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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(1) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

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

(3) M. D. Newton, F. P. Boer, W. E. Palke, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **53**, 1089 (1965).

(4) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2353 (1966).

(5) F. P. Boer, M. D. Newton, and W. N. Lipscomb, *ibid.*, **88**, 2361 (1966).

(6) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *ibid.*, **88**, 2367 (1966).

(7) C. A. Coulson, "Valence," 2nd ed, Oxford University Press, London, 1961, p 40.

(8) W. E. Palke and W. N. Lipscomb, to be published.

(9) R. M. Pitzer, to be published (personal communication).

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

Table I. Wave Function of Methane

MO	Orbital energy	Coefficients								
		H1	H2	H3	H4	1sC	2sC	$2p_zC$	$2p_xC$	$2p_yC$
$1a_1$	−11.2714	0.0057	0.0057	0.0057	0.0057	−0.9953	−0.0275	0	0	0
$2a_1$	−0.9320	0.1590	0.1590	0.1590	0.1590	−0.2012	0.6644	0	0	0
$1t_{2z}$	−0.5418	0.2850	−0.2850	−0.2850	0.2850	0	0	0.5943	0	0
$1t_{2x}$	−0.5418	0.2850	0.2850	−0.2850	−0.2850	0	0	0	0.5943	0
$1t_{2y}$	−0.5418	0.2850	−0.2850	0.2850	−0.2850	0	0	0	0	0.5943
$2t_{2z}$	0.6441	0.6472	−0.6472	−0.6472	0.6472	0	0	−1.1316	0	0
$2t_{2x}$	0.6441	0.6472	0.6472	−0.6472	−0.6472	0	0	0	−1.1316	0
$2t_{2y}$	0.6441	0.6472	−0.6472	0.6472	−0.6472	0	0	0	0	−1.1316
$3a_1$	0.6887	0.7108	0.7108	0.7108	0.7108	0.2049	−1.7253	0	0	0
	Electronic energy		−53.5059	Kinetic energy 39.9045						
	Nuclear repulsion		13.3918							
	Total energy		−40.1141							

Table II. Population Analysis for Methane

Orbital	Population	Orbital	Population
H	0.867	$C2p_z$	1.088
C1s	1.996	$C2p_x$	1.088
C2s	1.274	$C2p_y$	1.088

Table III. Hamiltonian Matrix of CH_4[a]

H1	H2	H3	H4	C1s	C2s	$C2p_z$	$C2p_x$	$C2p_y$
−0.507	−0.274	−0.274	−0.274	−0.787	−0.730	−0.253	−0.253	−0.253
−0.274	−0.507	−0.274	−0.274	−0.787	−0.730	0.253	−0.253	0.253
−0.274	−0.274	−0.507	−0.274	−0.787	−0.730	0.253	0.253	−0.253
−0.274	−0.274	−0.274	−0.507	−0.787	−0.730	−0.253	0.253	0.253
−0.787	−0.787	−0.787	−0.787	−11.268	−2.640	0	0	0
−0.730	−0.730	−0.730	−0.730	−2.640	−1.432	0	0	0
−0.253	0.253	0.253	−0.253	0	0	−0.349	0	0
−0.253	−0.253	0.253	0.253	0	0	0	−0.349	0
−0.253	0.253	−0.253	0.253	0	0	0	0	−0.349

[a] All the Hamiltonian matrices are given as square matrices with the rows in the same order as the columns. The labels on the rows are omitted.

for 1s of B, 1.3 for 2s and 2p of B, 5.7 for 1s of C, 1.625 for 2s and 2p of C, 6.7 for 1s of N, and 1.95 for 2s and 2p of N. Atomic units of distance, a = 0.529172 A, and of energy, $E = 2R$ = 27.2098 ev, have been used throughout this study.

Procedure and Results

Computer Programs. Most of the required molecular integrals were computed with the use of programs based upon ζ-function methods.[11] Some of these programs were written at the Solid State and Molecular Theory Group at MIT, while others were developed here in conjunction with the MIT group as described earlier.[2,12] Four-center integrals over two p orbitals were computed from Shavitt's program[13] which employs the Gaussian transform procedure developed by Shavitt, Kern, and Karplus.[14] Control programs have now been written to produce these integrals in an optimum order, and to transform from the coordinates in which they are computed to the coordinate system of the molecule. Hence, no hand manipulation of integrals is required as the complete list is written onto magnetic tape.

All integrals have been computed to an accuracy of five or more decimal places. In checking this over-all program, we have reproduced McLean's results[15] on acetylene, Merrifield's results[16] on water, and the ethane calculation[2] all to four decimal places or better. Also we have reproduced Foster and Boys' results[17] for the energy to three decimal places and the molecular orbital coefficients to two decimal places on formaldehyde, for which integrals were believed to be good only to ±0.002. Several of Ransil's diatomic calculations[18] have been reproduced, and the earlier calculations for hydrogen cyanide[19] and for ethylene[20] (from a Gaussian basis) seem quite reasonable in comparison with our results. Thus, we feel that the programs are working correctly.

Methane. Atomic coordinates for H_1 at aaa, H_2 at $a\bar{a}\bar{a}$, H_3 at $\bar{a}a\bar{a}$, and H_4 at $\bar{a}\bar{a}a$, where a = 1.1930942 au, were obtained by inscribing the tetrahedral molecule inside a cube of side $2a$ and scaling[21] with the use of the

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(11) M. P. Barnett, "Methods of Computational Physics," Vol. II, Academic Press Inc., New York, N. Y., 1963, p 95; also M. P. Barnett and C. A. Coulson, *Phil. Trans. Roy. Soc.* (London), **243**, 221 (1951).

(12) Several of these programs have been submitted to the Quantum Chemistry Program Exchange at the University of Indiana.

(13) I. Shavitt, "Methods in Computational Physics," Vol. II, Academic Press Inc., New York, N. Y., 1963, p 1.

(14) I. Shavitt and M. Karplus, *J. Chem. Phys.*, **36**, 550 (1962); M. Karplus and I. Shavitt, *ibid.*, **38**, 1256 (1963); I. Shavitt and M. Karplus, *ibid.*, **43**, 398 (1965); C. W. Kern and M. Karplus, *ibid.*, **43**, 415 (1965).

(15) A. D. McLean, *ibid.*, **32**, 1595 (1960).

(16) D. Merrifield, personal communication of unpublished results.

(17) (a) J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 303 (1960). (b) P. L. Goodfriend, F. W. Birss, and A. B. F. Duncan, *ibid.*, **32**, 307 (1960), have also produced results for formaldehyde, but our recalculation of this function has yielded somewhat different results (M. Newton and W. E. Palke, to be published).

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

(19) A. D. McLean, *J. Chem. Phys.*, **37**, 627 (1962).

(20) J. W. Moscowitz, *ibid.*, **43**, 60 (1965).

(21) In order to permit detailed future checks on our results, a number of molecular parameters, particularly input geometrical coordinates, are given to a number of decimal places far beyond experimental significance.

Table IV. Wave Function of Acetylene

MO	Orbital energy	H1	H2	1sC1	2sC1	$2p_zC1$	$2p_xC1$	$2p_yC1$	1sC2	2sC2	$2p_zC2$	$2p_xC2$	$2p_yC2$
		Coefficients											
$1\sigma_g$	−11.2978	−0.0030	−0.0030	0.7041	0.0111	−0.0005	0	0	0.7041	0.0111	0.0005	0	0
$1\sigma_u$	−11.2951	0.0032	−0.0032	−0.7044	−0.0223	−0.0051	0	0	0.7044	0.0223	−0.0051	0	0
$2\sigma_g$	−1.0048	−0.1141	−0.1141	0.1744	−0.4754	−0.1758	0	0	0.1744	−0.4754	0.1758	0	0
$2\sigma_u$	−0.7513	−0.3070	0.3070	0.1125	−0.3444	0.2932	0	0	−0.1125	0.3444	0.2932	0	0
$3\sigma_g$	−0.6563	−0.3167	−0.3167	−0.0011	−0.0894	0.4645	0	0	−0.0011	−0.0894	−0.4645	0	0
$1\pi_{ux}$	−0.4056	0	0	0	0	0	0.6122	0	0	0	0	0.6122	0
$1\pi_{uy}$	−0.4056	0	0	0	0	0	0	0.6122	0	0	0	0	0.6122
$1\pi_{gx}$	0.3058	0	0	0	0	0	0.8664	0	0	0	0	−0.8664	0
$1\pi_{gy}$	0.3058	0	0	0	0	0	0	0.8664	0	0	0	0	−0.8664
$3\sigma_u$	0.4758	−0.8196	0.8196	−0.1431	1.2150	0.0040	0	0	0.1431	−1.2150	0.0040	0	0
$4\sigma_g$	0.6541	0.9987	0.9987	0.0625	−0.7283	0.6801	0	0	0.0625	−0.7283	−0.6801	0	0
$4\sigma_u$	1.3426	−0.6147	0.6147	0.0508	−1.1567	−1.6009	0	0	−0.0508	1.1567	−1.6009	0	0

Electronic energy	−101.3559	Kinetic energy 76.3161
Nuclear repulsion	24.7394	
Total energy	−76.6165	

equilibrium C–H bond distance.[22] The wave function and energies are shown in Table I, the population analysis in Table II, and the SCF Hamiltonian matrix in Table III. We were unable to reproduce Sinai's results,[23] but we did obtain with the use of his parameters (C–H = 2 au and exponent 1.0 for H) a molecular energy of −40.0444 au, which has independently been obtained by Pitzer.[24] Our results yield a charge of +0.113 on each H, and a C–H overlap population of 0.780. The wave function and energies compare well with results obtained by Pitzer,[24] who found optimum exponents of 2s and 2p of C to be 1.76. Comparison of our results with those of Woznick[25] is reasonable, but more complex; he used a combination of three 1s functions with different exponents for 1s of C, but our H exponent is more nearly optimal than is his choice of 1.0 or 1.5 in his "minimal representation." Also his choices of 1.5525 for 2s of C and 1.5793 for 2p of C are not as close to the optimal value as our Slater exponent of 1.625. Hence, for the most nearly comparable calculations, our energy is lower than those (−40.001 to −40.073 au) for his minimal representation, but Woznick's calculations with a larger basis set gave energies as low as −40.181 au, which is a considerable further improvement over our results.

Acetylene. Coordinates of the ground-state equilibrium distances[26] are z = 0 for C1, 2.281 for C2, −2.002 for H1, and 4.283 for H2. Results are given in Table IV for wave function and energy, in Table V for the population analysis, and in Table VI for the SCF Hamiltonian matrix. The resulting charge on H is +0.188, and overlap populations are 0.820 for C–H, 0.874 for C–C_σ, and 1.001 for C–C_π. Values from McLean's "best atom" calculation[27] are +0.213 for the charge of H, and 0.824, 0.892, and 1.051 for the C–H, C–C_σ, and C–C_π overlap populations, respectively. A calculation by Moscowitz,[20] who used an extended set of Gaussian functions, yields a charge of +0.205 on H, and total energy of −76.741 au, which is lower than our value (−76.6165 au) from a minimum basis set of Slater orbitals.

Table V. Population Analysis for Acetylene

Orbital	Population	Orbital	Population
H	0.812	$C2p_z$	1.086
C1s	1.997	$C2p_x$	1.0
C2s	1.105	$C2p_y$	1.0

Ethylene. Coordinates for the equilibrium geometry[22] of the ground state are given in Table VII, wave function and energies in Table VIII, population analysis in Table X, and the SCF Hamiltonian matrix in Table IX. The charge on H is +0.140, which is to be compared to the charge of +0.180 obtained by Moscowitz.[20] We obtain overlap populations of 0.812 for C–H, 0.791 for C–C_σ, and 0.420 for C–C_π.

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(22) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p 439.

(23) J. J. Sinai, *J. Chem. Phys.*, **39**, 1575 (1963).

(24) R. M. Pitzer, personal communication of unpublished results.

(25) B. J. Woznick, *J. Chem. Phys.*, **40**, 2860 (1964).

(26) G. Herzberg, ref 22, p 398.

(27) A. D. McLean, B. J. Ransil, and R. S. Mulliken, *J. Chem. Phys.*, **32**, 1873 (1960).

Table VI. Hamiltonian Matrix of C_2H_2

H1	H2	1C1s	1C2s	1C2p_z	1C2p_x	1C2p_y	2C1s	2C2s	2C2p_z	2C2p_x	2C2p_y
−0.564	−0.032	−0.848	−0.771	0.436	0	0	−0.059	−0.203	0.251	0	0
−0.032	−0.564	−0.059	−0.203	−0.251	0	0	−0.848	−0.771	−0.436	0	0
−0.848	−0.059	−11.294	−2.645	−0.005	0	0	−0.003	−0.775	1.298	0	0
−0.771	−0.203	−2.645	−1.460	−0.184	0	0	−0.775	−0.940	0.783	0	0
0.436	−0.251	−0.005	−0.184	−0.749	0	0	−1.298	−0.783	0.271	0	0
0	0	0	0	0	−0.169	0	0	0	0	−0.372	0
0	0	0	0	0	0	−0.169	0	0	0	0	−0.372
−0.059	−0.848	−0.003	−0.775	−1.298	0	0	−11.294	−2.645	0.005	0	0
−0.203	−0.771	−0.775	−0.940	−0.783	0	0	−2.645	−1.460	0.184	0	0
0.251	−0.436	1.298	0.783	0.271	0	0	0.005	0.184	−0.749	0	0
0	0	0	0	0	−0.372	0	0	0	0	−0.169	0
0	0	0	0	0	0	−0.372	0	0	0	0	−0.169

Table VII. Geometry of Ethylene[a]

Atom	x	y	z
C1	0	0	0
C2	0	0	2.5511602
H1	1.7511301	0	−1.0110153
H2	−1.7511301	0	−1.0110153
H3	1.7511301	0	3.5621755
H4	−1.7511301	0	3.5621755

[a] This coordinate system differs from the recommendation that the molecule lies in the yz plane: R. S. Mulliken, *J. Chem. Phys.*, **23**, 1997 (1955).

Ethane. The atomic coordinates[28] listed in Table XI are identical with those of the previous study[2] which used 1.0 as the orbital exponent for H. The present study is concerned only with the staggered geometry. Wave functions and energies (Table XX), population analysis (Table XII), and the SCF Hamiltonian matrix (Table XXI) are all reasonable in comparison with the earlier results.[2] In the present study a charge of +0.124 on H, a C–H overlap population of 0.785, and a C–C overlap population of 0.710 may be compared with the earlier results (with a different exponent for H) of +0.114, 0.777, and 0.704 for these three quantities, respectively.

Borane (BH_3). Because BH_3 dimerizes rapidly to B_2H_6, no direct evidence for the geometry of BH_3 is known, but a planar structure is most reasonable[29] and is supported by a theoretical study.[30] In a series of calculations to be reported elsewhere,[8] detailed variation of orbital exponents and B–H distance in BH_3 has yielded an optimum B–H distance of 2.25 au, which is very close to the B–H (terminal) distance of 2.26 au in diborane.[31] Coordinates in the x,y plane are H1 at $x = 2.25$ and $y = 0$, H2 at $x = -1.125$ and $y = 1.9485572$, and H3 at $x = -1.125$ and $y = -1.9485572$. Wave functions and energies (Table XIII), population analysis (Table XV), and SCF Hamiltonian matrix (Table XIV) yield a charge of +0.057 on each H, and a B–H overlap population of 0.837.

Diborane. The molecular geometry (Table XVII) is taken from the recent electron diffraction study of Bartell and Carroll.[31] Wave functions, energies, population analysis, and SCF Hamiltonian matrix are given in Tables XXII, XVIII, and XXIV. Our results are substantially different from those of Yamazaki,[32] and from the earlier four-center results of Hamilton,[33] both of whom found that the charge on H(bridge) was about −0.2. In contrast, we find the charge on the bridge H atoms is +0.099 and on the terminal H atoms is +0.092. When the orbital exponents on H and B have been optimized, as reported previously,[3] the charges are −0.001 on H(bridge) and −0.032 on H(terminal). Overlap populations of 0.864 for B–H(terminal), B–H(bridge) of 0.399, and B–B of 0.291 are especially interesting in view of the moderately strong direct B–B interaction.[34]

Ammonia. Coordinates are chosen with N at the origin and three H atoms in the $z = 0.71996$ plane, with H1 at $x = 1.776$ and $y = 0$, H2 at $x = -0.888$ and $y = 1.538$, and H3 at $x = -0.888$ and $y = -1.538$. Wave functions and energies (Table XXV), population analysis (Table XVI), and the SCF Hamiltonian matrix (Table XXVI) lead to a charge of +0.155 on each H, and a N–H overlap population of 0.677. The molecular dipole moment of 1.72 D. is computed from the detailed wave function, not from the charges of the population analysis. The observed value[35] is 1.47 D. Orbital energies are in the same order and in qualitative agreement with results obtained by Kaplan,[36] who obtained an energy of −56.266 au and a dipole moment of 1.82 D. with the use of Hartree–Fock atomic orbitals and a single determinantal wave function. On the other hand, we have repeated the calculation with the exponent of 1.0 for H in an attempt to reproduce Duncan's results,[37] but we obtained an energy of −55.9645 au. Although our values of one- and two-center integrals agree with his values, our three- and four-center integrals are not in agreement with his.

Hydrogen Cyanide. The equilibrium geometry[36] has C at the origin, H at $z = -2.0$, and N at 2.187. The wave function and energies (Table XXIII), population analysis (Table XIX), and SCF Hamiltonian matrix (Table XXVII) yield a charge of +0.216 on H, −0.141 on C, and −0.075 on N. The dipole moment computed from the detailed wave function is 2.11 D., as compared with the observed value[38] of 2.95 D.

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(28) G. E. Hansen and D. M. Dennison, *J. Chem. Phys.*, **20**, 313 (1952).

(29) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin Co., New York, N. Y., p 166.

(30) W. L. Clinton and B. Rice, *J. Chem. Phys.*, **29**, 445 (1958).

(31) L. S. Bartell and B. L. Carroll, *ibid.*, **42**, 1135 (1965).

(32) M. Yamazaki, *ibid.*, **27**, 1401 (1957).

(33) W. C. Hamilton, *Proc. Roy. Soc.* (London), **A235**, 395 (1956).

(34) A molecular orbital calculation for diborane using an extended set of gaussian orbitals has recently been completed by L. Burnelle and J. J. Kaufman (*J. Chem. Phys.*, **43**, 3540 (1965)). They obtained a charge of +0.045 on the terminal H and a nearly neutral bridge H. Their B–H overlap populations agree well with ours; however, they obtain a B–B overlap population of 0.064 which is surprisingly low.

(35) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963, p 27.

(36) H. Kaplan, *J. Chem. Phys.*, **26**, 1704 (1957).

(37) A. B. F. Duncan, *ibid.*, **27**, 423 (1957).

(38) Reference 35, p 39.

Table VIII. Wave Function of Ethylene

MO	Orbital energy	Coefficients													
		H1	H2	H3	H4	1sC1	2sC1	$2p_z$C1	$2p_x$C1	$2p_y$C1	1sC2	2sC2	$2p_z$C2	$2p_x$C2	$2p_y$C2
$1a_g$	−11.2875	0.0039	0.0039	0.0039	0.0039	−0.6990	−0.0137	0.0018	0	0	−0.6990	−0.0137	−0.0018	0	0
$1a_u$	−11.2868	0.0040	0.0040	−0.0040	−0.0040	−0.6988	−0.0232	−0.0041	0	0	0.6988	0.0232	−0.0041	0	0
$2a_g$	−1.0144	0.0995	0.0995	0.0995	0.0995	−0.1604	0.4715	0.1090	0	0	−0.1604	0.4715	−0.1090	0	0
$2a_u$	−0.7823	0.2058	0.2058	−0.2058	−0.2058	−0.1256	0.4394	−0.2021	0	0	0.1256	−0.4394	−0.2021	0	0
$1b_{3u}$	−0.6438	−0.2377	0.2377	−0.2377	0.2377	0	0	0	−0.4060	0	0	0	0	−0.4060	0
$3a_g$	−0.5616	0.2010	0.2010	0.2010	0.2010	0.0128	−0.0048	−0.5171	0	0	0.0128	−0.0048	0.5171	0	0
$1b_{2g}$	−0.5061	0.3270	−0.3270	−0.3270	0.3270	0	0	0	0.4241	0	0	0	0	−0.4241	0
$1b_{2u}$	−0.3709	0	0	0	0	0	0	0	0	−0.6286	0	0	0	0	−0.6286
$1b_{3g}$	0.2426	0	0	0	0	0	0	0	0	−0.8251	0	0	0	0	0.8251
$2b_{3u}$	0.5868	−0.6754	0.6754	−0.6754	0.6754	0	0	0	0.7397	0	0	0	0	0.7397	0
$4a_g$	0.6206	0.6783	0.6783	0.6783	0.6783	0.0990	−0.8903	0.5199	0	0	0.0900	−0.8903	−0.5199	0	0
$3a_u$	0.6395	−0.6920	−0.6920	0.6920	0.6920	−0.1373	1.1571	−0.1920	0	0	0.1373	−1.1571	−0.1920	0	0
$4a_u$	0.8453	−0.1358	−0.1358	0.1358	0.1358	0.0876	−0.9413	−1.2199	0	0	−0.0876	0.9413	−1.2199	0	0
$2b_{2g}$	0.8917	0.6805	−0.6805	−0.6805	0.6805	0	0	0	−1.0226	0	0	0	0	1.0226	0

Electronic energy	−111.2167	Kinetic energy 77.5275
Nuclear repulsion	33.3824	
Total energy	−77.8343	

Table IX. Hamiltonian Matrix of C_2H_4

H1	H2	H3	H4	1C1s	1C2s	$1C2p_z$	$1C2p_x$	$1C2p_y$	2C1s	2C2s	$2C2p_z$	$2C2p_x$	$2C2p_y$
−0.537	−0.260	−0.088	−0.049	−0.829	−0.758	0.206	−0.387	0	−0.084	−0.232	0.250	−0.080	0
−0.260	−0.537	−0.049	−0.088	−0.829	−0.758	0.206	0.387	0	−0.084	−0.232	0.250	0.080	0
−0.088	−0.049	−0.537	−0.260	−0.084	−0.232	−0.250	−0.080	0	−0.829	−0.758	−0.206	−0.387	0
−0.049	−0.088	−0.260	−0.537	−0.084	−0.232	−0.250	0.080	0	−0.829	−0.758	−0.206	0.387	0
−0.829	−0.829	−0.084	−0.084	−11.284	−2.643	−0.002	0	0	−0.001	−0.567	0.956	0	0
−0.758	−0.758	−0.232	−0.232	−2.643	−1.463	−0.106	0	0	−0.567	−0.772	0.680	0	0
0.206	0.206	−0.250	−0.250	−0.002	−0.106	−0.549	0	0	−0.956	−0.680	0.294	0	0
−0.387	0.387	−0.080	0.080	0	0	0	−0.411	0	0	0	0	−0.232	0
0	0	0	0	0	0	0	0	−0.146	0	0	0	0	−0.324
−0.084	−0.084	−0.829	−0.829	−0.001	−0.567	−0.956	0	0	−11.284	−2.643	0.002	0	0
−0.232	−0.232	−0.758	−0.758	−0.567	−0.772	−0.680	0	0	−2.643	−1.463	0.106	0	0
0.250	0.250	−0.206	−0.206	0.956	0.680	0.294	0	0	0.002	0.106	−0.549	0	0
−0.080	0.080	−0.387	0.387	0	0	0	−0.232	0	0	0	0	−0.411	0
0	0	0	0	0	0	0	0	−0.324	0	0	0	0	−0.146

Table X. Population Analysis for Ethylene

Orbital	Population	Orbital	Population
H	0.860	C2p$_z$	1.013
C1s	1.996	C2p$_x$	1.072
C2s	1.197	C2p$_y$	1.0

Table XI. Geometry of Ethane

Atom	x	y	z
C1	0	0	0
C2	0	0	2.9158761
H1	1.9616301	0	−0.6991481
H2	−0.9808151	1.6988215	−0.6991481
H3	−0.9808151	−1.6988215	−0.6991481
H4	−1.9616301	0	3.6150242
H5	0.9808151	−1.6988215	3.6150242
H6	0.9808151	1.6988215	3.6150242

Table XII. Population Analysis for Ethane

Orbital	Population
H	0.876
C1s	1.995
C2s	1.248
C2p$_z$	0.981
C2p$_x$	1.074
C2p$_y$	1.074

Table XVII. Geometry of Diborane

Atom	x	y	z
B1	0	0	0
B2	0	0	3.3542969
H1	1.9473999	0	−1.1471018
H2	−1.9473999	0	−1.1471018
H3	1.9473999	0	4.5013987
H4	−1.9473999	0	4.5013987
H5	0	1.8947127	1.6771484
H6	0	−1.8947127	1.6771484

Table XVIII. Population Analysis for Diborane

Orbital	Population	Orbital	Population
H1	0.908	B2p$_z$	0.727
H5	0.901	B2p$_x$	1.085
B1s	1.995	B2p$_y$	0.451
B2s	1.025		

Table XIX. Population Analysis for Hydrogen Cyanide

Orbital	Population	Orbital	Population
H	0.784	N1s	1.998
C1s	1.997	N2s	1.764
C2s	1.090	N2p$_z$	1.351
C2p$_z$	1.014	N2p$_x$	0.981
C2p$_x$	1.019	N2p$_y$	0.981
C2p$_y$	1.019		

Table XIII. Wave Function of Borane

MO	Orbital energy	Coefficients							
		H1	H2	H3	1sB	2sB	2p$_z$B	2p$_x$B	2p$_y$B
1a$_1$′	−7.6795	0.0048	0.0048	0.0048	−0.9960	−0.0233	0	0	0
2a$_1$′	−0.7129	0.2457	0.2457	0.2457	−0.1902	0.5932	0	0	0
1e$_x$	−0.5104	0.4614	−0.2307	−0.2307	0	0	0	0.5545	0
1e$_y$	−0.5104	0	0.3996	−0.3996	0	0	0	0	0.5545
1a$_1$″	0.1139	0	0	0	0	0	1.0	0	0
3a$_1$′	0.6094	0.8484	0.8484	0.8484	0.1701	−1.6279	0	0	0
2e$_x$	0.6475	1.1296	−0.5648	−0.5648	0	0	0	−1.2871	0
2e$_y$	0.6475	0	0.9783	−0.9783	0	0	0	0	−1.2871
	Electronic energy		−33.7742						
	Nuclear repulsion		7.4365	Kinetic energy 26.1784					
	Total energy		−26.3377						

Table XIV. Hamiltonian Matrix of BH_3

H1	H2	H3	B1s	B2s	B2p$_z$	B2p$_x$	B2p$_y$
−0.465	−0.176	−0.176	−0.584	−0.569	0	−0.406	0
−0.176	−0.465	−0.176	−0.584	−0.569	0	0.203	−0.352
−0.176	−0.176	−0.465	−0.584	−0.569	0	0.203	0.352
−0.584	−0.584	−0.584	−7.677	−1.719	0	0	0
−0.569	−0.569	−0.569	−1.719	−0.969	0	0	0
0	0	0	0	0	0.114	0	0
−0.406	0.203	0.203	0	0	0	−0.345	0
0	−0.352	0.352	0	0	0	0	−0.345

Table XV. Population Analysis for Borane

Orbital	Population	Orbital	Population
H	0.943	B2p$_z$	0
B1s	1.997	B2p$_x$	1.027
B2s	1.121	B2p$_y$	1.027

Table XVI. Population Analysis for Ammonia

Orbital	Population	Orbital	Population
H	0.845	N2p$_z$	1.760
N1s	1.997	N2p$_x$	1.056
N2s	1.598	N2p$_y$	1.056

McLean,[19] in his "best atom" calculation on HCN, obtained charges of 0.24 on H, −0.16 on C, and −0.08 on N, in excellent agreement with our values. Our π-electron transfer of 0.038 electron (negative charge) from N to C compares well with his transfer of 0.06 electron in the same direction. Finally, our overlap populations of 0.800 for C–H, 0.544 for C–N$_\sigma$, and 0.918 for C–N$_\pi$ agree well with his values of 0.801, 0.520, and 0.953, respectively.

Discussion

The most extended series of comparable molecules in this paper is the group, C_2H_2, C_2H_4, C_2H_6, and CH_4.

Table XX. Wave Function of Ethane

MO	Orbital energy	Coefficients															
		H1	H2	H3	H4	H5	H6	1sC1	2sC1	$2p_zC1$	$2p_xC1$	$2p_yC1$	1sC2	2sC2	$2p_zC2$	$2p_xC2$	$2p_yC2$
$1a_{2u}$	−11.2791	0.0040	0.0040	0.0040	−0.0040	−0.0040	−0.0040	−0.7035	−0.0226	−0.0026	0	0	0.7035	0.0226	−0.0026	0	0
$1a_{1g}$	−11.2790	−0.0039	−0.0039	−0.0039	−0.0039	−0.0039	−0.0039	0.7040	0.0157	−0.0025	0	0	0.7040	0.0157	0.0025	0	0
$2a_{1g}$	−1.0016	−0.0929	−0.0929	−0.0929	−0.0929	−0.0929	−0.0929	0.1497	−0.4682	−0.0592	0	0	0.1497	−0.4682	0.0592	0	0
$2a_{2u}$	−0.8276	0.1552	0.1552	0.1552	−0.1552	−0.1552	−0.1552	−0.1332	0.4734	−0.1468	0	0	0.1332	−0.4734	−0.1468	0	0
$1e_{ux}$	−0.5935	0.2929	−0.1465	−0.1465	−0.2925	0.1465	0.1465	0	0	0	0.4106	0	0	0	0	0.4106	0
$1e_{uy}$	−0.5935	0	0.2537	−0.2537	0	−0.2537	0.2537	0	0	0	0	0.4106	0	0	0	0	0.4106
$3a_{1g}$	−0.4919	−0.1392	−0.1392	−0.1392	−0.1392	−0.1392	−0.1392	−0.0155	0.0628	0.5469	0	0	−0.0155	0.0628	−0.5469	0	0
$1e_{gx}$	−0.4809	0.3744	−0.1872	−0.1872	0.3744	−0.1872	−0.1872	0	0	0	0.4277	0	0	0	0	−0.4277	0
$1e_{gy}$	−0.4809	0	0.3243	−0.3243	0	0.3243	−0.3243	0	0	0	0	0.4277	0	0	0	0	−0.4277
$2e_{ux}$	0.5865	0.7521	−0.3761	−0.3761	−0.7521	0.3761	0.3761	0	0	0	−0.7312	0	0	0	0	−0.7312	0
$2e_{uy}$	0.5865	0	0.6514	−0.6514	0	−0.6514	0.6514	0	0	0	0	−0.7312	0	0	0	0	−0.7312
$3a_{2u}$	0.5992	0.1246	0.1246	0.1246	−0.1246	−0.1246	−0.1246	−0.0663	0.4995	1.0502	0	0	0.0663	−0.4995	1.0502	0	0
$4a_{1g}$	0.6462	0.5501	0.5501	0.5501	0.5501	0.5501	0.5501	0.1211	−1.0094	0.4376	0	0	0.1211	−1.0094	−0.4376	0	0
$4a_{2u}$	0.7002	0.5633	0.5633	0.5633	−0.5633	−0.5633	−0.5633	0.1540	−1.2680	0.0686	0	0	−0.1540	1.2680	0.0686	0	0
$2e_{gx}$	0.7098	0.7244	−0.3622	−0.3622	0.7244	−0.3622	−0.3622	0	0	0	−0.8846	0	0	0	0	0.8846	0
$2e_{gy}$	0.7098	0	0.6274	−0.6274	0	0.6274	−0.6274	0	0	0	0	−0.8846	0	0	0	0	0.8846

Electronic energy −121.0013 Kinetic energy 78.6202
Nuclear repulsion 41.9324

Total energy −79.0689

Table XXI. Hamiltonian Matrix of C_2H_6

H1	H2	H3	H4	H5	H6	1C1s	1C2s	$1C2p_z$	$1C2p_x$	$1C2p_y$	2C1s	2C2s	$2S2p_z$	$2C2p_x$	$2C2p_y$
−0.501	−0.268	−0.268	−0.042	−0.076	−0.076	−0.773	−0.727	0.139	−0.413	0.	−0.071	−0.190	0.198	−0.071	0
−0.268	−0.501	−0.268	−0.076	−0.043	−0.076	−0.773	−0.727	0.139	0.207	−0.358	−0.071	−0.190	0.198	0.035	−0.061
−0.268	−0.268	−0.501	−0.076	−0.076	−0.043	−0.773	−0.727	0.139	0.207	0.358	−0.071	−0.190	0.198	0.035	0.061
−0.043	−0.076	−0.076	−0.501	−0.268	−0.268	−0.071	−0.190	−0.198	0.071	0	−0.773	−0.727	−0.139	0.413	0
−0.076	−0.043	−0.076	−0.268	−0.501	−0.268	−0.071	−0.190	−0.198	−0.035	0.061	−0.773	−0.727	−0.139	−0.207	0.358
−0.076	−0.076	−0.043	−0.268	−0.268	−0.501	−0.071	−0.190	−0.198	−0.035	−0.061	−0.773	−0.727	−0.139	−0.207	−0.358
−0.773	−0.773	−0.773	−0.071	−0.071	−0.071	−11.277	−2.641	0	0	0	0	−0.364	0.619	0	0
−0.727	−0.727	−0.727	−0.190	−0.190	−0.190	−2.641	−1.449	−0.029	0	0	−0.364	−0.575	0.540	0	0
0.139	0.139	0.139	−0.198	−0.198	−0.198	0	−0.029	−0.386	0	0	−0.619	−0.540	0.301	0	0
−0.413	0.207	0.207	0.071	−0.035	−0.035	0	0	0	−0.354	0	0	0	0	−0.168	0
0	−0.358	0.358	0	0.061	−0.061	0	0	0	0	−0.354	0	0	0	0	−0.168
−0.071	−0.071	−0.071	−0.773	−0.773	−0.773	0	−0.364	−0.619	0	0	−11.277	−2.641	0	0	0
−0.190	−0.190	−0.190	−0.727	−0.727	−0.727	−0.364	−0.575	−0.540	0	0	−2.641	−1.449	0.029	0	0
0.198	0.198	0.198	−0.139	−0.139	−0.139	0.619	0.540	0.301	0	0	0	0.029	−0.386	0	0
−0.071	0.035	0.035	0.413	−0.207	−0.207	0	0	0	−0.168	0	0	0	0	−0.354	0
0	−0.061	0.061	0	0.358	−0.358	0	0	0	0	−0.168	0	0	0	0	−0.354

Table XXII. Wave Function of Diborane

MO	Orbital energy	Coefficients															
		H1	H2	H3	H4	H5	H6	1sB1	2sB1	$2p_zB1$	$2p_xB1$	$2p_yB1$	1sB2	2sB2	$2p_zB2$	$2p_xB2$	$2p_yB2$
$1a_u$	−7.7082	0.0035	0.0035	−0.0035	−0.0035	0	0	−0.7038	−0.0237	−0.0057	0	0	0.7038	0.0237	−0.0057	0	0
$1a_g$	−7.7082	0.0038	0.0038	0.0038	0.0038	0.0066	0.0066	−0.7038	−0.0175	−0.0006	0	0	−0.7038	−0.0175	0.006	0	0
$2a_g$	−0.9002	0.0814	0.0814	0.0814	0.0814	0.2137	0.2137	−0.1341	0.3273	0.1347	0	0	−0.1341	0.3273	−0.1347	0	0
$2a_u$	−0.6564	0.2249	0.2249	−0.2249	−0.2249	0	0	−0.1240	0.4428	−0.1441	0	0	0.1240	−0.4428	−0.1441	0	0
$1b_{2u}$	−0.5763	0	0	0	0	−0.4442	0.4442	0	0	0	0	−0.3146	0	0	0	0	−0.3146
$1b_{3u}$	−0.5601	0.2397	−0.2397	0.2397	−0.2397	0	0	0	0	0	0.4021	0	0	0	0	0.4021	0
$3a_{6g}$	−0.5351	−0.2358	−0.2358	−0.2358	−0.2358	0.1889	0.1889	0.0355	−0.1745	0.3826	0	0	0.0355	−0.1745	−0.3826	0	0
$1b_{2g}$	−0.4869	0.2967	−0.2967	−0.2967	0.2967	0	0	0	0	0	0.4278	0	0	0	0	−0.4278	0
$1b_{3g}$	0.1272	0	0	0	0	0	0	0	0	0	0	0.8091	0	0	0	0	−0.8091
$4a_g$	0.4103	−0.3105	−0.3105	−0.3105	−0.3105	0.8417	0.8417	0.0279	−0.0932	−0.6709	0	0	0.0279	−0.0932	0.6709	0	0
$3a_u$	0.4125	−0.2181	−0.2181	0.2181	0.2181	0	0	−0.1318	1.2356	0.9126	0	0	0.1318	−1.2356	0.9126	0	0
$2b_{3u}$	0.5123	0.6855	−0.6855	0.6855	−0.6855	0	0	0	0	0	−0.7769	0	0	0	0	−0.7769	0
$2b_{2u}$	0.6195	0	0	0	0	−0.9863	0.9863	0	0	0	0	0.8502	0	0	0	0	0.8502
$4a_u$	0.6339	0.6922	0.6922	−0.6922	−0.6922	0	0	0.0738	−0.6643	0.7557	0	0	−0.0738	0.6643	0.7557	0	0
$5a_g$	0.7356	0.6550	0.6550	0.6550	0.6550	0.6626	0.6626	0.1287	−1.2115	0.2239	0	0	0.1287	−1.2115	−0.2239	0	0
$2b_{2g}$	0.7840	0.7127	−0.7127	−0.7127	0.7127	0	0	0	0	0	−1.0774	0	0	0	0	1.0774	0

Electronic energy	−84.4265	Kinetic energy	52.2536
Nuclear repulsion	31.7483		
Total energy	−52.6782		

Table XXIII. Wave Function of Hydrogen Cyanide

MO	Orbital energy	Coefficients									
		H	1sC	2sC	$2p_zC$	$2p_xC$	$2p_yC$	1sN	2sN	$2p_zN$	$2p_xN$	$2p_yN$
1σ	−15.6471	−0.0010	0.0002	−0.0086	−0.0074	0	0	0.9961	0.0219	−0.0078	0	0
2σ	−11.3353	0.0045	−0.9960	−0.0210	−0.0017	0	0	0.0005	0.0053	−0.0012	0	0
3σ	−1.2181	0.0629	−0.1498	0.3504	0.2050	0	0	−0.1923	0.6205	−0.2326	0	0
4σ	−0.7770	0.4104	−0.1326	0.4806	−0.4172	0	0	0.0784	−0.2777	−0.0576	0	0
5σ	−0.5287	0.1509	0.0651	−0.2129	−0.3328	0	0	−0.1216	0.7002	0.6755	0	0
$1\pi_x$	−0.4764	0	0	0	0	−0.6284	0	0	0	0	−0.6128	0
$1\pi_y$	−0.4764	0	0	0	0	0	−0.6284	0	0	0	0	−0.6128
$2\pi_x$	0.2949	0	0	0	0	−0.8383	0	0	0	0	0.8497	0
$2\pi_y$	0.2949	0	0	0	0	0	−0.8383	0	0	0	0	0.8497
6σ	0.4882	1.2019	0.1501	−1.3653	0.3043	0	0	−0.0598	0.4337	−0.5109	0	0
7σ	1.2173	−0.7826	0.0387	−0.7202	−1.6483	0	0	−0.1070	1.3215	−1.0673	0	0

Electronic energy	−116.4665	Kinetic energy	92.6803
Nuclear repulsion	23.8762		
Total energy	−92.5903		

Table XXIV. Hamiltonian Matrix of B_2H_6

H1	H2	H3	H4	H5	H6	1B1s	1B2s	1B2p_z	1B2p_x	1B2p_y	2B1s	2B2s	2B2p_z	2B2p_x	2B2p_y
−0.464	−0.179	−0.032	0.018	−0.175	−0.175	−0.580	−0.584	0.188	−0.355	0	−0.026	−0.134	0.166	−0.052	0
−0.179	−0.464	−0.018	−0.032	−0.175	−0.175	−0.580	−0.584	0.188	0.355	0	−0.026	−0.134	0.166	0.052	0
−0.032	−0.018	−0.464	−0.179	−0.175	−0.175	−0.026	−0.134	−0.166	−0.052	0	−0.580	−0.584	−0.188	−0.355	0
−0.018	−0.032	−0.179	−0.464	−0.175	−0.175	−0.026	−0.134	−0.166	0.052	0	−0.580	−0.584	−0.188	0.355	0
−0.175	−0.175	−0.175	−0.175	−0.593	−0.217	−0.426	−0.564	−0.372	0	−0.301	−0.426	−0.564	0.372	0	−0.301
−0.175	−0.175	−0.175	−0.175	−0.217	−0.593	−0.426	−0.564	−0.372	0	0.301	−0.426	−0.564	0.372	0	0.301
−0.580	−0.580	−0.026	−0.026	−0.426	−0.426	−7.706	−1.728	−0.009	0	0	0	−0.317	0.538	0	0
−0.584	−0.584	−0.134	−0.134	−0.564	−0.564	−1.728	−1.081	−0.104	0	0	−0.317	−0.536	0.497	0	0
0.188	0.188	−0.166	−0.166	−0.372	−0.372	−0.009	−0.104	−0.439	0	0	−0.538	−0.497	0.281	0	0
−0.355	0.355	−0.052	0.052	0	0	0	0	0	−0.388	0	0	0	0	−0.160	0
0	0	0	0	−0.301	0.301	0	0	0	0	−0.183	0	0	0	0	−0.280
−0.026	−0.026	−0.580	−0.580	−0.426	−0.426	0	−0.317	−0.538	0	0	−7.706	−1.728	0.009	0	0
−0.134	−0.134	−0.584	−0.584	−0.564	−0.564	−0.317	−0.536	−0.497	0	0	−1.728	−1.081	0.104	0	0
0.166	0.166	−0.188	−0.188	0.372	0.372	0.538	0.497	0.281	0	0	0.009	0.104	−0.439	0	0
−0.052	0.052	−0.355	0.355	0	0	0	0	0	−0.160	0	0	0	0	−0.388	0
0	0	0	0	−0.301	0.301	0	0	0	0	−0.280	0	0	0	0	−0.183

As saturation increases, the negative charge on C varies monotonically as −0.188 in C_2H_2, −0.280 in C_2H_4, −0.372 in C_2H_6, and −0.452 in CH_4, while the charge on each H decreases as +0.188 in C_2H_2, +0.140 in C_2H_4, +0.124 in C_2H_6, and +0.113 in CH_4. The C–H overlap population is remarkably constant, ranging from 0.820 to 0.812 in C_2H_2 and C_2H_4, respectively, and from 0.785 to 0.790 in C_2H_6 and CH_4. These small variations in overlap population are in accord with the bond lengths of 2.002 au in C_2H_2, 2.022 au in C_2H_4, 2.066 au in CH_4, and 2.082 au in C_2H_6. The total carbon–carbon overlap populations are 1.875 for C_2H_2, 1.211 for C_2H_4, and 0.710 for C_2H_6. Thus the C–H overlap population seems reasonably independent of bonding on the other side of the C atom. Even in HCN the C–H overlap population is 0.800, the charge of C is −0.141, somewhat lower than that in C_2H_2, and the charge on H is +0.216, somewhat higher than in C_2H_2. Hence, HCN fits into the series as HCN, C_2H_2, C_2H_4, C_2H_6, CH_4.

Wave functions with an orbital exponent of 1.0 on H, already available for C_2H_6, have also been computed for NH_3, CH_4, and C_2H_4. The C–H overlap populations change only slightly with this change in the H exponent; however, the N–H overlap population changes from 0.677 for exponent 1.2 to 0.640 for exponent 1.0. Surprisingly, the C–C overlap population in C_2H_4 changes from 0.791 to 0.853 on changing the H exponent from 1.2 to 1.0. In each case the total energy is lower for an exponent of 1.2 on H. In NH_3 the difference between the energy with 1.0 and 1.2 exponents is 0.0407 au (0.0136 au per H atom). For CH_4 this difference is 0.0535 au (0.0134 au per H atom), and for C_2H_6 it is 0.0777 au (0.0130 au per H atom). On the other hand, the difference in ethylene is 0.0723; this last result is in the same direction but is 0.0181 au per H atom in magnitude. Another very interesting study is the effect of changing the exponent of H on the barrier to rotation in ethane and such a calculation is in progress by Dr. R. M. Pitzer.

Several numbers have been computed from the ethane wave functions which, however, do not yet give a simple interpretation of the internal rotation barrier. The total noncylindrical charge[39] obtained by numerical integration over the electron density in staggered[2] ethane is 4.129 electrons (e) of which 2.320 e are in H 1s orbitals including H–H overlap regions, and 1.809 e are in C–H overlap. (None are on C by symmetry.) Values for eclipsed[2] ethane are 4.154 e (total) and 2.333 e (on H). For our model with an H exponent of 1.2, values for staggered ethane are 4.570 e (total) and 2.460 e (on H). Thus the protons of CH_3 do not seem to be moving in a sea of cylindrical electron density. The total charge (also obtained by numerical integration) which is spherically symmetrical about each H is 0.834 e (both staggered[2] and eclipsed[2]) and 0.789 e (staggered, H exponent 1.2). Thus the H nucleus is well shielded. Hence we doubt that discussions of nuclear contributions separately from electronic contributions will yield a simple interpretation of the barrier. We note further that an increase in the C–C–H angle of only 0.0022 radian (less than zero-point amplitudes)

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(39) Thus this integration sums over all charge density which is greater than the cylindrical minimum values, and thus is not equivalent to the first term of an expansion in cylindrical harmonics.

Table XXV. Wave Function of Ammonia

MO	Orbital energy	Coefficients							
		H1	H2	H3	1sN	2sN	$2p_zN$	$2p_xN$	$2p_yN$
$1a_1$	−15.5230	0.0050	0.0050	0.0050	−0.9957	−0.0225	−0.0041	0	0
$2a_1$	−1.1014	−0.1554	−0.1554	−0.1554	0.2096	−0.7390	−0.1375	0	0
$1e_x$	−0.5824	0.5034	−0.2517	−0.2517	0	0	0	0.5901	0
$1e_y$	−0.5824	0	0.4359	−0.4359	0	0	0	0	0.5901
$3a_1$	−0.3661	−0.1247	−0.1247	−0.1247	−0.0830	0.4506	−0.8921	0	0
$4a_1$	0.5844	0.7114	0.7114	0.7114	0.1683	−1.2708	−0.5626	0	0
$2e_x$	0.6905	1.0071	−0.5036	−0.5036	0	0	0	−1.0562	0
$2e_y$	0.6905	0	0.8722	−0.8722	0	0	0	0	−1.0562
	Electronic energy	−67.9386		Kinetic energy	56.3959				
	Nuclear repulsion	11.9334							
	Total energy	−56.0052							

Table XXVI. Hamiltonian Matrix of NH_3

H1	H2	H3	N1s	N2s	$N2p_z$	$N2p_x$	$N2p_y$
−0.563	−0.348	−0.348	−1.008	−0.887	−0.221	−0.434	0
−0.348	−0.563	−0.348	−1.008	−0.887	−0.221	0.217	−0.375
−0.348	−0.348	−0.563	−1.008	−0.887	−0.221	0.217	0.375
−1.008	−1.008	−1.008	−15.519	−3.742	−0.025	0	0
−0.887	−0.887	−0.887	−3.742	−1.859	−0.119	0	0
−0.221	−0.221	−0.221	−0.025	−0.119	−0.356	0	0
−0.434	0.217	0.217	0	0	0	−0.328	0
0	−0.375	0.375	0	0	0	0	−0.328

Table XXVII. Hamiltonian Matrix of HCN

H	C1s	C2s	$C2p_z$	$C2p_x$	$C2p_y$	N1s	N2s	$N2p_z$	$N2p_x$	$N2p_y$
−0.591	−0.853	−0.794	0.443	0	0	−0.070	−0.188	0.207	0	0
−0.853	−11.333	−2.655	−0.008	0	0	−0.003	−0.694	1.157	0	0
−0.794	−2.655	−1.526	−0.232	0	0	−0.933	−1.035	0.793	0	0
0.443	−0.008	−0.232	−0.868	0	0	−1.574	−1.022	0.391	0	0
0	0	0	0	−0.212	0	0	0	0	−0.413	0
0	0	0	0	0	−0.212	0	0	0	0	−0.413
−0.070	−0.003	−0.933	−1.574	0	0	−15.644	−3.760	0.031	0	0
−0.188	−0.694	−1.035	−1.022	0	0	−3.760	−1.936	0.279	0	0
0.207	1.157	0.793	0.391	0	0	0.031	0.279	−0.657	0	0
0	0	0	0	−0.413	0	0	0	0	−0.199	0
0	0	0	0	0	−0.413	0	0	0	0	−0.199

causes the nuclear repulsion of eclipsed ethane to be equal to that of undistorted staggered ethane. Surely some small change[40] in geometry of the CH_3 group occurs during internal rotation. We therefore feel that a study of this change and the development of criteria which do not separate nuclear repulsions from electronic contributions are promising directions for further study of the nature of the barrier.

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(40) E. B. Wilson, Jr., *Proc. Natl. Acad. Sci. U. S.*, **43**, 816 (1957).