitative π-electron calculations, so long as the σ core is represented properly .This conclusion is also that of Silbey and co-workers [31], who compared linear combinations of carbon SCF AO's with highly accurate π MO's of C_2 [5].

Furthermore, the resolution of the Hückel α and β parameters into more nearly fundamental parts (Table 6) provides a look at the question of electronic reorganization resulting from a change in the electronic state of the molecule. It can be seen that a change (improvement) in the representation of the core causes a change (diminishing) in the σ-π interactions, manifested in the coulombic repul-

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[5] A promising approach which goes beyond the SCF AO level for π-electron calculations has been reported recently. In studies on the planar methyl radical CH_3 [32] and the planar molecular fragment NH_3^+ [33], it has been demonstrated that there is a considerable difference between a free-atom SCF $2p\pi$ function and the atomic-like, molecular fragment $2p\pi$ functions, optimized within the molecular fragment.

sion term. It is normal that a subsequent adjustment in the peel should follow, manifested in the kinetic energy and nuclear attraction terms. But this peel deformation causes another reorganization in the core, manifested in another coulombic repulsion adjustment. As seen in columns I and II of Table 6, the net effect of the peel deformation and subsequent core reorganization is small because of the noticeable cancellation among all energy terms. Thus, in spite of the distinctive changes in the peel and peel-core interactions, the two levels of calculations show little net difference because of a fortuitous cancellation of energy contributions.

This sort of cancellation is not a coincidence of the idealized systems of this work. In studies on acetylene, Griffith and Goodman [34] suggested that the success of the π-electron approximation is based essentially on the cancellation of σ and π reorganization energy terms with the σ-π interaction ones. They observed that the total reorganization energy was small in comparison with the change in the σ-π interaction term. Orloff and Sinanoğlu [35] included σ-π changes in their study of the atomic valence-state reaction $2C \rightarrow C^- + C^+$, appropriate to π-electron systems. They noted a partial cancellation of σ-π interaction by σ core changes. Moreover, they included correlation effect and noted a cancelling of σ correlation and σ-π correlation effects. Similarly, Hermann and co-workers [32] noted that the constant core approximation partly compensated for the neglect of correlation effects in the planar methyl radical. Thus it appears that the adequacy of SCF computations for qualitative π-electron studies may be due to a fortuitous cancellation of electronic energy terms.

Finally, the question of calibrating Hückel parameters must be considered. The solution of the Hückel secular equation depends upon the empirically calibrated α and β parameters, and thus the resulting LCAO–MO wave functions are dependent upon the experimental conditions selected. The use of wave functions determined in this manner for interpreting electron spin resonance spectra is just one example where empirically-derived wave functions have been used commonly and productively[6]. Yet, if the calibration results are doubtful, the resulting wave functions may lead to invalid conclusions.

For the analog π systems of this paper, it was shown how only one set of calibrated parameters was obtained. But the calibrated Hückel parameters are more appropriately the averages $\bar{\alpha} = \frac{1}{2}(\alpha_u + \alpha_g)$ and $\bar{\beta} = \frac{1}{2}(\beta_u + \beta_g)$, respectively, for either singlet or triplet transition. Salem [36] demonstates convincingly the difficulty of obtaining unique, transferable Hückel parameters for some conventional π systems. From empirical resonance energies β is determined to be about $-2/3$ eV for benzene, while from transition energies it is determined to be about -4 eV for a series of alternant hydrocarbons, one of which is benzene. Clearly, then, even for these idealized π systems, calibrations must be done cautiously with the knowledge that only the gross features of the Hückel calculations are meaningful.

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[6] Hyperfine-splitting of ESR spectra of conjugated hydrocarbons is due to the interaction of an unpaired π electron with the proton of the hydrocarbon. The unpaired electron density ϱ_π is often correlated with the hyperfine-splitting constant of the proton a_H by the relationship $a_H = Q\varrho_\pi$, where Q is a constant. The density at a particular carbon atom can be calculated directly by squaring the corresponding carbon AO coefficients of a Hückel LCAO-MO wave function. Calculated and experimental a_H ratios often exhibit good agreement and, consequently, the interpretation of hyperfine structure of ESR spectra has been accomplished via simple Hückel calculations [36, 37].

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