relatively better than those obtained by Dewar and de Llano. For most of the compounds, *e.g.*, phenanthrene, chrysene, and triphenylene, our values for both heats of formation and resonance energies come out to be identical with those obtained experimentally. Moreover, in several cases, *e.g.*, naphthacene and pyrene, the differences between calculated and observed values, which are significant in the work of Dewar and de Llano, have been minimized in our work. The success of the IOC-ω technique is indicated here, and the heats of formation and resonance energies indicate the correctness of the $E_{\pi\mathrm{b}}$ values.

Further, in the case of polyphenyls, the calculation shows that their resonance energies are approximately integral multiples of the resonance energy of benzene. For example, the resonance energy of biphenyl (1.501 eV), where two benzene rings are joined by a C–C bond, is nearly twice that of benzene (0.719 eV); similarly, in the case of terphenyls, where three benzene rings are joined by two C–C bonds in various manners, the resonance energies are approximately three times that of benzene, etc. This proves that the bonds joining the benzene rings in polyphenyls are essentially single, localized bonds.

Further light is thrown on the case of open-chain classical polyenes where all C—C and C═C bonds are localized. The E_{R} values for those polyenes according to definition and expectation should be equal to zero. However, our calculation suffers in this case for two reasons: (1) the value of E_{C} has been assumed to be the same for all σ bonds in an aromatic hydrocarbon, while it should be a function of bond length, and (2) in the polyenes, unlike aromatic hydrocarbons, the differences between the lengths of C—C and C═C bonds are significant. The E_{R} values for these polyenes generally are slightly different from zero. However, the differences are so small (irrespective of sign) that they signify nothing except that that value of E_{C} is not appropriate in the case of polyenes, and that E_{C} should be a function of bond length. The above results and discussion lead to the conclusion that the IOC-ω technique, on being properly handled, is quite successful in accounting for experimental facts and theoretical predictions.

Polarization and Overlap Population. A Reanalysis of Molecular Orbital Theory of SN2 Reactions[1]

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Abstract: The effects of charge polarization on Mulliken overlap populations are analyzed. The results show that a bond population change cannot be accounted for by simply summing the effects of empty MO's mixed in and filled MO's mixed out, except in special cases. It is possible for an empty MO which is antibonding in a given bond to be mixed in, in a way to strengthen that bond. A reanalysis of the SN2 reaction shows how the charge polarization to the leaving atom, due to an approaching negative base, results in a weakening of the bond to the leaving atom and a strengthening of the bonds to the other hydrogens of methane. The calculations indicate that C–H bonds at tetrahedral carbons should generally be strengthened or weakened as they are polarized negative or positive, respectively. It is argued that effects of charge transfer on bond strengths also require consideration of more than contributions due to gain or loss of electron population in individual MO's of the separated molecules.

Consider the attack by a hydride ion on a methane molecule. Let the hydride ion approach along a C_3 axis (a C–H bond axis) from the carbon side (*i.e.*, "backside" attack). This system is a model for SN2 reactions. As an aid in predicting the stereochemical nature of SN2 reactions, one can ask which bonds in the methane molecule will be strengthened or weakened by the interactions with hydride. Two potentially important interactions may be cited: polarization of methane induced by the charged hydride, and, at fairly close approach, some transfer of electronic charge from hydride to methane.

In an earlier paper,[2] we analyzed the ways in which filled and empty MO's of methane or methyl fluoride are intermixed to effect charge polarization due to approach by negative bases. We found that the empty MO's mixed in are antibonding predominantly in the bond to the leaving group, while loss of the filled MO's occurs mainly in MO's which are bonding for that bond. It was argued from this that polarization by the negative base, in driving charge to the backside atom, simultaneously weakens the bond to that atom. This general approach further predicts that the bonds to the three front-side hydrogens should also be weakened although to a much lesser extent.

This approach has great intuitive appeal. It has also been applied in a limited way to the process of charge transfer in SN2 reactions.[3] Nevertheless, as we show below, it is not generally a complete approach and *can lead to predictions that bonds should be weakened when calculated bond orders show them to be strengthened and vice versa.* It was just such disagreements that led us to examine the problem more closely.

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[2] J. P. Lowe, *J. Amer. Chem. Soc.*, **93**, 301 (1971).

[3] For a clear review, see L. Salem, *Chem. Brit.*, **5**, 449 (1969).

Table I. Resolution of Filled MO's of Perturbed Methane (Backside Attack by H⁻) in Terms of Unperturbed Methane[a]

Perturbed methane MO	Unperturbed methane MO 1	2	3	4	5	6	7	8
1	+0.1000+1	0.0	−0.5925−2	0.0	0.1734−3	0.3405−4	0.3533−2	0.0
2	−0.5874−2	0.0	−0.9999+0	0.0	0.6892−2	−0.2057−4	0.7832−2	0.0
3	0.0	0.0	0.0	−0.1000+1	0.0	0.0	0.0	−0.3259−2
4	−0.3424−4	0.9999+0	−0.2046−4	0.0	−0.3644−4	0.3520−2	0.2036−4	0.0
5	−0.4206−3	0.0	−0.6935−3	0.0	0.1013−2	0.0	0.4080−3	0.0

[a] Read −0.3424−4 as −0.3424 × 10⁻⁴.

Polarization and Overlap Population

Suppose we wished to calculate the effect on the overlap population[4] in H_2^+ of an external electric field along the internuclear axis. The field causes charge polarization in the molecule and a skewed wave function. Within the minimal basis set of atomic orbitals (AO's) framework, Rayleigh–Schrödinger perturbation theory describes this skewed wave function as being mainly the original bonding molecular orbital (MO), Ψ_+, with some admixture of the antibonding MO Ψ_-. The normalized polarized wave function, then, is

$$\Psi = (1 - c^2)^{1/2}\Psi_+ + c\Psi_- \tag{1}$$

where

$$\Psi_\pm = N_\pm(1s_a \pm 1s_b) \tag{2}$$

and $N_\pm$ are normalizing factors. In calculating the overlap population, we square Ψ and integrate, obtaining

$$\int\Psi^2 d\tau = (1 - c^2)\int\Psi_+^2 d\tau + c^2\int\Psi_-^2 d\tau + 2c(1 - c^2)^{1/2}\int\Psi_+\Psi_- d\tau \tag{3}$$

The first two integrals on the right indicate that we have lost c^2 times the overlap population due to Ψ_+ and gained c^2 times that due to Ψ_-. The cross term is

$$2c(1 - c^2)^{1/2}N_+N_-\left[\int(1s_a^2 - 1s_b^2 + 1s_a1s_b - 1s_b1s_a)d\tau\right] \tag{4}$$

The last two terms in the integrand of eq 4 yield overlap population terms, but they cancel. But they cancel only because (a) the bond in H_2^+ is bisected by a symmetry element for the molecule, and (b) the two wave functions being mixed, Ψ_+ and Ψ_-, are of opposite symmetry for this symmetry operation. When we recognize that, in H_2^+, the "bond overlap population operator," P_{ab}, has the symmetry of the molecule, the vanishing of $\int\Psi_+P_{ab}\Psi_- d\tau$ is recognized as a familiar quantum mechanical theorem.[5] Thus, in H_2^+, we can conveniently describe changes in overlap population as being due to empty and filled MO's of the unperturbed molecule. But a C–H bond in methane does not have the symmetry qualifications required for the cross term to vanish, and the effects of the cross term can therefore be expected to dominate since this term is first order in c. But this term is neglected in the predictive method described above and used in ref 2.

When the cross term between MO's 1 and 2 is present, its contribution to the overlap population between AO's a and b is (neglecting c^2)

$$2ncS_{ab}(c_{1a}c_{2b} + c_{2a}c_{1b}) \tag{5}$$

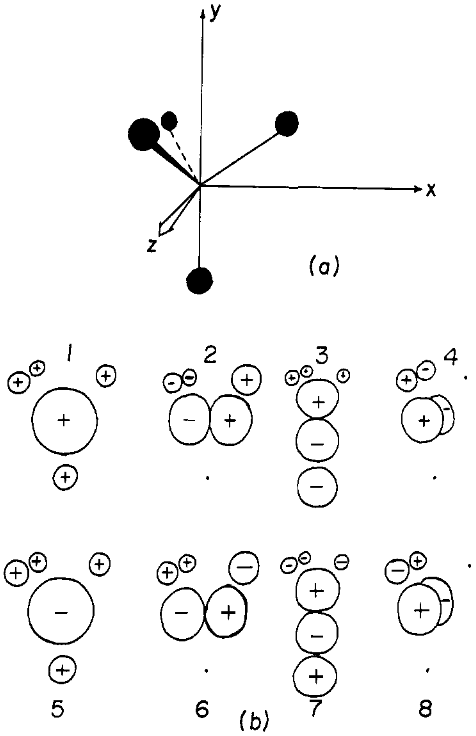

Figure 1. (a) Orientation of methane with respect to Cartesian coordinates. (b) Sketches of methane MO's.

where S_{ab} is the overlap between AO's, n is the number of electrons in the perturbed MO, and c_{ij} is the coefficient for the jth AO in the normalized ith MO.

Hydride Attack on Methane

In Figure 1 are sketched the MO's for unperturbed methane. AO coefficients for these MO's, obtained by a CNDO/2 calculation,[6] appear in ref 2. A second CNDO/2 calculation was performed for the case where a hydride ion is located at 5 Å on the $+y$ axis (see Figure 1). This gave MO's for polarized methane which were then resolved in terms of the unperturbed methane MO's. The results of this resolution are here reproduced (with some corrections) as Table I. This table is to be read as follows. MO number 2 of *polarized* methane is equal to -0.5874×10^{-2} times unperturbed MO number 1, plus −0.9999 times unperturbed MO number 3, plus 0.6892×10^{-2} times unperturbed MO number 5, . . . etc. By inspecting Table I, one can easily pick out the major interactions between filled and empty MO's.[7] These are depicted in Figure 2 of this

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(4) R. S. Mulliken, *J. Chem. Phys.*, 23, 1833, 1841 (1955).

(5) H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," Wiley, New York, N. Y., 1944, p 188.

(6) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 43, S136 (1965).

(7) Intermixing of the type $c_1\varphi_1 + c_2\varphi_2$ together with $c_1\varphi_2 - c_2\varphi_1$ where φ_1 and φ_2 are both filled unperturbed methane MO's introduces no change in charge distribution. Such mixtures are equivalent orbitals. Hence, the sizable entries in positions 2,1 and 1,3 of Table I do not affect bond strengths.

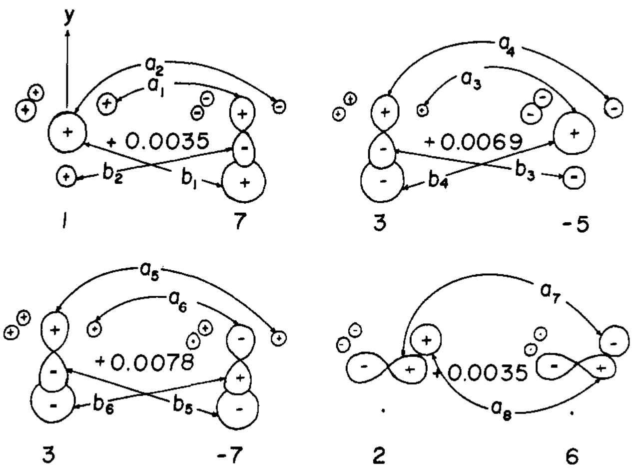

Figure 2. Four significantly mixed MO combinations for C_3 attack in methane. Arrows indicate AO interactions contributing to overlap population from cross-term expression 5 of text.

paper. The 1–7, 3–5, and 3–7 interactions all result in transfer of charge to the backside hydrogen, which is most distant from the hydride ion. The 2–6 interaction moves charge away from the three equivalent hydrogens and onto the carbon. A 4–8 interaction (not shown) ensures that this latter process is carried out symmetrically. Effects of these mixings on CNDO/2 "unnormalized bond populations"[8] and on regular Mulliken overlap populations are given in Table II.

Table II. Contributions to Overlap Populations Caused by Polarization of CH_4

	Effect on overlap population			
MO's mixed	Frontside		Backside	
1–7	a_1	0.0006	b_1	0.0032
	a_2	−0.0010	b_2	−0.0017
		−0.0004		0.0015
3–5	a_3	0.0020	b_3	0.0034
	a_4	−0.0012	b_4	−0.0060
		0.0008		−0.0026
3–7	a_5	0.0007	b_5	0.0065
	a_6	−0.0007	b_6	−0.0066
		0.0000		−0.0001
2–6	a_7	−0.0026		
	a_8	0.0026		
		0.0000		
Net		+0.0004		−0.0012
		(+0.0009)[a]		(−0.0025)[a]

[a] Values in parentheses result from coefficients which are renormalized so that $C^{\dagger}SC = 1$. All other values are from CNDO/2 coefficients, for which $C^{\dagger}C = 1$.

The net effect is a population decrease in the backside C–H bond (in agreement with the arguments in ref 2) and roughly one-third as great a population *increase* in each of the three frontside C–H bonds (in disagreement with our prediction in ref 2). These net results are understandable in terms of the interactions in Figure 2. Consider first the contributions to backside bond population, labeled b_1–b_6. Each mixture of MO's produces a bonding and an antibonding interaction. These two interactions largely cancel in the 3–7 mixture ($b_5 \cong -b_6$) because the AO coefficients for the two interactions are almost identical (Table I of ref 2), and because the overlap integral is identical in the two interactions. The interactions in the 1–7 mixture do not cancel, nor do those in the 3–5 mixture. In each of these cases, the carbon 2s–hydrogen 1s interaction (b_1 and b_4) dominates. This comes about because the backside hydrogen AO coefficient in p-type MO's 3 and 7 is roughly double that in MO's 1 and 5, while the overlaps and also the coefficients for carbon 2s or $2p_y$ AO's are nearly equal. So b_1 and b_4 dominate b_2 and b_3. The 1–7 mixture, then, is an example of a case where mixing in an *antibonding* MO contributes an *increase* in bond population. Finally, b_4 dominates b_1 because MO's 3 and 5 are more strongly mixed ($c = 0.0069$) than are MO's 1 and 7 ($c = 0.0035$). This is at least partly due to the fact that MO's 3 and 5 lie closer together in energy ($\Delta\epsilon = 1.08$ au) than do MO's 1 and 7 ($\Delta\epsilon = 1.59$ au). The domination by b_4 gives a bond-weakening effect. This is a somewhat surprising result because it indicates that the *empty* MO primarily involved in weakening this bond *via polarization* is the totally symmetric MO 5 rather than MO 7.

The strengthening of the frontside bonds can be analyzed similarly. The 3–7 and 2–6 interactions are ineffective because of internal cancellation, just as in the 3–7 case above. [We have chosen to analyze the C–H bond lying in the *xy* plane (Figure 1) so we can ignore the 4–8 interaction involving the $2p_z$ AO.] The carbon 2s–hydrogen 1s interactions a_2 and a_3 dominate the a_1 and a_4 interactions in the 1–7 and 3–5 MO mixtures. This is traceable to the very small overlap between carbon $2p_y$ AO and any of the three frontside hydrogens; the carbon 2s AO overlaps them three times as effectively. As before, a_3 dominates a_2 because 3–5 mixes more strongly than 1–7. The net result is bond strengthening. That the population decrease of the backside bond is about three times as great as the increase for any frontside bond is due to the three-to-one ratio of coefficients on backside *vs.* frontside hydrogens in MO's 3 and 7, and the three-to-one overlap factor mentioned above. (Note in Table II that $b_1 = -3a_2$, etc.)

These results differ in several ways from those based on a second-order argument using only properties of MO's gained and lost. The second-order argument automatically predicts a weakening of all C–H bonds, but mainly the backside one, whereas we have seen that the first-order treatment shows the frontside bonds to be strengthened. For the C_2 axis approach discussed in ref 2, the second-order effect is again to weaken all four bonds, whereas overlap population calculations (not included here) indicate that the backside bonds weaken and the frontside bonds strengthen. Thus, the nature of the empty MO's mixed in by the perturbation is not an adequate indicator of the bond changes. Rather, it is the *way* the filled and empty MO's interact that is important. Also, we note that the greatest mixing coefficient will not always be associated with the greatest effect on bonding. The strongest mixing here is the 3–7 one, which has almost no effect on the overlap populations.

An interesting implication of these results is that there should be a general tendency in polarized hydro-

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[8] CNDO/2 coefficients are normalized consistent with the neglect of differential overlap. Hence the sum of bond and atom populations calculated from these coefficients will not equal the total number of valence electrons in the molecule. As Table II shows, however, the effect of renormalizing the MO's does not alter the sense of change in bond strength in this instance.

carbons for C–H bond weakening where hydrogens become negative and bond strengthening where they become positive. (Attack by a positive ion would tend to mix the same MO's as in Figure 2, but with a mixing coefficient of opposite sign, so that b_4 would now be a bonding interaction, etc.)

Effects of Charge Transfer on Bonding

As the base molecule draws closer to the substrate, significant overlap between their wave functions develops and some of the electronic charge of the base becomes delocalized over the reacting pair. Many papers have been published concerning this process.[3,9] These mostly consider the interaction *energy* between base and substrate, *i.e.*, the activation energy barrier to bond formation between base and substrate. Perturbation treatments of this process indicate that the highest occupied MO (HOMO) of base and the lowest unoccupied MO (LUMO) of substrate play a dominant role in the energetics and symmetry of this process. This view has led to successful predictions about many reactions.

However, our concern is with a different, but related, question. How are bonds in the substrate (or in the base) strengthened or weakened by charge transfer? We feel that a useful answer will frequently require consideration of cross terms analogous to those described above. A simple illustrative example can be obtained by considering the approach of a one-center base, H^-, toward one end of a three-center acid, H_3^+ (see Figure 3). The *extreme* of approach (not necessarily achieved in all acid–base interactions) is the four-center molecule H_4. Treating this reaction in the simple Hückel approximation gives LCAO–MO coefficients familiar from the analogous π systems, allyl cation and butadiene.

Initially the two bonds of H_3^+ ($\alpha\beta$ and $\beta\gamma$ of Figure 3) are of equal strength by symmetry. How do they change as H^- approaches the end labeled γ? Let us consider the effect of only a single MO, the HOMO of H_4. Figure 3 indicates that the HOMO of H_4 consists mostly of the LUMO of H_3^+ in combination with the HOMO of H^-. This is consistent with perturbation arguments.[9] But if we consider *only* the effect of the LUMO of H_3^+ on the $\alpha\beta$ and $\beta\gamma$ bonds, we can obtain no change at all since the MO is nonbonding in both of these bonds. Furthermore, if we consider the effects of all three MO's of H_3^+ individually, it is clear that any change in $\alpha\beta$ must be equalled by a change in $\beta\gamma$ because of the symmetry of these three MO's. Yet Figure 3 shows that the HOMO of H_4 is bonding in $\alpha\beta$ and antibonding in $\beta\gamma$. Hence, in this case, only the cross-term contributions, some of which are shown in Figure 3, can contribute to the question of interest, namely the *difference* in changes of $\alpha\beta$ and $\beta\gamma$ bond strengths as the transfer proceeds.

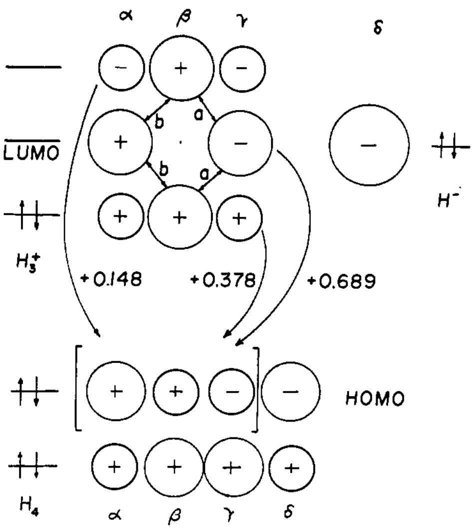

Figure 3. Orbital diagram for $H^- + H_3^+ \rightarrow H_4$. HOMO of H_3 fragment in H_4 is mostly (0.689) made up of LUMO of H_3^+, but the nature of the bonding in the HOMO in H_4 is only understandable in terms of cross terms between all MO's of H_3^+. Antibonding and bonding interactions (not all of which are illustrated) are labeled a and b, respectively.

Acknowledgment. It is a pleasure to thank Professor Oakley H. Crawford of this university for a very helpful discussion.

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(9) A few recent examples are: K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jap.*, **42**, 3399 (1969); L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1968); R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.