Molecular Orbitals for Organic Systems Parametrized from SCF Model Calculations[1]

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Abstract: A new molecular orbital method, in which parameters are taken from SCF results for closely related simpler molecules and all electrons are included, has been applied to some hydrocarbons, carbonyls, and heterocycles. Energy criteria such as the virial theorem and binding energies are tested, and our results are found to reproduce trends in experimental ionization potentials and dipole moments. We examine relative energies and the spatial distribution of σ and π electrons in conjugated systems, suggesting a reinterpretation of the Rydberg series in benzene and pyridine. Charge transfer is studied, in terms of exact dipole moments and Mulliken charges. The calculated directions of the dipole moments of propylene, acrolein, and acetaldehyde are in close agreement with microwave results. By examining overlap populations, we conclude that hyperconjugation is not an important contribution to alkyl group electron donation in the ground state. Lone-pair MO's in a large series of carbonyls and heterocycles are found to have appreciable delocalization and antibonding character. Our nonempirical framework enables us to question the validity of certain previous results, based on empirical parameters.

I. Introduction

The many applications of the molecular orbital (MO) method to complex organic systems during the past decades have been based largely upon empirical parameters, and usually limited to π electrons only.[3] The extended Hückel method[4] has resulted in some appreciation of the importance of explicit inclusion of the σ electrons and has yielded a wide range of approximate results, particularly for ground-state molecular properties. In a study[5,6] originally aimed toward an understanding and improvement of the logical foundations of extended Hückel theory, we have developed[7,8] an essentially nonempirical[7] MO theory in which a primary aim is the approximation of LCAO Hartree–Fock (HF) self-consistent-field (SCF) wave functions[9] for complex molecules using SCF results[10] for closely related simpler molecules with explicit inclusion of all electrons. Here we use our method to calculate a variety of properties of organic molecules, including hydrocarbons, aldehydes, ketones, and heterocycles. First, tests of internal consistency (*e.g.*, virial theorem) and of reproducibility of the SCF results by our theory are briefly considered. Then the transferability of parameters discussed earlier[7] is used to provide parameters from simpler molecules for complex molecules, in which we examine dissociation energies, ionization potentials, aspects of charge distribution (charge transfer, dipole moments, conjugation, hyperconjugation, π- and σ-electron densities), and the concept of the lone pair. A reassignment of the benzene and pyridine Rydberg spectra[11] is also suggested.

II. Method and Parameters

A. General Discussion. In applying our method to organic compounds, we have followed the procedure outlined in the Summary at the end of paper I.[7] The SCF results[10] on which these studies are based were computed for a minimum basis set of Slater-type orbitals,[12] including 1s on all atoms, and having exponents of 1.2 for H and Slater values[12] for all others. These molecules include[10] CH_4, C_2H_2, C_2H_4, C_2H_6, H_2CNH (hypothetical), NH_3, and H_2CO. The assumptions of molecular geometry for larger molecules are summarized in Table I and Appendix I. We chose methyl group conformations which presumably correspond to energy minima, based on previous experimental work.[13] For a series of alkylbenzenes, we present results for several conformations, since we found some properties to be rather sensitive to conformational changes in these compounds.

Our approximation of the SCF Hamiltonian matrix requires two steps:[7] (1) choice of diagonal elements (α's); (2) calculation of the potential energy part of the off-diagonal elements, using the Mulliken approximation[14] modified by certain coefficients K_{ij}, as indicated in eq 5 and 6 of paper I. Kinetic energy integrals are calculated exactly. In applying this method the question arises as to whether the α's for compounds of interest should be modified by some function of the net atomic charges (q_i), which vary from one compound to another. Unfortunately, our study of the variation of α's for model SCF calculations places in great doubt the existence of any simple relationship[15] between α_i

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[1] Paper III in a series of four papers.

[2] National Science Foundation Predoctoral Fellow, 1964–1966.

[3] For a recent review of these methods, see "The Quantum Theory of Molecular Electronic Structure," R. G. Parr, Ed., W. A. Benjamin, Inc., New York, N. Y., 1963.

[4] (a) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2047, 2474, 2480 (1964); (b) R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962).

[5] F. P. Boer, M. D. Newton, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **52**, 890 (1964).

[6] M. D. Newton, F. P. Boer, W. E. Palke, and W. N. Lipscomb, *ibid.*, **53**, 1089 (1965).

[7] Paper I: M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2353 (1966).

[8] Paper II: F. P. Boer, M. D. Newton, and W. N. Lipscomb, *ibid.*, **88**, 2361 (1966).

[9] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[10] (a) Paper IV: W. E. Palke and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2384 (1966). (b) Two formaldehyde wave functions have been obtained by M. D. Newton and W. E. Palke (to be published), using the parameters from the calculations cited in ref 39 and 40. (c) A wave function for CH_2NH (C–N = 1.305 A, N–H = 1.000 A) has been obtained by M. D. Newton, unpublished results.

[11] M. F. A. El-Sayed, M. Kasha, and Y. Tanaka, *J. Chem. Phys.*, **34**, 334 (1961).

[12] J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

[13] The appropriate experimental work is cited in the first paper of ref 4a.

[14] R. S. Mulliken, *J. Chim. Phys.*, **46**, 497, 675 (1949).

[15] (a) Several workers have used the ω technique, which assumes a linear relationship between α and q_i for π-electron systems: N. Muller,

$H{-}C'{\equiv}C''{-}C'''{\equiv}H_3$

$\alpha_{C'} = -0.169$ $\quad q_{C'} = -0.176$
$\alpha_{C''} = -0.169$ $\quad q_{C''} = +0.102$
$\alpha_{C'''} = -0.364$ $\quad q_{C'''} = -0.044$
$\alpha_{H_3} = -0.323$ $\quad q_{H_3} = +0.188$

Figure 1. α's (au) and net Mulliken charges (q's) for the propyne π system (8 electrons). Core charges are given in text.

and q_i (Figures 1-3 of paper I). Also the difference between α's for σ and π orbitals, first noted by Mulliken[14] (and since, ignored!), has been shown[7] to be much more important than the variation of α_i with charge. Until more exact results are available which elucidate the functional form of the dependence of α_i on charge,[15b] or some other function of the MO's, our procedure is simply to take α's from LCAO SCF Hamiltonians of the most appropriate model compounds.[10]

Table I. Bond Distances (A)

A. Carbon–Carbon Bonds	
1. Single bonds	
1.540	Tetrahedral–tetrahedral
1.520	Tetrahedral–trigonal[a]
1.480	Trigonal (phenyl)–trigonal (carbonyl)[b]
1.460	Trigonal (vinyl)–trigonal (carbonyl)
1.459	Tetrahedral–digonal
2. Aromatic	
1.400	(All phenyl rings)
3. Double and triple bonds	
1.340	(Ethylene, butadiene)
1.360	(Vinyl conjugated with carbonyl group, and propylene)
1.206	(Alkyne)
B. Carbon–Hydrogen Bonds	
1.100	Paraffin
1.084	Aromatic
1.070	Olefin
1.064	Alkyne
1.115	Aldehyde
C. Carbon–Oxygen	
1.230	All carbonyls except tropone

[a] Propylene was given C–C = 1.490 A. [b] Also, butadiene.

We have previously discussed the requirement that our wave functions be invariant under any transformation which rotates the 2p orbitals on the various atoms.[7] A sufficient condition that our approximate wave functions possess such invariance is that: (1) an average value of α be used for all three 2p orbitals on a given atom; (2) the coefficients K_{ij} governing s–p and p–p interactions be the same for all three 2p orbitals on each atom. In the case of the diborane wave function, this was a large approximation,[8] but until an unambiguous procedure is developed for the preservation of local atomic anisotropies in the higher hydrides, this seemed to be the best procedure. In the present paper these requirements were somewhat relaxed for planar unsaturated systems, where symmetry allows a unique separation of 2p orbitals into σ and π types. Hence the invariance requirement was applied only to rotations in the molecular plane, and different values of α and K_{ij} were assigned to the σ and π 2p orbitals. In the case of alkyl-substituted planar systems, the σ–π anisotropy was maintained for interactions between the atoms of the planar, unsaturated residue, while isotropic α_{2p}'s and K_{ij}'s were used for all other interactions.

B. Choice of α's.[16] Values (in atomic units) of the diagonal elements α_{1s} and α_{2s} for C are very similar in all model compounds, except for the C atom in H_2CO. Hence, the values $\alpha_{1s} = -11.284$ and $\alpha_{2s} = -1.463$ for ethylene were used for all C atoms, except for those in carbonyl groups, for which the values for H_2CO were employed (respectively −11.352 and −1.545). All alkyl C atoms were assigned the α_{2p} value of −0.364, which is an average of the values of −0.385, −0.354, and −0.354 for C_2H_6. For planar systems, the carbon $\alpha_{2p\pi}$ value was taken either from C_2H_4 (−0.146) or H_2CO (−0.199), while the corresponding $\alpha_{2p\sigma}$'s are −0.480 and −0.580, obtained respectively by averaging the SCF C_2H_4 and H_2CO in-plane α_{2p}'s. The propyne α_{2p}'s were taken directly from C_2H_2. Nitrogen α_{1s} and α_{2s} values were taken from NH_3, respectively −15.519 and −1.859. Since at first no SCF wave function involving carbon doubly bonded to nitrogen was available, we used the following device to obtain nitrogen $\alpha_{2p\sigma}$ and $\alpha_{2p\pi}$ values for the azabenzenes. Noticing that in both C_2H_4 and H_2CO the ratio of $\alpha_{2p\pi}$ to $\alpha_{2p\sigma}$ is about 0.35, and also that the average of the three α_{2p}'s of C_2H_4 is about equal to α_{2p} of CH_4, we assumed a similar relationship to hold between the NH_3 nitrogen and doubly bonded nitrogen, obtaining $\alpha_{2p\sigma} = -0.427$ and $\alpha_{2p\pi} = -0.149$. Subsequently an SCF wave function for the hypothetical $CH_2{=}NH$ was obtained,[10c] whose α_{2p}'s agreed with the above values to within 0.02 au, thus vindicating the above *ad hoc* procedure. In addition, this SCF calculation revealed that the carbon α's are little different from the ethylene values, as opposed to the large inductive effect observed in formaldehyde. Hence, along with the nitrogen parameters from NH_3, we used ethylene carbon α's for all heterocycle calculations. In lieu of a more suitable model for the pyrrole nitrogen, the average of the NH_3 α_{2p}'s (−0.334) was assigned. For the carbonyl oxygen, the SCF H_2CO calculation yielded: $\alpha_{1s} = -20.588$, $\alpha_{2s} = -2.449$, $\alpha_{2p\sigma} = -0.503$, $\alpha_{2p\pi} = -0.179$. The α_{1s} for H could easily have been given different values for H bonded to different types of carbon atoms, but we chose the ethylene value of −0.537 which seemed to be an appropriate average, except for the aldehyde proton, for which the H_2CO value of $\alpha_{1s} = -0.570$ was used.

C. Choice of K_{ij}'s. Table III of paper I[7] reveals that the values of K_{ij} obtained from our reference SCF calculations are all roughly constant for each type of overlap situation and independent of the atoms involved except for H, which is treated separately. Thus we felt justified in simply using the ethylene K_{ij}'s for all our calculations, noting that they are quite close to the averages for the K_{ij}'s of all the models.

L. W. Pickett, and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 4770 (1954); A. Streitwieser, *ibid.*, **82**, 4123 (1960); and S. Ehrenson, *ibid.*, **83**, 4493 (1961). See also G. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949). (b) In the absence of accurate values of the individual integrals which make up the α's, extensions of the ω technique, in which α_i for a given center is made dependent on the changes on other centers, may prove useful: *e.g.*, A. Streitweiser, ref 15a, eq 11, and A. Streitweiser, A. Heller, and M. Feldman, *J. Phys. Chem.*, **68**, 1224 (1964).

(16) The interatomic distances used in the model calculations differ slightly from some of the values adopted for our calculations. We have ascertained, however, that our parameters are not very sensitive to these small differences; *e.g.*, the α's for ethylene at the ethylene and benzene C–C distances differ by less than 0.02 au.

Table II. Sensitivity of H_2CO and C_2H_4 Wave Functions[a]

	A SCF	B Correct α's, correct ZO elements	C Correct α's, ZO elements = 0	D Averaged α's, correct ZO elements	E Averaged α's, ZO elements = 0	F General method $K^{ZO} = 0.400$
			H_2CO			
$-\epsilon$ (au)	0.385	0.352	0.352	0.393	0.393	0.394
$-\Sigma\epsilon$ (au)	36.252	36.303	36.446	36.335	36.465	36.385
KE (au)	114.096	114.165	114.201	114.380	114.370	114.237
q_c	−0.163	−0.110	−0.424	−0.184	−0.490	−0.246
q_o	−0.079	−0.092	−0.076	−0.138	−0.118	−0.085
q_H	0.121	0.101	0.250	0.161	0.304	0.166
μ_{CL} (D.)	1.080	1.049	1.716	1.622	2.237	1.341
μ_A (D.)	1.440	1.047	0.091	1.099	0.206	1.212
μ_B (D.)	−1.537	−1.209	−0.467	−1.292	−0.625	−1.202
μ_{tot} (D.)	0.983	0.887	1.340	1.429	1.818	1.351
			C_2H_4			
$-\epsilon$ (au)	0.371	0.371	0.371		0.371	0.371
$-\Sigma\epsilon$ (au)	26.453	26.492	26.512		26.515	26.504
KE (au)	77.527	77.557	77.820		77.923	77.700
q_c	−0.280	−0.236	−0.424	See column F	−0.490	−0.308
q_H	0.140	0.118	0.212		0.245	0.154
$\mu_A{}^C$ (D.)	−0.312	−0.139	−0.729		−0.551	0.029
$\mu_B{}^C$ (D.)	−1.315	−1.360	−0.470		−0.858	−1.490

[a] The symbols in column 1 refer: (a) for H_2CO, to the eigenvalue of the highest occupied orbital, the sum over MO's of the eigenvalues of the occupied orbitals, the kinetic energy, Mulliken charges on carbon, oxygen, and hydrogen, the classical, atomic, and bond components of the dipole moment, and the total dipole moment; (b) for C_2H_4, to the same quantities except for $\mu_A{}^C$ and $\mu_B{}^C$ which refer respectively to the carbon atomic dipole, and the sum of all the bond moments to carbon. Positive dipole components for H_2CO denote C^+O^- polarity; positive components for the ethylene carbon denote $C^-H_2{}^+$. Averaging of α's is described in section IIB. The zero-overlap (ZO) elements and K^{ZO} are discussed in section IIC. The method for origin-invariant dipole partitioning is given by K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962). The SCF H_2CO and C_2H_4 wave functions are respectively from ref 10b and 10a, and the geometries for all the calculations were those given in the latter references.

We have previously shown[7] that, consistent with the requirements of three-dimensional rotational invariance, a two-center Hamiltonian matrix element involving two 2p orbitals may be partitioned (eq 7 of paper I) into a σ–σ and a π–π component (neglecting cross terms),[17] determined respectively by $K_{2p\sigma 2p\sigma}$ and $K_{2p\pi 2p\pi}$, provided that the two values of K remain constant for all such interactions between a given pair of atoms. A similar neglect of cross terms for 2s–2p two-center interactions[17] implies that for each pair of atoms only the σ component (along interatomic axis) of a 2p orbital contributes to the Hamiltonian element. If only two-dimensional rotational invariance is required (*vide supra*), different values of $K_{2p\pi 2p\pi}$ may be used for in-plane and out-of-plane interactions. In the absence of a larger body of SCF calculations to help us decide which value of $K_{2p\pi 2p\pi}$ is appropriate in a given situation, we think it reasonable to postulate the following: $K_{2p\pi 2p\pi} = 1.10$ when both 2p orbitals are π orbitals of trigonal carbons in a planar conjugated system. Otherwise the other ethylene value, 0.73, is assigned. We shall examine the sensitivity of some of our results to this choice. Although we have just shown that certain Hamiltonian elements corresponding to vanishing overlap integrals can be safely neglected,[17] the one-center 2s–2p elements have appreciable magnitudes and we calculate them according to eq 6 of paper I, using the value of K^{ZO} for ethylene.

D. Reproduction of Model Wave Functions. Since our final choice of α's and K's represents an average set of values, we now examine the ability of these parameters to reproduce the models before considering complex systems. Table II shows some properties of the C_2H_4 and H_2CO wave functions, reproduced under the approximations of our method and several other approximations. In particular, the assumption that $K^{ZO} = 0$ leads to sharp disagreement with SCF results. Even though column C for H_2CO yields essentially the SCF dipole moment, the partitioning into bond and atomic moments shows that this apparent agreement is fortuitous. On the other hand, our results for H_2CO (column F) yield both charges and moments close to the SCF values. The eigenvalues (not shown), at worst off by 0.08 au, are generally good to about 0.02 au. Results for ethylene are comparable, with the highest eigenvalue good to 0.00 au and one discrepancy of 0.06 au. For ethane, the use of the ethylene values of K_{ij} somewhat exaggerates the C–C interaction, gives $q_H = -0.13$ (SCF value, -0.06), and yields eigenvalues (not shown) generally good to 0.04 au, the highest one off by 0.02 au and the worst off by 0.05 au. Results for acetylene are comparably reproduced by our method. In all cases the correct order of the eigenvalues is obtained.

III. Eigenvalues and Energies

A. Total Energy Criteria. Our method permits the calculation of eigenvalues and total kinetic energies. The relationship between eigenvalues and ionization potentials is discussed in a later section. Two tests can be made of our results on the basis of over-all energy relationships: the approximate molecular binding energy and the virial theorem. Both of these tests depend upon an additional assumption not required in other sections of this paper: namely, the near cancellation between molecular nuclear repulsion energy (N) and one-half the difference of the total one-electron energy (kinetic and nuclear attraction) of the molecule

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(17) The Mulliken approximation obviously neglects matrix elements between orthogonal orbitals. Our CH_2NH wave function allows us to examine several of these zero-overlap Hamiltonian elements. We find that all such elements have magnitudes less than 0.03 au, except for the one-center 2s–2p elements, which are included in our method.

and its constituent ground-state atoms.[5] To the extent that this cancellation holds (see Appendix III), the binding energy A is given simply as one-half the difference of the sum over electrons of the molecular eigenvalues (ϵ_i^{m}) and those of the reference atoms (ϵ_i^{a})

$$A = \sum_i (\epsilon_i^{\mathrm{m}} - \epsilon_i^{\mathrm{a}})/2$$

This test is quite crude and depends, of course, on the choice of wave functions for the reference atoms. A corollary of this procedure is that the total molecular energy E_{tot} is one-half of the sum of the total one-electron energy of the constituent atoms plus one-half of the sum over electrons of the molecular eigenvalues

$$E_{\mathrm{tot}} = \sum_i (E_i^{\mathrm{a}} + \epsilon_i^{\mathrm{m}})/2$$

where E_i^{a} is the kinetic and nuclear attraction energy of the ith atomic orbital. This energy can be compared with the exact kinetic energy in a test of the virial theorem. Although the relation $T = -E_{\mathrm{tot}}$ holds only for a molecule in the nuclear configuration of lowest energy,[18] this relation should still be approximately valid for small deviations from equilibrium geometry.

Results of the application of these energy criteria are presented in Appendix II, while Appendix III reveals for several polyatomic SCF calculations,[10] the value of

$$\Delta = \left[\sum_i (E_i^{\mathrm{m}} - E_i^{\mathrm{a}})/2\right] + N$$

assumed equal to zero in Appendix II. We see that Δ is usually only a small fraction of A. It is clear from the quantitative results of Appendix II that binding energies are fairly reasonable (within 25%), and that the virial theorem is obeyed to better than 99%, about the range of agreement of unscaled exact SCF calculations.[10,19] We realize that the above procedure is far from rigorous. However, we feel it is significant that, for the first time, approximate, large-molecule wave functions can be shown to be in reasonable conformity with certain energy criteria.

B. Conformational and Isomerization Energies. When one realizes that molecular binding energies represent differences between relatively very large energies, it seems remarkable that our nonempirical[7] method can obtain these binding energies to within 25%, in terms of only molecular eigenvalues and atomic integrals. Since, however, the cancellation relied upon above may fail by several electron volts (see values of Δ in Appendix III), extreme caution must be taken when using eigenvalues to detect energy differences of the order of kilocalories or electron volts. When interatomic distances are varied, there is frequently no simple correlation between changes in the total energy (E_{tot}) and the sum of eigenvalues of occupied MO's ($\sum_i \epsilon_i^{\mathrm{m}}$) in SCF calculations. For example, in an SCF calculation for CH_4,[20] $\sum_i \epsilon_i^{\mathrm{m}}$ increases monotonically in magnitude as the CH distance is decreased, but the total energy shows a minimum. This same lack of correlation between E_{tot} and $\sum_i \epsilon_i^{\mathrm{m}}$ occurs as the basis set is varied.[20] In the application of the extended Hückel method[4] some success has been found in location of energy minima using $\sum_i \epsilon_i^{\mathrm{m}}$, but in those studies the same values of α's have been used for all distances. There is a general tendency for α's to become more negative as distances are decreased, although the behavior for p orbitals is somewhat more complex. In some of our studies of diatomic molecules these changes of α with distance are of the same order of magnitude as the changes in E_{tot} and $\sum_i \epsilon_i^{\mathrm{m}}$.

The only complete SCF results for a conformational energy difference are those for ethane,[19] although there are many such studies by the extended Hückel method.[4] In the SCF study of C_2H_6 the difference of $\sum_i \epsilon_i^{\mathrm{m}}$ is twice the difference in E_{tot} for the two conformations. An examination of the Hamiltonian matrices for ethane reveals that the difference in α's for staggered and eclipsed conformations is only about 20% of the barrier for most basis orbitals. The largest difference, 44% of the barrier, occurs for the α's of the 2p orbitals perpendicular to the C–C axis. Perhaps, then, there are circumstances when the use of constant α's may be a reasonable approximation to SCF results, and perhaps in these cases the differences in Hamiltonian matrices can be expressed solely in terms of geometrical factors (*i.e.*, overlap integrals), but in general there is no assurance that changes in $\sum_i \epsilon_i^{\mathrm{m}}$ will even occur in the same direction as changes in the total energy of the molecule undergoing conformational change. In spite of these qualifications, our $\sum_i \epsilon_i^{\mathrm{m}}$ values (Appendix II) appear to be qualitatively useful in predicting stabilities of conformers; thus, *s-trans* isomers are usually found more stable than are *s-cis* isomers, a reasonable ethane barrier is obtained, and the least eclipsed alkylbenzenes are predicted as more stable, with slight exceptions for *t*-butylbenzene (the barrier is only 1 kcal) and toluene (negligible barrier).

Positional isomers are a different matter. No SCF calculations are available, the entended Hückel method exaggerates steric effects,[4a] and we find our method unreliable here. Probably dispersion forces, a correlation phenomenon outside of the MO framework, are important factors in these isomerization energies[21] (possibly also in conformational and distance variation). It is clear, then, that in attempting to obtain small energy changes in terms of approximate eigenvalues one is at the mercy of a tenuous balance of errors.

IV. Eigenvalues and Ionization Potentials

A. General Background. The practice of using absolute values of MO eigenvalues to approximate vertical ionization potentials (IP) has developed from arguments by Koopmans[22] and Mulliken.[14] In general, however, some modification of the un-ionized wave function has been found necessary for close agreement with experiment. For example, in π-electron theory these methods

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[18] See footnote 12 of ref 7.

[19] R. M. Pitzer and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 1995 (1963).

[20] B. J. Woznick, *ibid.*, 40, 2860 (1964).

[21] See K. S. Pitzer and E. Catalano, *J. Am. Chem. Soc.*, **78**, 4844 (1956). We have briefly examined nonbonded interactions in our method by observing changes in $\sum_i \epsilon_i^{\mathrm{m}}$ for two methane molecules (D_{2d} configuration) and for two neon atoms separated by various distances. No stabilization (relative to infinite separation) was observed, and repulsions became appreciable at distances smaller than van der Waals contacts.

[22] T. Koopmans, *Physica*, **1**, 104 (1934).

Table III. Eigenvalues and Ionization Potentials (ev)

	Calcd[a]	Experimental[b]	
	ϵ	PI	EI
CH_4	15.16	12.98, 12.99[c]	13.4[f]
C_2H_6 (θ = 60°)	12.45	11.65, 11.49[c]	11.76,[g] 11.9[f]
(θ = 0°)	12.24		
C_3H_8	11.66	11.07, 11.07[c]	11.21,[g] 11.4[f]
n-C_4H_{10}	11.12	10.63, 10.50[c]	10.80,[g] 11.0[f]
i-C_4H_{10}	11.85	10.57 (?), 10.78[c]	10.79,[h] 10.7[f]
n-C_5H_{12}	10.39	10.35 (?)	10.55[g]
i-C_5H_{12}	10.89	10.32 (?)	10.60[h]
neo-C_5H_{12}	11.75	10.35 (?)	10.29[h]
n-C_6H_{14}	9.85	10.18 (?)	10.43[g]
n-C_7H_{16}	9.44	10.08 (?), 10.20[c]	10.35[g]
n-C_8H_{18}	9.13	...	10.24[g]
Cyclohexane	10.24	9.88, 9.79[c]	9.95[i]
Adamantane	9.69	...	8.0[i]
Congressane[j]	8.79[k]	...	7.3[i]

	ϵ_n	ϵ_π	ϵ_σ	PI	EI
C_2H_2	...	11.31	19.54	11.41, 11.41[c]	11.41[l]
$CH_3C{\equiv}CH$	...	10.21 (15.92)	16.58	10.36	10.36[l]
C_2H_4	...	10.15	13.82	10.515, 10.48[c]	10.80[l]
$CH_3CH{=}CH_2$	...	8.98 (15.81)	12.66	9.73	9.94[l]
s-trans-Butadiene	...	7.34 (13.17)	12.78	9.07,[d] 9.08[c]	9.18[l]
s-cis-Butadiene	...	7.03 (13.27)	13.00	8.75[d]	
Fulvene	...	5.74 (16.14)	12.33	...	...
Dimethylfulvene	...	5.74 (17.34)	11.11	...	...
Azulene	...	4.61 (16.89)	11.03	...	7.72[m]
C_6H_6	...	8.33 (15.58)	12.10	9.24,[e] 9.25[c]	9.52,[n] 9.52[o]
$CH_3C_6H_5$ (θ = 0°)	...	7.62 (16.63)	11.78	8.82	9.20[n]
(θ = −30°)	...	7.62			
$C_2H_5C_6H_5$ (θ = 90°)	...	7.61		8.76	9.12[o]
(θ = 0°)		7.64			
i-$C_3H_7C_6H_5$ (θ = 60°)	...	7.51		8.69	9.13[o]
(θ = 30°)		7.56			
(θ = 0°)		7.62			
(θ = −30°)		7.64			
t-$C_4H_9C_6H_5$ (θ = 0)	...	7.53		8.68	9.35[o]
(θ = −30)		7.54			
o-$(CH_3)_2C_6H_4$	...	7.30 (17.53)	11.19	8.56	8.96[n]
m-$(CH_3)_2C_6H_4$	...	7.40 (16.99)	11.59	8.56	9.01[n]
p-$(CH_3)_2C_6H_4$	...	6.98 (16.95)	11.62	8.445	8.86[n]
Naphthalene	...	5.90 (17.01)	10.74	8.12, 8.14[e]	8.26[m]
H_2CO	11.04	13.20	16.25	10.87	10.88[p]
CH_3CHO	10.64	11.75 (16.27)	13.79	10.21	10.26,[p] 10.28[o]
s-trans-$(CH_2{=}CH)CHO$	10.51	8.38 (15.02)	13.84	10.10	10.25,[p] 10.34[o]
s-cis-$(CH_2{=}CH)CHO$	10.70	8.19 (15.08)	13.66		
s-trans-$(CH_3CH{=}CH)CHO$	10.23	7.57 (16.05)	12.92	9.73	9.81[p]
s-cis-$(CH_3CH{=}CH)CHO$	10.48	7.40 (16.08)	12.95		
C_6H_5CHO	10.36	7.33 (16.57)	11.95	9.53, 9.60[e]	9.82[o]
$(CH_3)_2CO$	10.13	11.11 (17.36)	13.33	9.69, 9.67[c]	9.89,[p] 9.92[o]
s-trans-$CH_3(CH_2{=}CH)CO$	10.08	8.38 (16.93)	12.98	...	9.91 (?)[o]
s-cis-$CH_3(CH_2{=}CH)CO$	10.16	8.12 (16.87)	13.06	...	
$CH_3(C_6H_5)CO$	9.85	7.32 (17.43)	11.64	9.27 (?), 9.65[e]	9.77[o]
p-Benzoquinone	9.96, 10.37	6.94 (17.38)	12.16	9.68[e]	...
o-Benzoquinone	9.48, 10.85	5.84 (17.78)	12.95	...	...
Tropone	9.49	4.32 (16.79)	11.98	...	9.68[q]
Pyrrole	7.48	5.46 (17.71)	13.22	8.20 (?)	8.97[n]
Pyridine	8.10	8.11 (16.21)	12.24	9.40,[e] 9.28[c]	9.76[n]
Pyrazine	7.03, 9.55	8.10 (16.60)	13.03	...	10.01[r]
Pyrimidine	7.26, 8.95	8.41 (16.93)	13.36	...	9.91[r]
Pyridazine	6.52, 10.10	8.62 (16.65)	13.65	...	9.86[r]

[a] For saturated hydrocarbons, ϵ of the hfmo is given. For planar unsaturated systems and their methyl derivatives, ϵ of the highest and (in parentheses) lowest π levels are listed together with ϵ of the highest σ level. When heteroatoms are present, the highest one or two σ levels are labeled n (exception: pyrrole, where n refers to the second highest π-level), σ denoting the next highest σ level. For the monoalkylbenzenes (aside from the eclipsed conformation of toluene) only the ϵ of the hfmo is given, designated as π, even when the alkyl group destroys the molecular plane. Conformations of alkyl groups are identified by θ, the angle of rotation (in degrees) from the eclipsed conformation (see Appendix IV). Conformers are listed in order of decreasing magnitude of $\frac{1}{2}\sum_i \epsilon_i^m$ (see Appendix II). [b] Unless otherwise noted, photoionization (PI) results are from K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectry. Radiative Transfer*, **2**, 369 (1963), while electron impact (EI) results are from a compilation by R. W. Kiser, "Tables of Ionization Potentials," USAEC Office of Technical Information, TID-6142. Aside from butadiene (footnote *d*) experimental results did not specify isomers in cases of conjugated double bonds. [c] Reference 30. [d] T. M. Sugden and A. W. Walsh, *Trans. Faraday Soc.*, **41**, 76 (1945). [e] F. I. Vileson, *Dokl. Akad. Nauk. SSSR*, **132**, 632 (1960). [f] R. W. Kiser, footnote *b*, ref 153. [g] R. W. Kiser, *ibid.*, ref 233. [h] R. W. Kiser, *ibid.*, ref 74 and 477. [i] R. S. Gohlke, private communication. [j] C. Cupas, P. von R. Schleyer, and D. J. Trecker, *J. Am. Chem. Soc.*, **87**, 917 (1965). [k] F. P. Boer and C. Cupas, unpublished results. [l] R. W. Kiser, footnote *b*, ref 72. [m] R. J. Van Brunt and M. E. Wacks, *J. Chem. Phys.*, **41**, 3195 (1964). [n] R. W. Kiser, footnote *b*, ref 3. [o] R. W. Kiser, *ibid.*, ref 364. [p] R. W. Kiser, *ibid.*, ref 393. [q] R. W. Kiser, *ibdi.*, ref 217. [r] R. W. Ksier, *ibid.*, ref 216.

have ranged from the ω technique[15] to Hoyland and Goodman's complete recalculation of the ionized state,[23] using Roothaan's open-shell theory,[24] modified with approximations due to Pople.[25] This last study[23] gave 1–3% agreement, which may be to some extent fortuitous and dependent on empirical parameters, since studies of diatomics by exact applications of Roothaan's method give agreement with experiment of only 5%.[26] In the above π-electron calculations,[23] Koopmans' theorem IP's were too *large* by ≈ 2 ev, a discrepancy which is partly due to the inherent approximation of the theorem, and partly to eigenvalue inaccuracies stemming from the use of empirical parameters in these approximate methods. Lorquet has noted[27] that full SCF calculations based upon Slater-type minimum basis sets usually yield values for IP's from Koopmans' theorem which are too *low* by about 2 ev. Perhaps a major portion of the discrepancy in π calculations is due to a failure to recognize that $\alpha_{2p\pi}$ is appreciably less negative than $\alpha_{2p\sigma}$. Furthermore, recent SCF results for diatomic molecules indicate that in going from minimum basis sets to near-complete sets, eigenvalues can change by several electron volts.[26] These diatomic wave functions, which offer the only fair basis to judge Koopmans' theorem for molecules, indicate that Koopmans' theorem is probably accurate to at least 10%. Thus at best, one might hope in the minimum basis framework to reproduce IP trends in related molecules. In Table III we present for various σ, π, and n (nonbonding) MO's[28] eigenvalues which we feel are generally closer to the exact SCF minimum basis results than those of any previous calculations for molecules of comparable size. In spite of some differences of 1–3 ev between IP's and the absolute values of our eigenvalues, we proceed to show how the latter nonempirical quantities can often be used in prediction and discussion of experimental data.

B. First Ionization Potentials. First we compare absolute values (ϵ) of the eigenvalues of the highest filled molecular orbitals (hfmo) with first ionization potentials (Table III). Koopmans' theorem[22] applies to vertical IP's, but it is not always clear to which process the experimental values refer (PI: photoionization, accurate to ±0.01 to ±0.05 ev; EI: electron impact, accurate to ±0.1 to ±0.3 ev). Nevertheless, we find that the trends of experimental values (when unambiguous) are always reproduced by our nonempirical molecular orbital ϵ's for *n*-alkanes, cyclohexane systems, olefins and alkynes, nonbenzenoid- and benzenoid-conjugated systems, saturated carbonyls, and conjugated carbonyls. In the heterocycles, correlation between ϵ's and IP's is poor except that the order of pyrrole relative to the azabenzenes is correctly given. For benzaldehyde, acetophenone, and *p*-benzoquinone, both the IP's and ϵ's are very close in magnitude, and experimental uncertainty may obscure the correct trend of IP's. The same applies to alkylbenzenes (C_6H_5R). Although the relative importance of the various conformations is not clear for these molecules, we note that in going from toluene to *t*-butylbenzene both the ϵ's and IP's (PI results) decrease about 0.1 ev. The experimental evidence is also inconclusive on our prediction that IP's increase as one goes from an *n*-alkane to its branched isomer, but it is apparent that the differences in ϵ's among isomeric alkanes exaggerate the corresponding differences in IP's. In conjugated hydrocarbon systems the ϵ's decrease faster than do the IP's as the size increases, and thus our ϵ's are smaller by 1–2 ev (3 ev for azulene) than experimental IP's. In the saturated carbonyl compounds, the hfmo is the lone pair or n MO (see section VI), for which ϵ is slightly greater than the IP, but the hfmo changes to π symmetry as unsaturated groups are added to the carbonyl; here the accompanying sharp decrease in the ϵ is not evident in the experimental IP's. In general, our ϵ's for conjugated carbonyls are about 2 ev less than IP's. The much larger difference in the case of tropone is unexplained.

The best agreement between ϵ's and IP's is found in the differences of IP's of certain unsaturated frameworks and the molecules obtained from them by replacing a hydrogen with an alkyl group. Price, *et al.*,[29] explain qualitatively the effect of alkyl groups on chromophore ionization potentials as follows. The pseudo-π orbital of the alkyl group interacts with the original π system to form a new hfmo which is antibonding with respect to the hfmo of the unsubstituted molecule. The decreased IP is then attributed to this antibonding effect in the un-ionized molecule and to the ability of the alkyl group to absorb some of the positive charge in the ion by delocalization in the ground-state hfmo. In Table IV we see quantitative justification of this reasoning in terms of ground-state MO's only. Even where our ϵ's and experimental IP's differ by 2 ev, the differences in IP for R = CH_3 and R = H are fairly closely reproduced by the ϵ's. The effect of replacing the carbonyl H in a conjugated aldehyde with a methyl group is predicted to be negligible, because for R = H, the π hfmo in the cases studied has very little contribution from the carbonyl π orbitals, so that the addition of the methyl group to the carbonyl carbon has little or no effect on the hfmo. The only IP available for

Table IV. Effect of Methyl Group on IP

	$IP_{R=H} - IP_{R=CH_3}$	
	Calcd	Exptl[a]
A. Attached to Carbon–Carbon Double (or Triple) Bond		
R—C≡CH	1.10	1.05
R—CH=CH_2	1.12	0.79
s-trans-R—CH=CH—CHO	0.81	0.37
R—C_6H_5	0.71	0.42
o-R(CH_3)C_6H_4	0.32	0.26
m-R(CH_3)C_6H_4	0.22	0.26
p-R(CH_3)C_6H_4	0.64	0.38
Dimethylfulvene	0.00	...
B. Attached to Carbonyl Carbon		
s-trans-R(CH_2=CH)CO	0.00	...
RC_6H_4CO	0.01	−0.05

[a] Experimental differences were taken from the PI data of Table III.

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(23) J. R. Hoyland and L. Goodman, *J. Chem. Phys.*, **36**, 12 (1962). Some of the parameters of this method were fitted to reproduce the C_2H_2, C_2H_4, and C_6H_6 first ionization potentials.

(24) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).

(25) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(26) A. C. Wahl, *J. Chem. Phys.*, **41**, 2600 (1964); W. M. Huo, *ibid.*, **43**, 624 (1965).

(27) J. C. Lorquet, *Rev. Mod. Phys.*, **32**, 312 (1960).

(28) The notation σ, π, and *n* is defined in Table III. The *n* or lone-pair MO's are discussed in section VI.

(29) W. C. Price, R. Bralsford, P. V. Harris, and R. G. Ridley, *Spectrochim. Acta*, **14**, 45 (1959).

Table V. Higher Ionization Potentials (ev)

C_3H_8		n-C_4H_{10}		i-C_4H_{10}		n-C_7H_{16}		Cyclohexane		s-*trans*-Butadiene		Acetone	
ϵ[a]	PE[b]	ϵ	PE	ϵ	PE	ϵ	PE	ϵ	PE	ϵ	PE	ϵ	PE
11.66	11.07	11.12	10.50	11.85	10.78	9.44	10.20	10.24	9.79	7.34	9.08	10.13	9.67
12.03		11.51		12.02									
13.12	13.17	12.39	12.36	12.46	12.54	11.28	14.38	11.88	(11.33)	12.78	11.25	11.11	12.16
						11.50							
14.06	15.17	13.28	14.13	14.33	14.51	11.92	15.18	12.25	12.22	13.17	12.14	13.33	(14.15)
												13.35	
15.21	15.70							13.97	14.37	14.43	13.23	14.35	15.55
										14.60			
										17.24	15.14		

[a] ϵ = absolute value of eigenvalue. [b] Ionization potentials obtained by photoelectron method, ref 30.

butenone is apparently somewhat uncertain, and our prediction of the closeness of the acrolein and butenone IP's awaits experimental verification. Fulvene has a hfmo which has a nodal plane containing the methylene carbon, and hence the addition of methyl groups to form dimethylfulvene has a negligible effect on ϵ; here we predict no appreciable decrease in IP, as opposed to the situation in the ethylene–isobutene series. Finally we observe that the difference in ϵ for *trans*- and *cis*-butadiene is close to the experimental difference in IP's.

C. Higher Ionization Potentials. The newly developed photoelectron (PE) method[30] yields values of higher ionization potentials which are compared in Table V with ϵ's for more strongly bound electrons. Since vibrational structure may extend over several tenths of an electron volt, we feel that some pairs of eigenvalues should be considered as effectively one level when comparing them with PE results, as indicated by the grouping in Table V. The agreement ranges from good (±0.5 ev) for cyclohexane to fair (±1.0 ev) for acetone and the smaller alkanes to poor for n-heptane and butadiene. For aliphatic compounds the experimental PE results consistently imply a much larger gap between the highest two electronic levels than do the ϵ's, especially for n-heptane (4.18 *vs.* 1.84 ev), and we therefore wonder if a higher resolution study would reveal more levels.

Table VI. Comparison of σ- and π-Electron Density in Benzene[a,b]

Height above benzene plane, au	Distance along C–C bond, au		
	0.00	0.66	1.32
2.00	0.023 (0.015)	0.020 (0.012)	0.017 (0.014)
1.06	0.119 (0.056)	0.076 (0.085)	0.043 (0.102)
0.66	0.154 (0.122)	0.076 (0.150)	0.033 (0.177)
0.00	0.000 (121.374)	0.000 (0.316)	0.000 (0.273)

[a] π-Electron and σ-electron (in parentheses) densities are listed for various points in the plane perpendicular to the molecular plane and containing a C–C bond. The points are defined by various distances along the C–C bond (measured from one of the carbon atoms) and various heights above the molecular plane (0.66 and 1.06 au correspond respectively to the heights of maximum π density at the carbon atom and at the bond midpoint). Densities are in units of electrons/au^3. Notice that the σ density exceeds the π density throughout much of the bonding region, including the region where the π-bond density is greatest. [b] We have also calculated the σ- and π-electron densities for C_2 ($^1\Sigma_g^+$, r_e = 2.347 au), using a Slater basis set. These densities are in essential agreement with the extended basis set densities for C_2 recently published by A. C. Wahl ("Pictorial Studies of Molecules," Argonne National Laboratory Technical Report, July 1965), although in the latter calculation the π density falls off somewhat more gradually than for the Slater basis set results at distances of 2 au or greater from the axis. This correspondence with a near Hartree–Fock calculation supports our conviction that the results in this table have general significance, in spite of the fact that they arise from a minimum basis set.

D. σ and π Levels and Rydberg Spectra. In a recent study by the extended Hückel method, Hoffmann found that the lowest π orbital of a series of aromatic molecules was lower in energy than several σ orbitals.[31] Our wave functions confirm and extend this result for all conjugated molecules studied (Table III). Usually the highest σ level is several electron volts higher than the lowest π level, and in the case of naphthalene there are eight σ levels above the lowest π level. Correspondingly, the spatial distribution of σ and π electrons in benzene (Table VI) confirms the earlier conclusion of Coulson, *et al.*,[32] that the π-electron density is to a large extent buried in the σ-electron density. This is also true for the SCF ethylene wave function.[10] It has not been demonstrated experimentally that some σ levels lie above some π levels in conjugated systems. Because of the open question of the interpretation of experimental values of higher IP's in benzene and pyridine, we compare in Table VII calculated values of ϵ's, limiting values of Rydberg series,[11] and PE ionization potentials.[30] Certainly the highest benzene level is of the π type. The Rydberg value at 11.48 ev was originally assigned to ionization of a σ electron (σ_{CH}) because of a blue shift of 250 A upon deuteration and because 11.48 ev is close to IP's for typical alkanes; but it was later argued that the existence of a similar blue shift for the lowest $\pi \rightarrow \pi^*$ transition in benzene, the sharpness of the series, and the small effect of deuteration on vibrational structure made the assignment of the series to a π-electron more reasonable.[11] By contrast, the other series, converging at 16.84 ev, was relatively diffuse and involved a ring mode excitation, suggesting that a σ_{CC} electron was involved.[11] The PE results give ionization potentials which are quite close to the corresponding spectral values, but the sharpness of the PE curve for the intensity of the 16.73-ev level seems inconsistent with the vibrational structure found in the Rydberg series.

In our calculation the $a_{2u}(\pi)$ eigenvalue is close to the spectral IP at 16.24 ev. In addition this is the most strongly binding (overlap population of 0.71) of

(30) M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 5141 (1963); 4434 (1964); 616 (1965).

(31) See the first paper of ref 4a.

(32) C. A. Coulson, N. H. March, and S. Altmann, *Proc. Natl. Acad. Sci. U. S.*, **38**, 372 (1952).

Table VII. Electronic Levels of Benzene and Pyridine

Benzene			Pyridine		
ϵ[a]	Rydberg[b]	PE[c]	ϵ[a]	Rydberg[b]	PE[c]
8.33 (π)	9.24 (π)	9.25 (π)	8.10 (n) 8.11 (π)	9.26 (π)	9.28 (π)
12.10 (σ)	11.48 (π)	11.49 (π)	9.07 (π)	10.3 (n or π)	10.54 (n)
15.27 (σ)		(12.19)	12.24 (σ)	11.56 (π)	12.22
15.48 (σ)		13.67 (14.44)	13.89 (σ) 14.81 (σ)		(13.43) 14.44
15.58 (π)	16.84 (σ)	16.73	15.64 (σ)		15.49
15.79 (σ)		18.75	16.21 (σ)		
21.02 (σ)			16.21 (π)		16.94

[a] ϵ = absolute value of eigenvalue. [b] Reference 11. [c] Reference 30.

all the MO's, consistent with the vibrational structure noted in the Rydberg series. Furthermore, the mere fact that the intermediate Rydberg series is not similar to diffuse alkane spectra does not rule out our predicted $e_2(\sigma)$ level as the source of the IP near 11.5 ev. This level has a small net overlap population (slightly C–H bonding, slightly C–C antibonding). Thus, we claim that our assignment, which places several σ levels above the $a_{2u}(\pi)$ level, is reasonable in terms of the presently available experimental results.[33] The semiempirical SCF results discussed above[23] predict an IP of 12.54 for the benzene a_{2u} electron. Since this method is calibrated with lowest IP's, it is not clear how valid it would be for higher IP's.

In the case of pyridine, two Rydberg series were assigned to the highest and lowest π-MO's (respectively a_2 and b_2).[11] An intermediate series was presumed to belong either to the nonbonding MO (a_1) or middle π level (b_2), although it was pointed out that Rydberg series involving the n electron are generally not observed.[11] The PE results indicate an n electron IP near the limit of the middle series. The MO calculation shows a splitting of the highest two π-levels about equal to the difference of the first two Rydberg limits (9.26 and 10.3 ev), while the n level is almost degenerate with the highest π level. Once again we suggest that the lowest π level is much lower than previously assumed, perhaps corresponding to the PE IP at 16.94 ev, while the lowest Rydberg limit (11.56 ev) is close to our predicted highest σ level (12.24).

E. Unoccupied Levels. As a final comment, we point out that in agreement with exact SCF closed-shell calculations for neutral ground-state molecules, we find that unoccupied (ghost) orbitals have positive eigenvalues. Most semiempirical methods, by contrast, tend to yield one or more negative eigenvalues for unfilled orbitals.[34]

V. Intramolecular Charge Transfer

A. General Remarks. Intramolecular charge transfer (Tables VIII–X) is generally described as a superposition of inductive (due to electronegativity differences) and mesomeric interactions.[35] In many previous treatments of this phenomenon, there has been a failure to consider σ electrons explicitly, combined with assumptions about the parameters of the theory and the relative importance of inductive and mesomeric effects.[36] Here, we develop these effects from our simulated SCF MO theory, which removes nearly all the arbitrariness, leaving only the assumption of the relevance of model SCF calculations for more complex systems. σ electrons were included in the extended Hückel method,[4] but the atomic parameters did not provide for inductive effects among different types of carbon atoms. Our choice of α's from model compounds allows for all appreciable inductive differences between atoms. We feel there is no reliable method at present for including finer differences due to charge transfer.[15]

Table VIII. Substituent Effects in Hydrocarbons[a,b]

Molecule	R	q_R	q_R^{π}
C_6H_5R	CH_3	−0.057	+0.022
	C_2H_5	−0.013	+0.019
	i-C_3H_7	+0.019	+0.017
	t-C_4H_9	+0.054	+0.015
o-$C_6H_4R_2$	CH_3	−0.055	+0.023
m-$C_6H_4R_2$	CH_3	−0.058	+0.023
p-$C_6H_4R_2$	CH_3	−0.058	+0.021
$R(CH{=}CH_2)$	CH_3	+0.050	+0.032
$R(C{\equiv}CH)$	CH_3	+0.139	+0.035
Fulvene	$CH_2{=}$	−0.165	+0.093
Dimethylfulvene	$(CH_3)_2C{=}$	+0.171	+0.306

[a] q_R is the net Mulliken charge for group R. The positive values of q_R^{π} indicate the amount of charge donated by R to the π orbitals of the unsaturated residue. [b] For the monoalkylbenzenes we have taken an unweighted average of the charges, since they were not especially sensitive to the alkyl group conformation.

For criteria of charge transfer we examine total dipoles computed exactly from the detailed wave function, Mulliken point charges,[37] and overlap populations.[37] The fact that dipole moments in terms of Mulliken charges are usually close to the exact results (see Table IX) seems to justify their use as a measure of charge distribution. In view of our reliance on dipole

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(33) A recently published limited Gaussian basis set benzene wave function (J. M. Schulman and J. W. Moskowitz, *J. Chem. Phys.*, **43**, 3287 (1965)) yields a gap of 4.5 ev between the two occupied π levels. However, the fact that this calculation predicts benzene less stable than its component, ground-state atoms by ~9 au makes the validity of the eigenvalues uncertain. The lowest six eigenvalues differ by ~0.5 au from typical values for MO's which are composed of carbon ls AO's.

(34) *E.g.*, ref 4, and B. Pullman and A. Pullman, "Quantum Biochemistry," John Wiley and Sons, Inc., New York, N. Y., 1963.

(35) I. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter II.

(36) In particular, we shall be interested in the work started by R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941), and extended by C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953); Y. I. Haya, *Bull. Chem. Soc. Japan*, **28**, 369, 376 (1955); and A. Lofthus, *J. Am. Chem. Soc.*, **79**, 24 (1957). In a future paper, we shall demonstrate that the method which these papers used to obtain second-order hyperconjugation energies (SHE) results in *negative* SHE values when applied to exact SCF wave functions.

(37) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

Table IX. Dipole Moments

	Calcd[a]		Experimental[b]			
	Total moment	π moment	Gas	Liquid	Benzene	Other
A. Hydrocarbons						
$CH_3(CH{=}CH_2)$	0.840 (0.986)	1.237 (0.920)	0.34–0.36	...	...	...
$CH_3(C{\equiv}CH)$	1.661 (2.333)	2.119 (1.747)	0.72–0.77	...	...	...
Fulvene	1.767 (1.457)	1.419 (1.419)	...	...	1.1	...
Dimethylfulvene	4.436 (4.206)	5.096 (4.458)	...	...	1.48	...
Azulene	4.787 (4.877)	4.162 (4.162)	...	...	1.0–1.08	...
$CH_3C_6H_5$ ($\theta = 0°$)	0.757 (0.722)	0.960 (0.703)	0.37	0.31–0.38	0.34–0.55	...
($\theta = -30°$)	0.760 (0.726	...				
$C_2H_5C_6H_5$ ($\theta = 90°$)	0.634 (0.718)	...	0.58	0.35–0.37	0.35	...
($\theta = 0°$)	0.708 (0.816)	...				
i-$C_3H_7C_6H_5$ ($\theta = 60°$)	0.602 (0.626)	...	0.65	0.37–0.39	0.38	...
($\theta = 30°$)	0.619 (0.682)					
($\theta = 0°$)	0.576 (0.713)					
($\theta = -30°$)	0.523 (0.719)					
t-$C_4H_9C_6H_5$ ($\theta = 0°$)	0.588 (0.686)		0.70	0.36	0.40–0.53	...
($\theta = -30°$)	0.576 (0.663)					
o-$(CH_3)_2C_6H_4$	1.402 (1.335)	1.939 (1.364)	0.62	0.44–0.54	0.52–0.58	...
m-$(CH_3)_2C_6H_4$	0.881 (0.792)	1.557 (0.917)[c]	...	0.30–0.36	0.37–0.46	...
B. Carbonyls						
H_2CO	1.261 (1.117)	0.039 (0.191)[d]	2.17–2.34	...	...	...
CH_3CHO	1.927 (1.986)	1.091 (0.564)	2.68–2.74	...	2.51	...
s-trans-$(CH_2{=}CH)CHO$	1.572 (1.431)	0.396 (0.229)	3.11,[e] 3.04	...	2.91	...
s-cis-$(CH_2{=}CH)CHO$	1.658 (1.936)	0.654 (0.446)				
s-trans-$CH_3{-}CH{=}CH{-}CHO$	2.714 (2.732)	1.991 (1.490)	3.7	...	3.50	3.58, 3.54
s-cis-$CH_3{-}CH{=}CH{-}CHO$	2.119 (2.277)	1.472 (1.189)				
C_6H_5CHO	1.768 (1.858)	0.723 (0.535)	...	2.72–2.97	2.78–2.99	2.89
$(CH_3)_2CO$	2.545 (2.620)	2.023 (1.168)	2.87–2.97	2.69–3.11	2.41–2.83	
s-trans-$CH_3(CH_2{=}CH)CO$	2.113 (1.969)	1.190 (0.668)	...	...	3.0	...
s-cis-$CH_3(CH_2{=}CH)CO$	2.336 (2.655)	1.620 (1.100)				
$CH_3(C_6H_5)CO$	2.369 (2.488)	1.572 (1.052)	3.03–3.06	3.00–3.40	2.60–2.99	2.63–3.18
Tropone	5.710 (5.831)	4.627 (4.481)	...	4.17–4.30	...	...
o-Benzoquinone	3.642 (3.951)	1.776 (1.441)	...	...	5.1	...
C. Heterocycles						
Pyrrole	4.979 (4.657)	4.304 (4.352)	1.55–1.84	1.54	1.72–2.2	1.76–2.15
Pyridine	1.140 (0.522)	0.101 (0.022)	2.15–2.25	2.23–2.43	1.96–2.28	2.22–2.39
Pyrimidine	1.166 (0.541)	0.079 (0.002)	...	...	2.0	2.44
Pyridazine	2.215 (1.063)	0.278 (0.152)	...	...	...	3.97

[a] The angle θ is defined in Appendix IV. Conformers are listed in order of decreasing magnitude of $^1/_2 \sum_i \epsilon_i{}^m$ (see Appendix II). The π moment is defined in section V. Quantities in parentheses are dipoles based on Mulliken point charges. [b] Experimental dipole moments were taken from A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman & Co., San Francisco, Calif., 1963. Unless otherwise noted, different conformations of a given molecule were not distinguished. [c] This π moment is quite sensitive to the methyl group conformations, becoming 0.174 (0.449) D. when each group is rotated 180° from the conformation assigned in Appendix I. The total moment becomes 0.603 (0.634) D. [d] The exact π moment has $C^+{-}O^-$ polarity, while the Mulliken π charges have a polarity $C^-{-}O^+$. [e] Dipole moment of *s-trans* isomer, ref 43.

moments, we must bear in mind that minimum basis sets are known to give molecular dipole moments in disagreement with experiment by as much as factors of 2 or so, even for exact SCF wave functions.[38] Nevertheless, one may expect that such SCF functions, or those well approximated by our method, might show trends in a series of related compounds. We have examined the situation in formaldehyde, for which two almost identical minimum basis sets, having only slightly different geometries, yielded dipole moments of opposite polarity, and have been able to obtain good agreement of our SCF results[10b] with those of Foster and Boys.[39] We differed appreciably with the other calculation[40] for formaldehyde, for which we obtain a dipole moment of 0.5 D. with C^+O^- polarity. Although the area of disagreement between the two functions is now narrowed considerably, the dipole moment of formaldehyde calculated from a minimum basis set is still less than half the observed value.

B. Unsaturated Hydrocarbons. We first consider the electron-donating ability of the alkyl group, with a view to further exploration of Hoffmann's surprising result that the methyl groups in toluene and the xylenes carry a net negative charge.[31] We feel that several previous π-electron studies of alkyl charge transfer illustrate the limitations of empirical parametrization.[36] Since these calculations assumed that the dipole moments of propylene, propyne, and toluene were resonance moments, it was felt necessary to make the α of the hydrogen pseudo-π orbital less negative than that for a carbon π orbital. In addition, the α_{2p} of the methyl carbon, to which the pseudo-H_3 atom was attached, was made a little less negative than the carbon $\alpha_{2p\pi}$, since an sp^3 carbon is less electronegative than an sp or sp^2 carbon. Muller, *et al.*, gave some theoretical justification for the H_3 α_π:[15] although a hydrogen 1s orbital is surely more electronegative than a carbon $2p\pi$ orbital, the antibonding combination of

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(38) B. J. Ransil, *Rev. Mod. Phys.*, **32**, 245 (1960).

(39) J. M. Foster and S. F. Boys, *ibid.*, **32**, 303 (1960).

(40) P. L. Goodfriend, F. W. Briss, and A. B. F. Duncan, *ibid.*, **32**, 307 (1960).

1s orbitals which comprises the pseudo-π orbital is calculated to have an ionization potential (IP) of 10.8 ev, compared to the valence-state ionization potential (VSIP) for a carbon $2p\pi$ electron of 11.2 ev. Having assigned α's by the above reasoning, the workers of ref 36, after relating off-diagonal Hamiltonian elements to the empirical parameter β, proceeded to obtain reasonable values of charge distributions, dipole moments, and resonance energies. We may now consider the above choice of α's in light of recently available exact SCF LCAO values of α for acetylene, ethylene, and ethane.[10a] Assuming that the C–C axes are along the z axis, with the ethylene hydrogens in the xz plane, the relevant α's (ev) are as follows: for ethane, $\alpha_{2pz} = -10.4$, $\alpha_{2px,y} = -9.5$, $\alpha_H = -13.60$, $\alpha_{H_3\pi} = -7.6$; for ethylene, $\alpha_{2pz} = -14.1$, $\alpha_{2px} = -12.0$, $\alpha_{2py} = -4.0$; and for acetylene, $\alpha_{2pz} = -20.0$, $\alpha_{2px,y} = -4.6$. The basic assumption of our method, stated above, is that in forming larger molecules, these α's may as a first approximation be transferred directly to the appropriate atoms in the new system. On the basis of this assumption, we infer the following about alkyl-substituted unsaturated molecules: (1) neglect of the σ core polarization is not justified, because the $\alpha_{2p\sigma}$'s of the various atoms differ by several electron volts; (2) while it is true, as Mulliken indicated, that the $\alpha_{H_3\pi}$ is smaller in magnitude than the atomic VSIP for C, it is actually much more negative than the most relevant numbers for comparison, which are the $\alpha_{2p\pi}$ values for ethylene and acetylene; (3) in accord with the empirical reasoning, the methyl α_{2p} is a little more negative than $\alpha_{H_3\pi}$. We are thus in the following paradoxical situation: whereas previous authors thought that methyl α's must be *less* negative than the carbon $\alpha_{2p\pi}$ (equating $\alpha_{2p\pi}$ with the VSIP of a $2p\pi$ electron), to ensure proper charge transfer we not only find evidence that the methyl α's should be *more* negative than the $\alpha_{2p\pi}$, but in addition discover that reasonable charge distributions are obtained, even when the latter assignment of α's is used. The charges and α's for propyne are illustrated in Figure 1, while the general results are presented below. Where the α's of Figure 1 differ from those of the above discussion, some averaging has been done as indicated in section IIA. Clearly the relationship between α's and charge transfer in the propyne π system is not a simple one.

Table VIII illustrates alkyl substituent effects in terms of total charges and those due only to π electrons. In part A of Table IX we give total dipole moments and resonance (*i.e.*, π-electron) dipole moments, calculated exactly, along with corresponding values in parentheses from Mulliken point charges.[37,38] In computing the π moment we have assigned to each atom a core charge equal to the number of π electrons (one or two) which it contributes. A core charge of $+0.5$ is assigned to each 1s orbital of the pseudo-π orbital (of the form $1s_{H_1} - 1s_{H_2}$), except for each methyl hydrogen of propyne to which a core charge of $+0.6667$ is assigned. These choices of core charges for π electrons then yield dipoles which represent the difference between the centroid of the actual π cloud and that obtained by localizing the π electrons on their respective centers. Although we present both total and π-only quantities, because of the assumed unique importance of π electrons in unsaturated molecules, we stress, in light of the results of section IVD, that the validity of σ–π separation should be reexamined. All dipoles, total or π only, point in a direction indicative of electron donation to the unsaturated residue (Appendix IV). While these directions seem reasonable, the magnitudes (Table IXA) are usually exaggerated. Nevertheless, the experimental trend is largely reproduced. For example, the dipole moment of propene is correctly calculated to be about one-half of that for propyne or of *o*-xylene, and about equal to that of toluene or of *m*-xylene. Our results for the monoalkylbenzenes show a slight decrease in dipole moment (about 0.2 D.) going from toluene to *t*-butylbenzene, in sharp disagreement with gas phase data, although other data indicate no decisive trend. Appendix IV reveals some sensitivity to conformational changes. The dipole component perpendicular to the alkyl–phenyl bond cannot be correlated with the angle of rotation of the alkyl group. The excessively large calculated dipoles for dimethylfulvene and azulene reemphasize the need for exact SCF calculations on more complex molecules to provide α's for carbon atoms in a wider variety of molecular environments than is presently available.

In general, the charge transfer indicated by the above dipoles is also reflected in the charges of Table VIII. The π charges always represent alkyl donation. Alkyl π donation for the benzene derivatives follows the hyperconjugative order,[41] whereas total alkyl donation obeys the inductive order. For methyl- and ethylbenzene the net alkyl charge is actually negative in spite of the fact that the alkyl group is at the positive end of the dipole. A similar situation arises in fulvene, where the methylene group has a negative charge. This paradox is resolved below in part E of this section.

C. Carbonyl Derivatives. We now consider our results for molecules containing the carbonyl group. Dipole moments and charges of various substituents are shown in Tables IXB and X, both for total electron density and for π density. In accord with experiment, we find that the replacement of a hydrogen atom of formaldehyde or acetaldehyde with a methyl, vinyl, or phenyl group results in donation of electrons to the oxygen atom, accompanied by a corresponding increase in dipole moment. The donating ability of the methyl group is exaggerated in our method, with the result that acetaldehyde, methyl vinyl ketone, and acetophenone dipoles are too large relative to those of formaldehyde, acrolein, benzaldehyde, and crotonaldehyde, although within the two groups of molecules the experimental trend in dipoles is reasonably well reproduced. It is difficult, however, to evaluate the plethora of experimental data. Acetone with its two methyl groups shows especially large exaggeration of electron donation. The *cis* isomers of methyl vinyl ketone and acrolein are predicted to have slightly larger dipole moments than the *trans* isomers, in conflict with previous reasoning in terms of bond dipole moments.[42] The fact that the dipole moment of *trans* acrolein, obtained from a microwave study,[43] is slightly larger than the dipole of an equilibrium mixture, obtained in another study,[44] offers some evidence that

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(41) J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1844 (1935).

(42) J. B. Bentley, K. B. Everard, R. J. B. Marsden, and L. E. Sutton, *ibid.*, 2957 (1949).

(43) R. Wagner, J. Fine, J. W. Simmons, and J. H. Goldstein, *J. Chem. Phys.*, **26**, 634 (1957).

(44) N. B. Hannay and C. P. Smyth, *J. Am. Chem. Soc.*, **68**, 1357 (1946).

Table X. Charges in Carbonyl Derivatives RR′CO

R	R′	q_R[a]	q_R^{π}[b]	$q_{R'}$[a]	$q_{R'}^{\pi}$[b]	q_O[c]	q_O^{π}[d]
H	H	+0.139	. . .	+0.139	. . .	−0.064	+0.032
H	CH_3	+0.081	. . .	+0.098	+0.031	−0.199	−0.041
H	CH_2=CH (*s-trans*)	+0.071	. . .	+0.076	+0.028	−0.225	−0.043
H	CH_2=CH (*s-cis*)	+0.057	. . .	+0.073	+0.027	−0.208	−0.043
H	CH_3—CH=CH (*s-trans*)	+0.070	. . .	+0.119	+0.056	−0.257	−0.074
H	CH_3—CH=CH (*s-cis*)	+0.056	. . .	+0.113	+0.055	−0.240	−0.074
H	C_6H_5	+0.064	. . .	+0.182	+0.043	−0.234	−0.055
CH_3	CH_3	+0.043	+0.028	+0.043	+0.028	−0.320	−0.106
CH_3	CH_2=CH (*s-trans*)	+0.032	+0.021	+0.010	+0.023	−0.327	−0.092
CH_3	CH_2=CH (*s-cis*)	+0.020	+0.027	+0.020	+0.027	−0.326	−0.106
CH_3	C_6H_5	+0.026	+0.025	+0.122	+0.039	−0.341	−0.113

[a] q_R denotes the net Mulliken charge for group R. [b] q_R^{π} denotes the Mulliken charge for group R due to the π-electron density, using the core charges defined in section VB. [c] Mulliken charge on oxygen atom. [d] Mulliken π-electron charge for oxygen.

the *trans* isomer should have a larger dipole. We find the latter situation in the case of crotonaldehyde. Of the two isomers formed from the vinyl and methyl group, we agree with experiment in finding the "in series" linkage in crotonaldehyde to yield a larger dipole than the "parallel" linkage in methyl vinyl ketone. Finally, *o*-benzoquinone and tropone are found to have dipoles appreciably larger than those already discussed.

Our predicted dipole directions may be compared with certain microwave results, which yield magnitudes of dipole components. For acrolein[43] and acetaldehyde[45] the most likely experimental directions made angles of respectively 14 or 34° and 14 or 52° with the C–O axis, the first value being preferred in each case. Our respective values of 6 and 11° are in agreement with these choices of the smaller angle. Similarly for propylene, we predict an angle of 36° between the dipole and the C–C single bond to be compared with experimental angles of 17 or 33° (preferred).[46]

D. N-Heterocycles. Table IXC lists dipole moments for several N-heterocycles. Values for the azabenzenes preserve the experimental trend, with nitrogen at the negative end of the dipole, though magnitudes are underestimated. We predict little contribution to the dipoles from the π density. A completely different situation exists for pyrrole where the electron-donating ability of the nitrogen π orbital is highly exaggerated. Charges are listed in Appendix V.

E. Conjugation and Hyperconjugation. We have seen that our nonempirical[7] wave functions, through their dipole moments and atomic charges, give a picture of the direction of charge transfer in good over-all agreement with experiment. We now consider briefly the importance of conjugation in this charge transfer by looking at appropriate π–π overlap populations. For all cases of trigonal carbons joined by "single" bonds,[47] we found π–π overlap populations of only ~0.10, as opposed to the value of 0.42 for the ethylene π bond. On the basis of these overlap populations we might expect valence structures of the type shown in Figure 2a to be present to a small but appreciable extent in our wave functions for vinyl- and phenyl-substituted carbonyl compounds. The distribution of π charges in these molecules, however, does not correspond to that in Figure 2a (see Appendix V). In addition, we notice that in acrolein and benzaldehyde, the σ system is responsible for a large portion of the dipole moment (Table IXB) and we discover from Table X that most of the charge donated to the carbonyl group by vinyl or phenyl groups is from the σ MO's. Hence we conclude that in assessing the electronic interactions of the vinyl and phenyl group with the carbonyl group, many valence structures other than ordinary conjugation between double bonds (Figure 2a) must be considered.

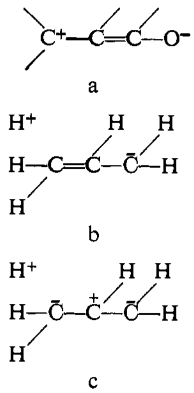

Figure 2. π-Electron valence structures: (a) valence structure for conjugated carbonyl group, (b) hyperconjugation in propylene, (c) dispersion-type ionic valence structure for propylene.

Turning now to the question of hyperconjugation, we find that in every case of an alkyl group bonded to a trigonal carbon, the overlap population between the 2pπ orbital of the trigonal carbon and the 2pπ orbital of the adjacent alkyl group carbon is slightly negative (*ca.* −0.01). Before discussing the implications of this failure to find evidence of hyperconjugation, we should point out that the proper value of $K_{2p\pi 2p\pi}$ for these interactions is perhaps somewhat uncertain. We have stressed that there are two distinct types of π–π interactions, with different values of $K_{2p\pi 2p\pi}$: that in ethane, where the 2p orbitals perpendicular to the C–C axis interact both with themselves and with hydrogens; and that in acetylene, where the 2pπ orbitals interact only with themselves (C_2H_4 and H_2CO have both types). Our assignment of the former value of $K_{2p\pi 2p\pi}$ to π–π interactions involving alkyl groups is at least self-consistent, since all the π–π overlap populations obtained are quite similar to the SCF ethane value (−0.005).[10a] Nevertheless, to obtain an upper limit

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(45) R. W. Kilb, C. C. Lin, and E. B. Wilson, *J. Chem. Phys.*, **26**, 1695 (1957).

(46) D. R. Lide and D. E. Mann, *ibid.*, **27**, 868 (1957).

(47) The term "single"bond refers to single bonds in principal valence bond structures, excluding the bonds in phenyl rings, naphthalene, azulene, and tropone.

to the amount of hyperconjugation, we performed some calculations assuming the other value of $K_{2p\pi 2p\pi}$. In a typical case we obtained a π–π overlap population for toluene of +0.056. Even this maximum estimate of hyperconjugation is only about 13% of the π–π overlap population in ethylene, as opposed to previous semiempirical work where a positive ethane π–π bond order (6% of the ethylene value) was obtained (Mulliken, *et al.*[36]), and where the toluene hyperconjugative bond order was 20% of the ethylene π–π bond order (Haya[36]).

We therefore conclude that hyperconjugation, if it exists at all in the ground states of the molecules studied, cannot be considered an important source of alkyl group charge-transfer effects. Indeed the π charges obtained for all our methyl-substituted unsaturated system (Appendix V) suggest strongly that more important than the valence structure in Figure 2b is what Mulliken has called the dispersion-type ionic structure (Figure 2c).[48] Such a structure offers an adequate explanation of the known direction of dipole moments in alkyl-substituted alkenes, alkynes, arenes, and carbonyls without invoking hyperconjugation (Figure 2b), and also without requiring actual donation of charge by the alkyl group. Thus our results, which are consistent with Dewar's claim that hyperconjugation is not necessary to account for the propylene dipole moment,[49] point to the importance of the polarizing effect of the alkyl group on the unsaturated residue, irrespective of whether or not electrons are donated.[50] In Tables VIII and X we have seen that alkyl groups *do* donate to the π orbitals. We recall, however, that the alkyl groups in toluene and ethylbenzene had net negative charges, although they were at the positive end of the dipole moments. In addition, the *ortho* and *para* positions in these molecules had net negative charges, in spite of the slight electron deficiency observed in the phenyl rings. Likewise in fulvene, the polarization of charge in the ring determined the dipole direction, despite a net negative charge on the methylene group. In short, we claim that the importance of polarization makes it impossible to infer the electron-donating or -accepting properties of alkyl groups, merely from a knowledge of dipole moment directions. Considering the methyl group in particular, we have found it to donate charge in varying degrees to unconjugated double bonds, while accepting charge from the phenyl ring. Of course, the latter situation could be expected to change in the presence of an electrophilic agent or other perturbing source.

VI. Lone Pairs and Nonbonding MO's

A number of authors have found the concept of the lone pair or nonbonded electron useful in interpreting spectra and ionization potentials of organic molecules containing heteroatoms.[51–53] It has been pointed out that discrepancies between free atom ionization potentials and "lone pair" ionization potentials in molecules do not necessarily rule out the existence of lone pairs, since electrostatic interactions (dipolar and charge transfer) can be invoked to account for some of these differences.[51] Absence of vibrational structure in some Rydberg series and in photoionization has been cited as evidence for the presence of nonbonding electrons.[30,51] Accordingly, starting with Mulliken's MO studies, semiempirical treatments of spectra involving heteroatoms have generally assumed the existence of a nonbonded lone pair as one of the MO's; *e.g.*, Sidman's study of n → π^* transitions of carbonyls assumed the n level to be a pure oxygen 2p orbital (in the molecular plane, perpendicular to C–O bond) with an orbital energy equal to the first ionization potential of formaldehyde.[54] Calculations which do not assume the existence of lone pairs include Hoffmann's semiempirical results (with explicit inclusion of σ electrons) which implied appreciable delocalization of lone pairs in several aza aromatics,[55] and exact SCF LCAO calculations[10] on H_2CO, NH_3, CH_2NH, and HCN. Let us first consider carbonyl derivatives. We notice (Table XIC) that the highest occupied MO of the SCF H_2CO wave function is 72% localized (in terms of Mulliken point charges) on the oxygen, with some antibonding character. Our method allows us to examine the extent to which this partial lone pair is preserved in a large series of carbonyl derivatives. The constancy of intensity of n–π^* transitions suggests that the n orbital is not essentially altered when aliphatic substituents are added to the carbonyl group. Our criteria for studying this orbital will be its eigenvalue, overlap population, Mulliken charge distribution, and its centroid of charge. Table XIA and the first column of figures in Table III reveal that in all the monocarbonyls there is a level with eigenvalue between 11.0 and 9.5 ev, with a slightly antibonding overlap population of -0.10 ± 0.04, 68 ± 8% localized on the oxygen atom, and with a centroid lying roughly along the carbonyl bond, 32 to 82% of the way to the carbon. The variation in eigenvalue is generally consistent with corresponding changes in dipole moment and piling up of charge on the oxygen atom (see Table X). The increase in delocalization seems for the most part merely to reflect the increasing size of the molecule as substituents are added. We also find that the 2s orbital contributes negligibly to the lone-pair orbital, even when it is allowed by symmetry to mix with the 2p orbital. This apparently justifies using the notation $U \leftarrow A$ for all carbonyl n → π^* transitions, regardless of molecular symmetry.[56] The oxygen lone-pair density is always found to be in a 2p orbital in the plane of the molecule, pointing in a direction 90 ± 10° from the CO axis. In the case of the quinones we find that the highest two levels are mostly confined to the oxygens. Since these levels are not degenerate, molecular symmetry prevents "lone pairs" by requiring both oxygens to contribute equally in each eigenfunctions. This situation does not, of course, prevent one from forming localized MO's with an appropriate unitary transformation; it simply means that when these electrons in quinones are excited, the effect is predicted to be delocalized over both oxygens. The same considerations apply to the diazabenzenes below.[57] In Table XIA we have

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(48) R. S. Mulliken, *Tetrahedron*, **5**, 253 (1959).

(49) M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962, pp 71–76.

(50) Of course, the alkyl group is also polarized (see ref 35).

(51) R. S. Mulliken, *J. Chem. Phys.*, **3**, 564 (1935).

(52) H. L. McMurry, *ibid.*, **9**, 231, 241 (1941).

(53) M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950).

(54) J. Sidman, *J. Chem. Phys.*, **27**, 429.

(55) R. Hoffmann, *ibid.*, **40**, 2047.

(56) Platt's notation, *ibid.*, **18**, 1168 (1950); see also review article: J. Sidman, *Chem. Rev.*, **58**, 689 (1958).

(57) Our results are in conflict with a recent discussion of pyrazine spectra by M. F. A. El-Sayed and G. W. Robinson, *Mol. Phys.*, **4**,

Table XI. Lone Pairs[a]

	q_{2s}[b]	q_{2p}[c]	r, A[d]	OP[e]
A. Carbonyl Results				
H_2CO	...	1.537	0.394	−0.086
CH_3CHO	...	1.465	0.509	−0.100
$(CH_2{=}CH)CHO$ (*s-trans*)	...	1.415	0.591	−0.108
(*s-cis*)	...	1.484	0.452	−0.100
$CH_3CH{=}CHCHO$ *s-trans*	...	1.229	1.013	−0.061
s-cis	...	1.333	0.656	−0.062
C_6H_5CHO	...	1.277	0.828	−0.086
$(CH_3)_2CO$	...	1.410	0.546	−0.122
$CH_3(CH_2{=}CH)CO$ (*s-trans*)	...	1.364	0.638	−0.153
(*s-cis*)	...	1.395	0.538	−0.124
$CH_3(C_6H_5)CO$	...	1.228	0.785	−0.144
Tropone	...	1.271	0.762	−0.112
o-Benzoquinone[f]	...	1.300, 1.100	...	−0.160, −0.030
p-Benzoquinone[f]	...	1.367, 1.239	...	−0.036, −0.278
B. N-Heterocycle Results				
Pyridine	0.119	1.280	0.276	−0.179
Pyrazine[f]	0.093, 0.147	1.225, 1.704	...	−0.227, −0.120
Pyrimidine[f]	0.062, 0.205	1.569, 1.184	...	−0.154, −0.234
Pyridazine[f]	0.206, 0.072	1.457, 1.320	...	−0.427, +0.044
Pyrrole	...	0.710	1.365	+0.157
C. Exact SCF Results				
H_2CO[g]	0.000	1.432	0.488	−0.103
NH_3[h]	0.219	1.701	0.127	−0.104
CH_2NH[i]	0.232	1.284	0.257	−0.212
HCN[h]	0.590	1.137	0.086	−0.290
N(sp)[j]	1.0	1.0	0.196	...
N(sp^2)[j]	0.667	1.333	0.185	...
N(sp^3)[j]	0.500	1.500	0.170	...

[a] The quantities listed refer to those high-lying MO's which are appreciably localized on the heteroatoms: the second highest π level of pyrrole; otherwise, the highest σ level, or highest two σ levels for quinones and diazines. [b] Mulliken charge in heteroatom 2s orbital. [c] Mulliken charge in heteroatom 2p orbital. [d] Centroid of MO, with origin at heteroatom. This centroid is always on the side of the heteroatom toward the rest of the molecule (lying approximately along the bond to the carbon atom for all carbonyls and CH_2NH), except in NH_3 and HCN. [e] Total overlap population (see ref 37). [f] The double entries refer respectively to the highest and second-highest σ MO's. [g] Reference 10b. [h] Reference 10a. [i] Reference 10c. [j] Pure atomic hybrids, using Slater exponents, listed for comparison with molecular lone pairs.

accordingly presented for both MO's the total charge in the oxygen in-plane 2p orbitals and the total overlap population.

The SCF "lone pairs" in NH_3, CH_2NH, and HCN are respectively 96, 76, and 86% localized on nitrogen (Table XIC). For multiply bonded nitrogen, this level is appreciably antibonding. Table XIB shows that the CH_2NH n level is essentially preserved in pyridine. Of particular interest in the diazines is the large antibonding overlap population of the highest MO in pyridazine. Goodman emphasized this as a feature of all *o*-azabenzenes.[58] On the average, our results indicate only 5% contribution of the nitrogen 2s orbital to the charge in these azine MO's. This is somewhat deceptive, however, illustrating a situation where Mulliken's charges are probably not meaningful, indicated by the fact that the centroids of these MO's are poorly approximated by the point charges.[59] More significant is the fact that the 2s and 2p coefficients of these MO's are in a ratio of almost 1:2.

In conclusion, we find the "lone pair" to be a useful qualitative concept, in spite of the fact that accurate quantitative work should take account of the appreciable delocalization. The term "nonbonding" in this context is apparently a misnomer to varying degrees. We stress the fact that the partial lone pair of the carbonyl oxygen is relatively constant in its properties over the wide range of molecular environments studied here, while the nitrogen lone pair has less 2s participation than one would predict on the basis of sp^2 hybridization.

VII. Conclusion

We believe that the ability of our method to yield reasonable binding energies, to allow correlations and predictions with regard to ionization potentials, and to give a good over-all account of charge transfer, justifies further development of this approach to complex molecules. We emphasize that we have been able to deal with this wide variety of physical properties with a single set of parameters not obtained from experimental values of these properties, but from essentially *a priori* quantum mechanical considerations. The possibilities of bettering our agreement with experiment through improved calculations of matrix elements or empirical corrections to the basic theory are presently being considered. Our study of exact models has revealed significant features (particularly anisotropies of atoms in molecular environments and the importance of including all electrons) which may not be entirely new to theoretical physicists but which go generally unrecognized in many approximate MO methods now in general use. We have shown these features to exert a strong influence on calculated molecular properties.

Some important implications of our present work are that new justification for consideration of π electrons

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273 (1961), where the two n MO's were assumed to be degenerate and localized.

(58) L. Goodman, *J. Mol. Spectry.*, **6**, 109 (1961).

(59) See section VI of paper I.

only in unsaturated molecules is called for, and that hyperconjugation is not required to account for the dipole moments of alkyl-substituted unsaturated molecules. Furthermore, by calculating the expectation value for the dipole moment exactly, we have found that the usual procedure based on Mulliken point charges is not always reliable. We are currently investigating methods for obtaining approximate values of integrals which, together with our wave functions, will allow calculation of polarizability and spectral and magnetic properties.

Acknowledgment. We are grateful to William E. Palke for the use of his SCF wave functions and to Roald A. Hoffmann for many inspiring discussions. Financial assistance was provided by the Office of Naval Research.

Appendix I

Molecular Geometries. With the exception of the molecules discussed below, geometries are based on idealized bond angles of 109° 28′, 120°, and 180°, and bond distances listed in Table I. The latter agree with those compiled by Sutton[a] to within ±0.020 A or better. Unless noted otherwise, all saturated hydrocarbon molecules and substituents are in the completely staggered conformation. All *n*-butane fragments are in the *anti* or *trans* conformation except for isopentane, where one skew butane interaction is present, and the series, cyclohexane, adamantane, and congressane.[b] All atoms in a conjugated system are coplanar. All methyl groups attached to trigonal carbon have one hydrogen in the plane of the molecule, eclipsing the double bond in the case of vinyl and carbonyl groups and in dimethylfulvene. In *o*- and *m*-xylene the in-plane hydrogen of one methyl group is directed away from the other methyl group, while the methyl groups of *p*-xylene are related by inversion.

The bond lengths for fulvene,[c] dimethylfulvene,[c] azulene,[d] and naphthalene[e,f] are taken from experimental data averaged to yield respectively C_{2v}, C_{2v}, C_{2v}, and D_{2h} symmetry. Tropone is taken as a regular heptagon of edge 1.41 A with a CO distance of 1.260 A.[g] The "single" and "double" bonds of *o*- and *p*-quinone are assigned lengths of 1.490 and 1.320 A, respectively.[h] Bond lengths for pyrrole,[i] pyridine,[j] and pyrazine[k] are taken directly from the literature. Bond lengths for several derivatives of 1,3-pyrimidine have been averaged to yield N_1–C_2 = 1.320, N_1–C_6 = 1.340, C_4–C_5 = 1.370 A.[l] For pyridazine, the N–N distance of 1.320 A is taken from *s*-tetrazine,[m] while the C–C and C–N distances are taken as 1.400 and 1.340 A. The C–H (trigonal) distance for all molecules mentioned in this paragraph are given the benzene value of 1.084 A, while the pyrrole N–H distance is 1.000 A.

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[a] L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958. Also see the Supplement to the above: Special Publication No. 18. [b] See footnote *j* of Table III, [c] N. Norman and B. Post, *Acta Cryst.*, **14**, 503 (1961). [d] J. M. Robertson, H. M. M. Shearer, G. A. Sim, and D. G. Watson, *ibid.*, **15**, 1. (1962). [e] L. E. Sutton, footnote *a*: [f] p M154 S; [g] p M138 S; [h] p M194; [i] p M108 S; [j] p M120 S; [k] p M104 S; [l] pp M160, M164, M181, and M107 S; [m] p M75 S.

Appendix II

Approximate Molecular Energies (au)[a]

	$-{}^1/_2\sum_i \epsilon_i{}^m$	$-A$	$-A_{\text{exptl}}$	$-E_{\text{tot}}$	Kinetic energy
	A. Hydrocarbons: Saturated				
CH_4	13.925	0.544	0.625	40.166	39.893
C_2H_6 (θ = 60°)	27.181	0.919	1.060	79.164	78.463
(θ = 0°)	27.175	0.913	...	79.158	78.503
C_3H_8	40.397	1.254	1.500	118.122	117.177
n-C_4H_{10}	53.627	1.604	1.941	157.093	155.852
i-C_4H_{10}	53.623	1.600	1.944	157.089	155.866
n-C_5H_{12}	66.858	1.954	2.382	196.066	194.521
i-C_5H_{12}	66.841	1.937	2.385	196.049	194.590
neo-C_5H_{12}	66.843	1.939	2.389	196.051	194.577
n-C_6H_{14}	80.088	2.303	2.824	235.037	233.190
n-C_7H_{16}	93.318	2.652	3.263	274.008	271.856
n-C_8H_{18}	106.547	3.001	3.704	312.979	310.517
Cyclohexane	79.399	2.114	2.641	233.848	231.908
Adamantane	130.914	3.106	...	387.329	384.142
		Unsaturated			
C_2H_2	25.859	0.597	0.618	76.842	76.382
$CH_3C{\equiv}CH$	39.059	0.917	1.066	115.783	114.912
C_2H_4	26.496	0.734	0.846	77.979	77.716
$CH_3CH{=}CH_2$	39.712	1.070	1.291	116.937	116.237
s-trans-butadiene	52.343	1.320	1.527	154.809	153.829
s-cis-butadiene	52.320	1.297		154.786	153.871
Fulvene	77.283	1.499	...	230.232	229.155
Dimethylfulvene	103.707	2.161	...	308.139	306.345
Azulene	128.176	2.366	3.243	382.586	380.475
C_6H_6	77.411	1.627	2.077	230.360	228.703
$CH_3C_6H_5$ (θ = 0°)	90.621	1.955	2.522	269.311	267.377
(θ = −30°)	90.621	1.955		269.311	267.376
$C_2H_5C_6H_5$ (θ = 90°)	103.835	2.289	2.962	308.267	306.030
(θ = 0°)	103.813	2.267		308.245	306.123

i-$C_3H_8C_6H_5$ ($\theta = 60°$)	117.037	2.610	3.405	347.211	344.755
($\theta = 30°$)	117.028	2.601		347.202	344.791
($\theta = 0°$)	117.017	2.590		347.191	344.826
($\theta = -30°$)	117.011	2.584		347.185	344.865
t-$C_4H_9C_6H_5$ ($\theta = 0°$)	130.217	2.909	...	386.132	383.559
($\theta = -30°$)	130.215	2.907		386.130	383.578
o-$(CH_3)_2C_6H_4$	103.824	2.277	2.967	308.256	306.064
m-$(CH_3)_2C_6H_4$	103.831	2.285	2.967	308.263	306.045
p-$(CH_3)_2C_6H_4$	103.830	2.284	2.967	308.262	306.047
Naphthalene	128.217	2.409	3.295	382.632	380.287
		B. Carbonyls[b]			
H_2CO	36.427	0.776	0.573	113.939	114.056
CH_3CHO	49.621	1.090	1.027	152.875	152.781
s-$trans$-$(CH_2{=}CH)CHO$	62.180	1.268	...	190.675	190.617
s-cis-$(CH_2{=}CH)CHO$	62.174	1.262		190.669	190.583
s-$trans$-$(CH_3{-}CH{=}CH)CHO$	75.397	1.604		229.634	229.209
s-cis-$(CH_3{-}CH{=}CH)CHO$	75.392	1.599		229.629	229.174
C_6H_5CHO	113.083	2.147	2.489	343.044	341.794
$(CH_3)_2CO$	62.803	1.391	1.481	191.798	191.567
s-$trans$-$CH_3(CH_2{=}CH)CO$	75.362	1.569	...	229.599	229.410
s-cis-$CH_3(CH_2{=}CH)CO$	75.364	1.571		229.601	229.386
$CH_3(C_6H_5)CO$	126.254	2.438	2.947	381.957	380.618
Tropone	112.964	2.029	...	342.925	342.539
o-Benzoquinone	122.867	2.043	...	378.857	378.944
p-Benzoquinone	122.872	2.048	...	378.862	378.961
		C. Heterocycles[b]			
Pyrrole	69.151	1.136	...	208.395	206.791
Pyridine	81.722	1.327	1.905	246.207	244.996
Pyrazine	86.080	1.074	1.708	262.101	261.014
Pyrimidine	85.955	0.949	1.708	261.976	261.383
Pyridazine	86.065	1.059	1.676	262.086	260.990

[a] The quantities $\sum_i \epsilon_i^{\mathrm{m}}$, A, and E_{tot} are defined in section IIIA. The reference ground-state atomic wave functions were taken from E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963). Conformational differences are indicated by θ, the angle of rotation from the eclipsed conformation, defined in Appendix IV. Values of A_{exptl} were obtained for 0°K from $\Delta H_f°$ values listed by F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel in "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, and from heats of atomization given by T. L. Cottrell in "The Strength of Chemical Bonds," 2nd Ed., Butterworth & Co., Ltd., London, 1958. A_{exptl} values for naphthalene and azulene were taken from E. Heilbronner in "Non-Benzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959. [b] For the carbonyls and heterocycles A_{exptl} could be obtained only for 25° using enthalpies from Cottrell, footnote *a*, and from J. H. S. Green, *Quart. Rev.* (London), **15**, 125 (1961), and J. Tjebbes, *Acta Chem. Scand.*, **16**, 916 (1962).

Appendix III

Values[a] of $\Delta = \left[\sum_i (E_i^{\mathrm{m}} - E_i^{\mathrm{a}})/2\right] + N$

Molecule	Δ, au	Molecule	Δ, au	Molecule	Δ, au
CH_4	−0.044	C_2H_6	−0.058	BH_3	0.011
C_2H_2	0.183	H_2CO	0.313	B_2H_6	0.326
C_2H_4	0.102	HCN	0.388	NH_3	−0.074

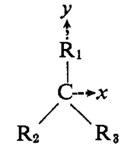
[a] Δ is calculated in terms of quantities defined in section IIIA and obtained from the SCF molecular calculations of ref 10 and from Clementi's optimized minimum basis set atomic wave functions. The sum is taken over the electrons of the molecule and the reference ground-state atoms.

Appendix IV

Dipole Moment Directions

Below we list the components of our calculated dipole moments (in Debye units) for those molecules where the dipole direction is not determined by molecular symmetry. A positive sign implies a dipole component pointing toward the negative end of the given axis, assuming the dipole is defined to point from positive charge to negative charge.

A. Alkylbenzenes, $(C_6H_5)CR_1R_2R_3$

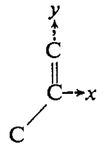


The phenyl group lies in the *yz* plane, at positive *z* relative to the alkyl group. The various conformations are obtained from the above eclipsed conformation by rotating the substituent through the angle θ (positive θ corresponds to clockwise rotation in the *xy* plane).

	θ, deg	μ_x	μ_y	μ_z
$CH_3C_6H_5$ ($R_1 = R_2 = R_3 = H$)	0	0	−0.086	−0.752
	−30	+0.091	0	−0.754

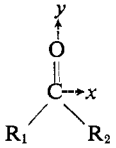
$C_2H_5C_6H_5$ (R_1 = CH_3; R_2 = R_3 = H)	+90	+0.097	0	−0.626
	0	0	+0.077	−0.703
i-$C_3H_7C_6H_5$ (R_1 = R_2 = CH_3; R_3 = H)	60	0	+0.363	−0.480
	30	−0.197	+0.264	−0.524
	0	−0.115	+0.061	−0.561
	−30	+0.005	0	−0.523
t-$C_4H_9C_6H_5$ (R_1 = R_2 = R_3 = CH_3)	0	0	−0.080	−0.571
	−30	+0.155	0	−0.567

B. Propylene



μ_x	μ_y	μ_z
−0.343	−0.767	0

C. Carbonyls



R_1	R_2	μ_x	μ_y	μ_z
CH_3	H	−0.368	−1.892	0
(*s-trans*)CH_2=CH	H	−0.161	−1.563	0
(*s-cis*)CH_2=CH	H	−0.089	−1.655	0
(*s-trans*)CH_3—CH=CH	H	−0.645	−2.636	0
(*s-cis*)CH_3—CH=CH	H	−1.101	−1.811	0
C_6H_5	H	−0.155	−1.761	0
(*s-trans*)CH_2=CH	CH_3	+0.251	−2.098	0
(*s-cis*)CH_2=CH	CH_3	+0.224	−2.325	0
C_6H_5	CH_3	+0.244	−2.356	0

Appendix V

Selected Values of Net Atomic Charges and Overlap Populations

We present net atomic charges and overlap populations for all the molecules discussed in sections II–VI. Quantities for π density only are in parentheses (core charges are defined in section V). Similar values have been averaged (indicated by ±). The nomenclature specifies the numbering system.

Net Atomic Charges	
A. Hydrogen atoms	
1. Saturated hydrocarbons and alkyl substituents	
CH_4	0.12
Primary hydrogens	0.07 ± 0.02
Secondary hydrogens	0.02 ± 0.02
Tertiary hydrogens	−0.03 ± 0.02
2. Unsaturated molecules	
Alkyne hydrogen	0.21 ± 0.01
Alkene hydrogen (=CH_2) and H_2CO	0.13 ± 0.02
Alkene hydrogen (=CH), azulene, tropone	
C_7-ring hydrogens, quinone hydrogens, and aldehyde hydrogens (except H_2CO)	0.07 ± 0.02
Naphthalene, phenyl, and pyrrole (NH) hydrogens	0.04 ± 0.01
Azabenzene hydrogens	0.02 ± 0.02
C_5-ring hydrogens in azulene, fulvene, and dimethylfulvene	0.01 ± 0.01
B. Carbon, nitrogen and oxygen atoms	
1. Saturated hydrocarbons	
Methane	C1, −0.49
Ethane	C1, −0.19
n-Propane	C1, −0.25; C2, −0.05
n-Butane	C1, −0.26; C2, 0.01
2-Methylpropane	C1, −0.28; C2, 0.30
n-Pentane	C1, −0.26; C2, 0.00; C3, −0.03
2-Methylbutane	C1, −0.28; C2, 0.27; C3, −0.01; C4, −0.26
2,2-Dimethylpropane	C1, −0.29; C2, 0.54
n-Hexane	C1, −0.26; C2, 0.00; C3, −0.04
n-Heptane	C1, −0.26; C2, 0.00; C3, −0.04; C4, −0.05
n-Octane	C1, −0.26; C2, 0.00; C3, −0.04; C4, −0.05

Cyclohexane	C1, −0.03
Adamantane	(CH_2), −0.09 (CH), +0.18
2. Unsaturated hydrocarbons	
Acetylene	C1, −0.22 (0.00)
1-Propyne	C1, −0.57 (−0.18); C2, 0.22 (0.10); C3, −0.04 (−0.04)
Ethylene	C1, −0.30 (0.00)
1-Propylene	C1, −0.48 (−0.10); C2, 0.04 (0.06); C3, −0.12 (−0.02)
1,3-Butadiene	C1, −0.42 (−0.05); C2, 0.10 (0.05)
5-Methylene-1,3-cyclopentadiene (fulvene)	C1, −0.15 (−0.08); C2, −0.02 (−0.01); C5, 0.52 (0.08); C6 (CH_2=), −0.44 (0.10)
5-Isopropylidene-1,3-cyclopentadiene (dimethylfulvene)	C1, −0.17 (−0.09); C2, −0.07 (−0.06); C5, 0.29 (−0.03); C6, 0.22 (0.23); C7 (CH_3), −0.22 (−0.04)
Decadehydrobicyclo[5.3.0]-decane (azulene)	C1, 0.27 (0.05); C2, −0.10 (0.08); C3, −0.09 (0.01); C4, −0.01 (0.06); C9, −0.01 (−0.00); C10, −0.29 (−0.17)
Benzene	C1, −0.04 (0.00)
1-Methylbenzene	C1, 0.25 (0.05); C2, −0.11 (−0.03); C3, −0.05 (0.00); C4, −0.06 (−0.02); C7 (CH_3), −0.23 (−0.03)
1-Ethylbenzene	C1, 0.22 (0.06 ± 0.01); C2, −0.13 ± 0.01 (−0.03); C3, −0.05 (0.00); C4, −0.06 (−0.02); C7 (CH_2), 0.02 ± 0.01; C8 (CH_3), −0.23 ± 0.01
1-Isopropylbenzene	C1, 0.19 ± 0.01 (0.06 ± 0.01); C2, −0.13 ± 0.02 (−0.02 ± 0.01); C3, −0.05 (0.0); C4, −0.06 (−0.02); C7 (CH), 0.25; C8 (CH_3), −0.28 ± 0.01
1-*t*-Butylbenzene	C1, 0.17 (0.06); C2, −0.14 ± 0.02 (−0.02); C3, −0.06 (0.00); C4, −0.06 (−0.02); C7, 0.46 ± 0.01; C8 (CH_3), −0.30 ± 0.01
1,2-Dimethylbenzene	C1, 0.17 (0.02); C3, −0.12 (−0.03); C4, −0.07 (−0.02); C7 (CH_3), −0.23 (−0.03)
1,3-Dimethylbenzene	C1, 0.24 (0.05); C2, −0.19 (−0.05); C4, −0.13 (−0.05); C5, −0.06 (0.01); C7 (CH_3), −0.23 (−0.03)
1,4-Dimethylbenzene	C1, 0.23 (0.03); C2, −0.12 (−0.02); C7 (CH_3), −0.23 (−0.03)
Decadehydrobicyclo[4.4.0]-decane (naphthalene)	C1, 0.24 (0.04); C2, −0.13 (−0.01); C3, −0.05 (−0.01)
3. Carbonyls (see also Table X)	
Methanal	C1, −0.21 (−0.03)
Ethanal	C1, +0.02 (+0.01); C2, −0.08 (−0.02)
2-Propenal	C1, 0.08 (0.02 ± 0.01); C2, 0.14 ± 0.01 (0.06); C3, −0.44 ± 0.01 (−0.03)
2-Butenal	C1, 0.07 (0.02), C2, 0.01 (−0.02); C3, −0.10 ± 0.01 (0.04); C4, −0.15 (−0.02)
2-Propanone	C1, −0.12 (−0.03); C2, 0.23 (0.05)
1-Buten-3-one	C1, −0.46 ± 0.01 (−0.03); C2, 0.10 (0.06); C3, 0.28 ± 0.01 (0.05); C4, −0.13 ± 0.01 (−0.03)
1-Formylbenzene	C1, 0.36 (0.05); C2, −0.11 (0.00); C3, −0.05 (0.00); C4, −0.04 (0.00); C7 (C=0), −0.01 (0.01)
1-Acetylbenzene	C1, 0.31 (0.05); C2, −0.12 (0.00); C3, −0.05 (0.00); C4, −0.04 (0.00); C7 (C=O), 0.20 (0.05); C8 (CH_3), −0.13 (−0.03)
1,2-Benzoquinone	C1, 0.31 (0.04); C3, −0.04 (0.00); C4, −0.05 (0.03); O1, −0.32 (−0.07)
1,4-Benzoquinone	C1, 0.28 (0.04); C2, −0.03 (0.02); O1, −0.32 (−0.08)
1,3,5-Cycloheptatrien-7-one	C1, −0.02 (0.06); C2, −0.06 (0.04); C3, −0.03 (0.04); C7, 0.38 (0.07); O1, −0.59 (−0.35)
4. N-Heterocycles	
Pyrrole	N1, 0.49 (0.56); C2, −0.06 (−0.10); C3, −0.20 (−0.18)
1-Azabenzene	N1, −0.20 (−0.01); C2, 0.11 (0.01); C3, −0.08 (−0.02); C4, −0.03 (0.02)
1,2-Diazabenzene	N1, −0.09 (−0.01); C3, −0.06 (0.01); C4, 0.08 (0.00)
1,3-Diazabenzene	N1, −0.25 (−0.02); C2, 0.30 (0.01); C4, 0.14 (0.03); C5, −0.09 (−0.03)
1,4-Diazabenzene	N1, −0.19 (0.00); C2, 0.08 (0.00)

Overlap Populations

A. With hydrogen atom	
Unsaturated hydrocarbons (CH)	0.78 ± 0.02
Alkanes (CH)	0.76 ± 0.02
Aldehyde (C–H)	0.74 ± 0.01
Pyrrole (NH)	0.72

B. Between carbon atoms 1. Molecules with "localized" bonds	"Single" bonds	"Double" or "triple" bonds
C (tetrahedral)–C (tetrahedral)	0.79 ± 0.01	...
Acetylene	...	1.89 (1.00)
Propyne	0.85 (−0.01)	1.87 (1.02)
Ethylene	...	1.18 (0.42)
Propylene	0.83 (−0.01)	1.20 (0.42)
C (tetrahedral)–C (trigonal) (other than propylene[a])	0.79 ± 0.01 (−0.01)	...
s-trans-Butadiene	0.95 (0.10)	1.13 (0.39)
s-cis-Butadiene	0.92 (0.09)	1.16 (0.39)
Dimethylfulvene ($(CH_3)_2C{=}C<$)	...	1.13 (0.33)
Fulvene, and other bonds in dimethylfulvene	0.94 ± 0.02 (0.12 ± 0.02)	1.07 ± 0.01 (0.34 ± 0.01)

Aliphatic α,β-unsaturated carbonyls and benzoquinones (C═C—C═O), and the C_6H_5—C═O(R) bond (R = H, CH_3)	0.89 ± 0.02 (0.09 ± 0.01)	1.15 ± 0.03 (0.38)
1,2-Benzoquinone		
C_1—C_2 bond	0.85 (0.06)	...
C_3—C_4 bond	0.93 (0.11)	...
2. Aromatic molecules (same numbering as above); all π–π overlap populations for phenyl rings are 0.240 ± 0.005 unless noted otherwise.		
1-Alkylbenzene	C1–C2, 1.07 ± 0.01; C2–C3, 1.04 ± 0.01; C3–C4, 1.06	
1,2-Dimethylbenzene	C1–C2, 1.08; C2–C3, 1.07; C3–C4, 1.04; C4–C5, 1.06	
1,3-Dimethylbenzene	C1–C2, 1.07; C3–C4, 1.08; C4–C5, 1.04	
1,4-Dimethylbenzene	C1–C2, 1.07; C2–C3, 1.03	
1-Formyl- or acetylbenzene	C1–C2, 1.05 (0.22); C2–C3, 1.04; C3–C4, 1.05	
Naphthalene	C1–C2, 1.00 (0.18); C2–C3, 1.07 (0.29); C1–C6, 1.04 (0.18); C3–C4, 1.01 (0.19)	
Azulene	C1–C7, 0.94 (0.09); C1–C10, 1.00 (0.21); C1–C2, 1.06 (0.22); C2–C3, 1.02 (0.24); C3–C4, 1.04 (0.23); C9–C10, 1.00 (0.23)	
Tropone	C1–C7, 0.95 (0.12); C1–C2, 1.08 (0.29); C2–C3, 0.98 (0.17); C3–C4, 1.09 (0.28)	
C. Carbon bonded to nitrogen and oxygen		
Pyrrole	0.98 (0.17)	
Azabenzenes	0.96 ± 0.01 (0.22 ± 0.01)	
Tropone	0.75 (0.25)	
Benzoquinones	0.79 (0.30)	
Other carbonyls	0.83 ± 0.03 (0.33 ± 0.02)	
D. Nitrogen bonded to nitrogen		
Pyridazine	0.89 (0.18)	

[a] Propylene is an exception because of its shorter bond length (see Table I).

Molecular SCF Calculations on CH_4, C_2H_2, C_2H_4, C_2H_6, BH_3, B_2H_6, NH_3, and HCN

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Abstract: Molecular self-consistent-field calculations with the use of accurate values of all molecular integrals for a minimum basis set have been made for the molecules CH_4, C_2H_2, C_2H_4, C_2H_6, BH_3, B_2H_6, NH_3, and HCN. The SCF wave function, the Hamiltonian matrix, and a population analysis are given for each molecule. Slater exponents are used except for the choice of 1.2 for the exponent of hydrogen.

The self-consistent-field (SCF) method based upon linear combinations of atomic orbitals (LCAO) for molecules[1] is likely to give a good account of those ground-state properties which are not strongly dependent upon electron correlation. Pending development of general molecular integral programs, the level of complexity of ethane has been explored[2] with the use of a minimum basis set of Slater atomic orbitals on each center. We report here SCF calculations on the ground states of a number of closely related molecules in order to provide as accurate wave functions as can be found with the use of a minimum basis set and accurate (we hope, and indeed expect) values of all molecular integrals. A consistent set of orbital exponents (Slater values for B, C, and N and 1.2 for H) also allows a comparison of systematic properties (*e.g.*, energy, charge transfer, and Mulliken overlap population) of these ground states. In addition, the Hamiltonian matrices from these SCF results have been employed to obtain atomic parameters for use in the nonempirical molecular orbital theory described in a preliminary communication[3] and in the three preceding papers.[4–6]

The exponents for Slater orbitals for B, C, and N were taken from Slater's rules,[7] rather than from the "best atom" values, because these rules give values which are closer to optimized exponents in B_2H_6,[3] in BH_3,[8] in CH_4,[9] and in many diatomic molecules[10] of the first row of the periodic table. In the same studies[3,8–10] the orbital exponents of 1.2 on H produced significantly lower total energies than did the value of 1.0 for H. Explicitly, these exponents are then 1.2 for 1s of H, 4.7

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