Semi-Empirical MO Methods

- the high cost of ab initio MO calculations is largely due to the many integrals that need to be calculated (esp. two electron integrals)
- semi-empirical MO methods start with the general form of ab initio Hartree-Fock calculations, but make numerous approximations for the various integrals
- many of the integrals are approximated by functions with empirical parameters
- these parameters are adjusted to improve the agreement with experiment

Semi-Empirical MO Methods

- core orbitals are not treated by semi-empirical methods, since they do not change much during chemical reactions
- only a minimal set of valence orbitals are considered on each atom (e.g. 2s, $2p_x$, $2p_y$, $2p_z$ on carbon)
- Extended Hückel, Zero Differential Overlap and Neglect of Diatomic Differential Overlap

Extended Hückel Theory

(Roald Hoffman, 1960's; implemented in YAeHOMP)

$$H\ C_i = S\ C_i\ E_i$$

- H — Hamiltonian Matrix
- C_i — column vector of molecular orbital coefficients
- E_i — orbital energies
- S — overlap matrix
- H_{ii} — use valence shell ionization potentials
- $H_{ij} = K\ S_{ij}\ (H_{ii} + H_{jj})/2$ with $K = 1.75$

TABLE 10-1 ► Cartesian Coordinates (in Angstroms) for Atoms of Methane Oriented as Shown in Fig. 10-1

Atom	x	y	z
C	0.0	0.0	0.0
H_a	0.0	0.0	1.1
H_b	1.03709	0.0	−0.366667
H_c	−0.518545	0.898146	−0.366667
H_d	−0.518545	−0.898146	−0.366667

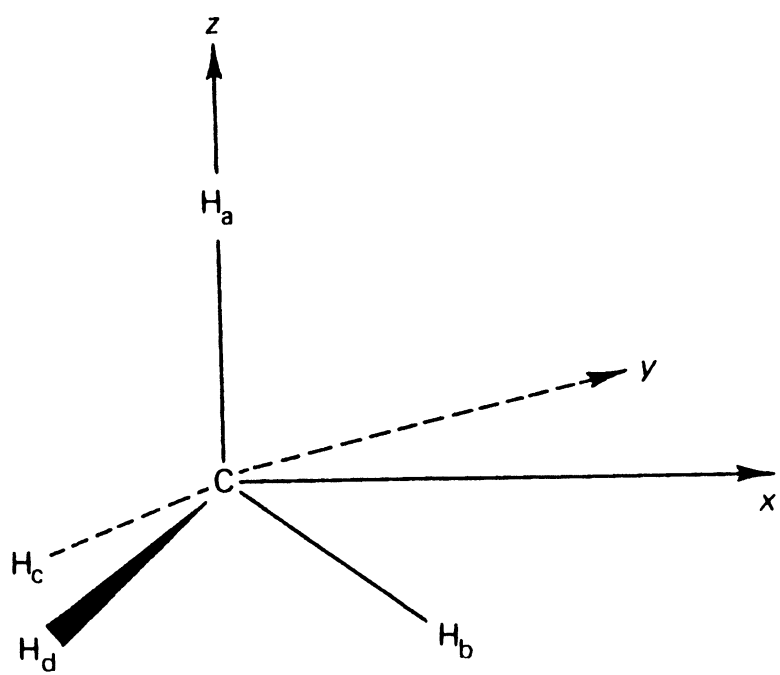


Figure 10-1 ► Orientation of methane in a Cartesian axis system.

TABLE 10-2 ► Basis AOs for Methane

AO no.	Atom	Type	n^a	l^a	m^a	exp
1	C	2s	2	0	0	1.625
2	C	$2p_z$	2	1	0	1.625
3	C	$2p_x$	2	1	$(1)^b$	1.625
4	C	$2p_y$	2	1	$(1)^b$	1.625
5	H_a	1s	1	0	0	1.200
6	H_b	1s	1	0	0	1.200
7	H_c	1s	1	0	0	1.200
8	H_d	1s	1	0	0	1.200

[a] n, l, m are the quantum numbers described in Chapter 4.

[b] $2p_x$ and $2p_y$ are formed from linear combinations of $m = +1$ and $m = -1$ STOs, and neither of these AOs can be associated with a particular value of m.

TABLE 10-3 ► Overlap Matrix for STOs of Table 10-2

	1	2	3	4	5	6	7	8
1	1.0000	0.0	0.0	0.0	0.5133	0.5133	0.5133	0.5133
2	0.0	1.0000	0.0	0.0	0.4855	−0.1618	−0.1618	−0.1618
3	0.0	0.0	1.0000	0.0	0.0	0.4577	−0.2289	−0.2289
4	0.0	0.0	0.0	1.0000	0.0	0.0	0.3964	−0.3964
5	0.5133	0.4855	0.0	0.0	1.0000	0.1805	0.1805	0.1805
6	0.5133	−0.1618	0.4577	0.0	0.1805	1.0000	0.1805	0.1805
7	0.5133	−0.1618	−0.2289	0.3964	0.1805	0.1805	1.0000	0.1805
8	0.5133	−0.1618	−0.2289	−0.3964	0.1805	0.1805	0.1805	1.000

TABLE 10-4 ► The Extended Hückel Hamiltonian Matrix for CH_4[a]

	1	2	3	4	5	6	7	8
1	−0.7144	0.0	0.0	0.0	−0.5454	−0.5454	−0.5454	−0.5454
2	0.0	−0.3921	0.0	0.0	−0.3790	0.1263	0.1263	0.1263
3	0.0	0.0	−0.3921	0.0	0.0	−0.3573	0.1787	0.1787
4	0.0	0.0	0.0	−0.3921	0.0	0.0	−0.3094	0.3094
5	−0.5454	−0.3790	0.0	0.0	−0.5000	−0.1579	−0.1579	−0.1579
6	−0.5454	0.1263	−0.3573	0.0	−0.1579	−0.5000	−0.1579	−0.1579
7	−0.5454	0.1263	0.1787	−0.3094	−0.1579	−0.1579	−0.5000	−0.1579
8	−0.5454	0.1263	0.1787	0.3094	−0.1579	−0.1579	−0.1579	−0.5000

[a] All energies in a.u.

TABLE 10-5 ► Energies for Methane by the Extended Hückel Method

MO no.	Energy (a.u.)	Occ. no.
8	1.1904	0
7	0.2068	0
6	0.2068	0
5	0.2068	0
4	−0.5487	2
3	−0.5487	2
2	−0.5487	2
1	−0.8519	2

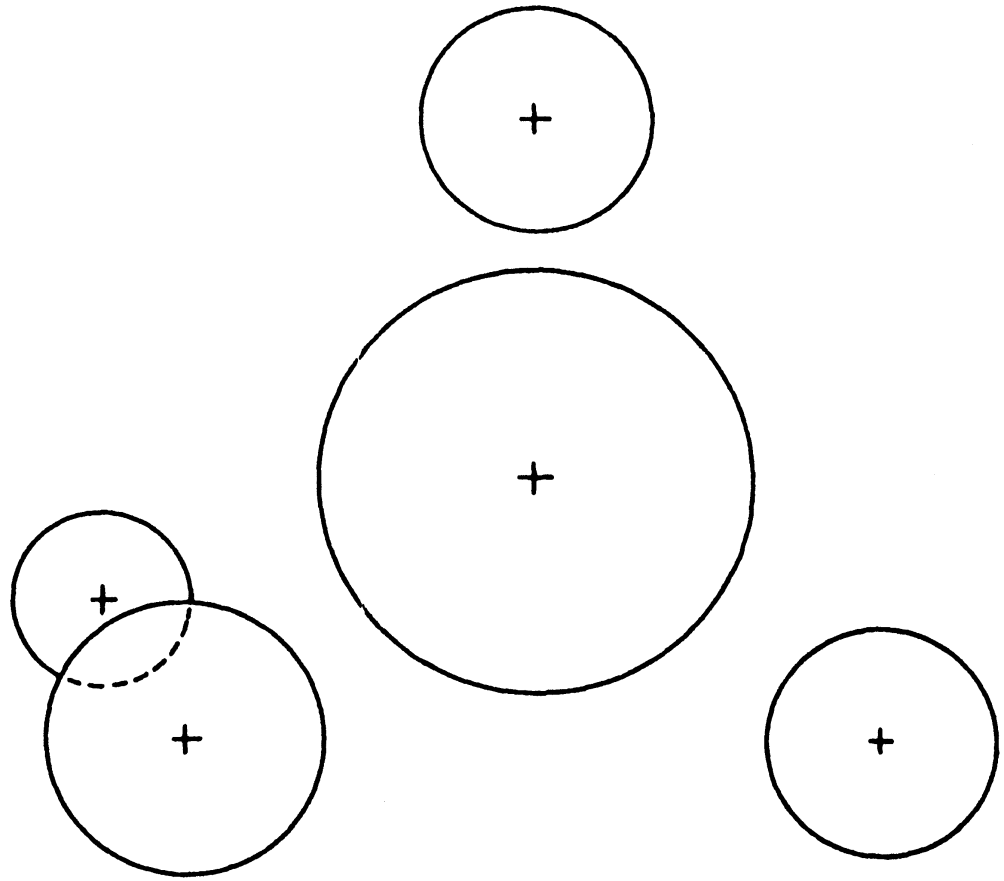


Figure 10-2 ▶ A drawing of the lowest-energy nondegenerate EHMO for methane. The AOs are drawn as though they do not overlap. This is done only to make the drawing simpler. Actually, the AOs overlap strongly.

TABLE 10-7 ► Coefficients for MOs φ_2', φ_3', φ_4'

	φ_2'	φ_3'	φ_4'
2s	0.0	0.0	0.0
$2p_z$	0.5313	0.0	0.0
$2p_x$	0.0	0.5313	0.0
$2p_y$	0.0	0.0	0.5313
$1s_a$	0.5547	0.0	0.0
$1s_b$	−0.1849	0.5228	0.0
$1s_c$	−0.1849	−0.2614	0.4529
$1s_d$	−0.1849	−0.2614	−0.4529

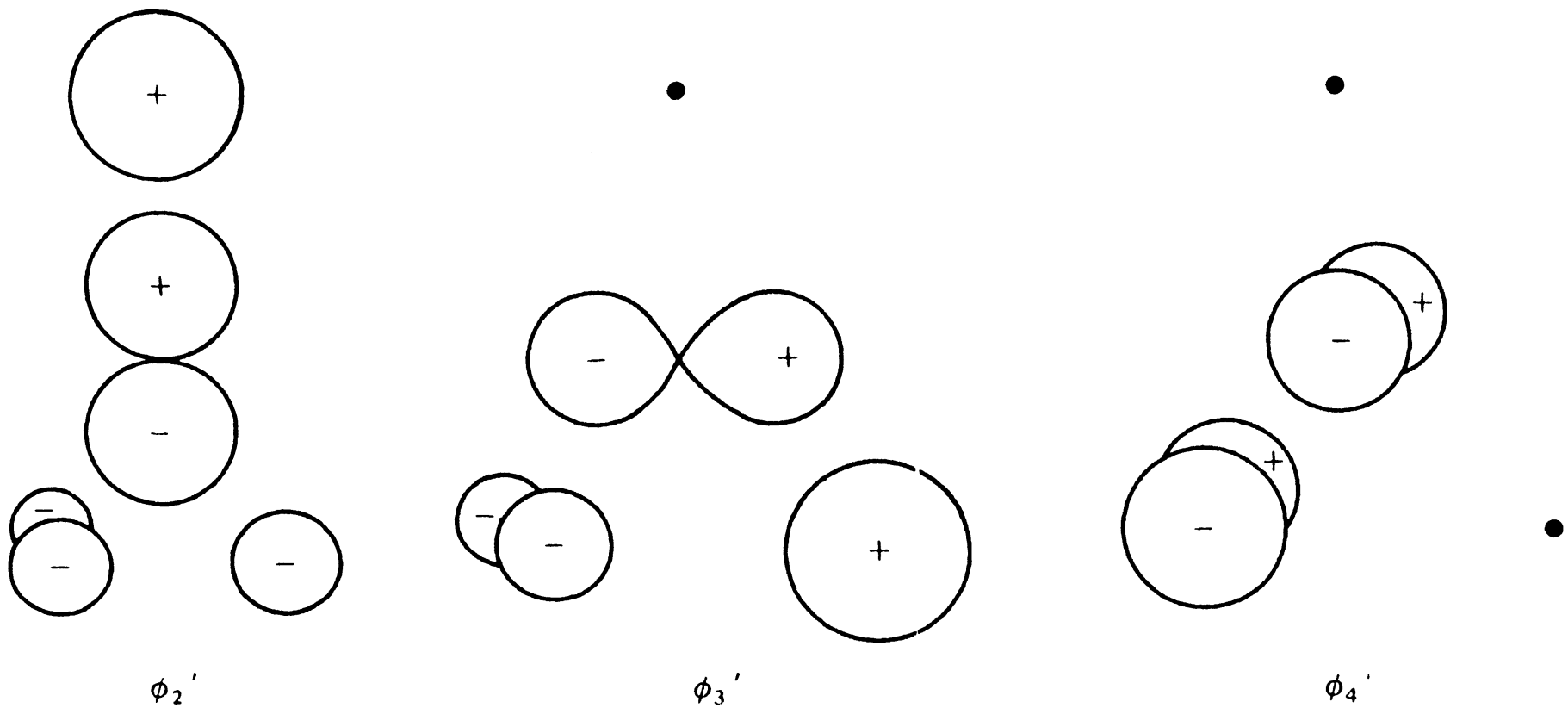


Figure 10-3 ▶ The three lowest-energy degenerate MOs of methane.

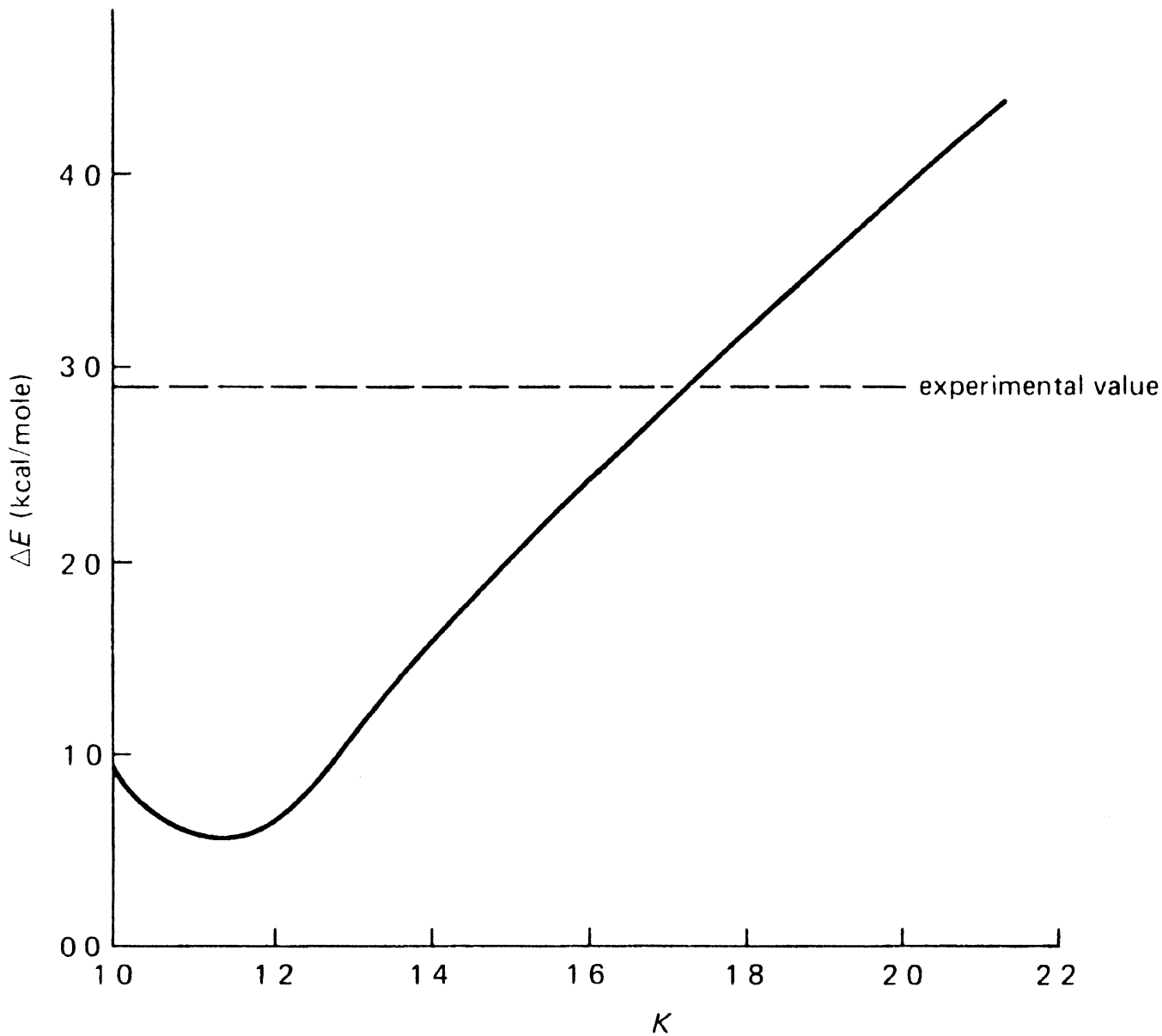


Figure 10-7 ► Extended Hückel energy difference between staggered and eclipsed ethanes as a function of K .

TABLE 10-11 ► Energy Barriers for Internal Rotation about Single Bonds[a]

Molecule	Barrier (kcal/mole)[b] Calculated	Experiment
$CH_3–CH_3$	3.04	2.88
$CH_3–NH_2$	1.66	1.98
$CH_3–OH$	0.45	1.07
$CH_3–CH_2F$	2.76	3.33
$CH_3–CHF_2$	2.39	3.18
$CH_3–CF_3$	2.17	3.25
$CH_3–CH_2Cl$	4.58	3.68
$CH_3–CHCH_2$	1.20	1.99
cis–CH_3–CHCHCl	0.11	0.62
$CH_3–CHO$	0.32	1.16
$CH_3–NCH_2$	0.44	1.97

[a] Calculated barriers are for rigid rotation, where no bond length or angle changes occur except for the torsional angle change about the internal axis.

[b] The stable form for the first seven molecules has the methyl C–H bonds staggered with respect to bonds across the rotor axis. For the last four molecules, the stable form has a C–H methyl bond eclipsing the double bond.

TABLE 10-8 ► Mulliken Net AO and Overlap Populations for Methane as Computed by the Extended Hückel Method

	2s	$2p_z$	$2p_x$	$2p_y$	$1s_a$	$1s_b$	$1s_c$	$1s_d$
2s	0.6827	0.0	0.0	0.0	0.2229	0.2229	0.2229	0.2229
$2p_z$		0.5645	0.0	0.0	0.5723	0.0636	0.0636	0.0636
$2p_x$			0.5645	0.0	0.0	0.5087	0.1272	0.1272
$2p_y$				0.5645	0.0	0.0	0.3815	0.3815
$1s_a$					0.6844	−0.0491	−0.0491	−0.0491
$1s_b$						0.6844	−0.0491	−0.0491
$1s_c$							0.6844	−0.0491
$1s_d$								0.6844

TABLE 10-10 ► Gross AO Populations, Gross Atomic Populations, and Net Atomic Charges for Methane

	Gross AO population	Gross atom population	Net atomic charge
C_{2s}	1.128	3.966	+0.0334
C_{2p}[a]	0.946		
H[a]	1.008	1.008	−0.0083

[a] All 2p AOs and all H AOs have identical values because they are equivalent through symmetry.

Zero Differential Overlap (ZDO)

- two electron repulsion integrals are one of the most expensive parts of ab initio MO calculations

$$(\mu\nu|\lambda\sigma) = \int \chi_\mu(1)\chi_\nu(1)\frac{1}{r_{12}}\chi_\lambda(2)\chi_\sigma(2)d\tau_1 d\tau_2$$

- neglect integrals if orbitals are not the same

$$(\mu\nu|\lambda\sigma) = (\mu\mu|\lambda\lambda)\ \delta_{\mu\nu}\ \delta_{\lambda\sigma}$$

$$where\ \delta_{\mu\nu} = 1\ if\ \mu = \nu,\ \delta_{\mu\nu} = 0\ if\ \mu \neq \nu$$

- approximate integrals by using s orbitals only
- CNDO, INDO and MINDO semi-empirical methods

Neglect of Diatomic Differential Overlap (NDDO)

- fewer integrals neglected

$$(\mu\nu\,|\,\lambda\sigma) = \int \chi_\mu(1)\chi_\nu(1)\frac{1}{r_{12}}\chi_\lambda(2)\chi_\sigma(2)d\tau_1 d\tau_2$$

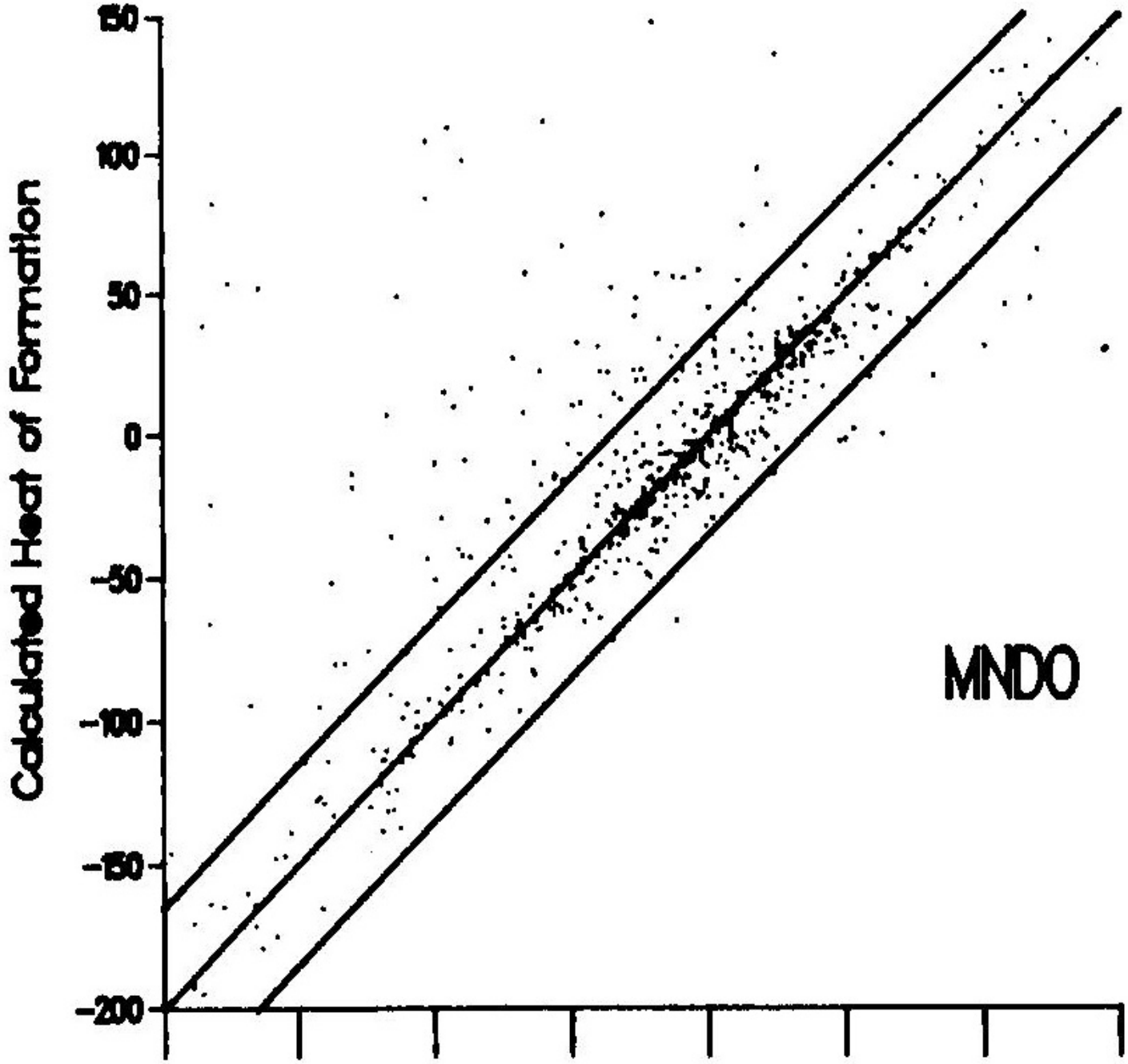
- neglect integrals if μ and ν are not on the same atom or λ and σ are not on the same atom
- integrals approximations are more accurate and have more adjustable parameters than in ZDO methods
- parameters are adjusted to fit experimental data and ab initio calculations
- MNDO, AM1 and PM3 semi-empirical methods
- recent improvements: PDDG and PM6

Table 3.2 Average errors in bond distances (Å)

Bonds to:	MNDO	AM1	PM3
H	0.015	0.006	0.005
C	0.002	0.002	0.002
N	0.015	0.014	0.012
O	0.017	0.011	0.006
F	0.023	0.017	0.011
Si	0.030	0.019	0.045

Table III. Statistical analysis of difference between experimental and calculated heats of formation.

Type of compounds	No. of compounds	Averages (unsigned)			Average (signed)			Root mean square		
		PM3	MNDO	AM1	PM3	MNDO	AM1	PM3	MNDO	AM1
Hydrogen	465	6.3	12.9	11.2	1.5	4.8	5.0	8.6	24.1	23.5
Carbon	463	6.2	12.8	11.1	1.1	3.4	3.9	8.8	23.1	22.1
Nitrogen	118	6.9	18.8	9.9	0.2	10.1	4.1	9.4	26.9	12.9
Oxygen	255	9.7	31.7	33.5	0.1	25.0	28.8	13.9	54.7	61.3
Fluorine	148	8.9	41.9	46.6	1.5	34.1	38.4	12.0	80.3	79.7
Aluminum	46	14.7	23.9	38.6	2.6	6.7	33.2	21.2	34.2	53.3
Silicon	78	10.1	22.4	14.5	1.9	13.0	3.6	14.2	32.9	20.8
Phosphorus	71	12.5	37.3	53.6	−0.5	23.8	44.8	16.1	55.1	83.0
Sulfur	101	12.0	50.3	53.5	−1.4	36.9	41.5	16.2	79.8	81.7
Chlorine	105	9.6	23.0	22.3	0.2	12.8	10.6	13.3	51.1	41.4
Bromine	70	11.5	28.8	27.1	1.1	17.1	14.9	15.7	47.1	44.7
Iodine	77	10.7	30.3	27.3	0.2	12.9	11.8	15.9	61.1	54.0
Set of Compounds used in Refs. 3 and 16	138	4.4	6.2	5.5	0.0	−1.4	0.7	6.3	9.1	7.3
Compounds of C, H, N, O, only	276	5.7	11.2	7.5	0.4	3.8	1.4	7.9	18.5	10.5
Nitro compounds	29	5.2	39.6	15.7	2.5	38.1	14.5	6.2	44.1	18.5
Organophosphorus-V compounds	15	10.9	53.9	75.6	3.6	50.2	75.6	14.3	56.7	80.1
Normal valent compounds	657	7.8	13.9	12.7	0.7	3.3	3.7	11.4	25.1	24.3
Hypervalent	106	13.6	75.8	83.1	−0.8	67.2	74.7	17.3	104.5	110.0
All compounds	763	8.6	22.5	22.4	0.5	12.1	13.6	12.4	45.5	46.8
All compounds except Al, P, and S	547	7.1	15.5	11.5	0.9	6.6	2.9	10.1	35.1	26.5


Calculated Heat of Formation
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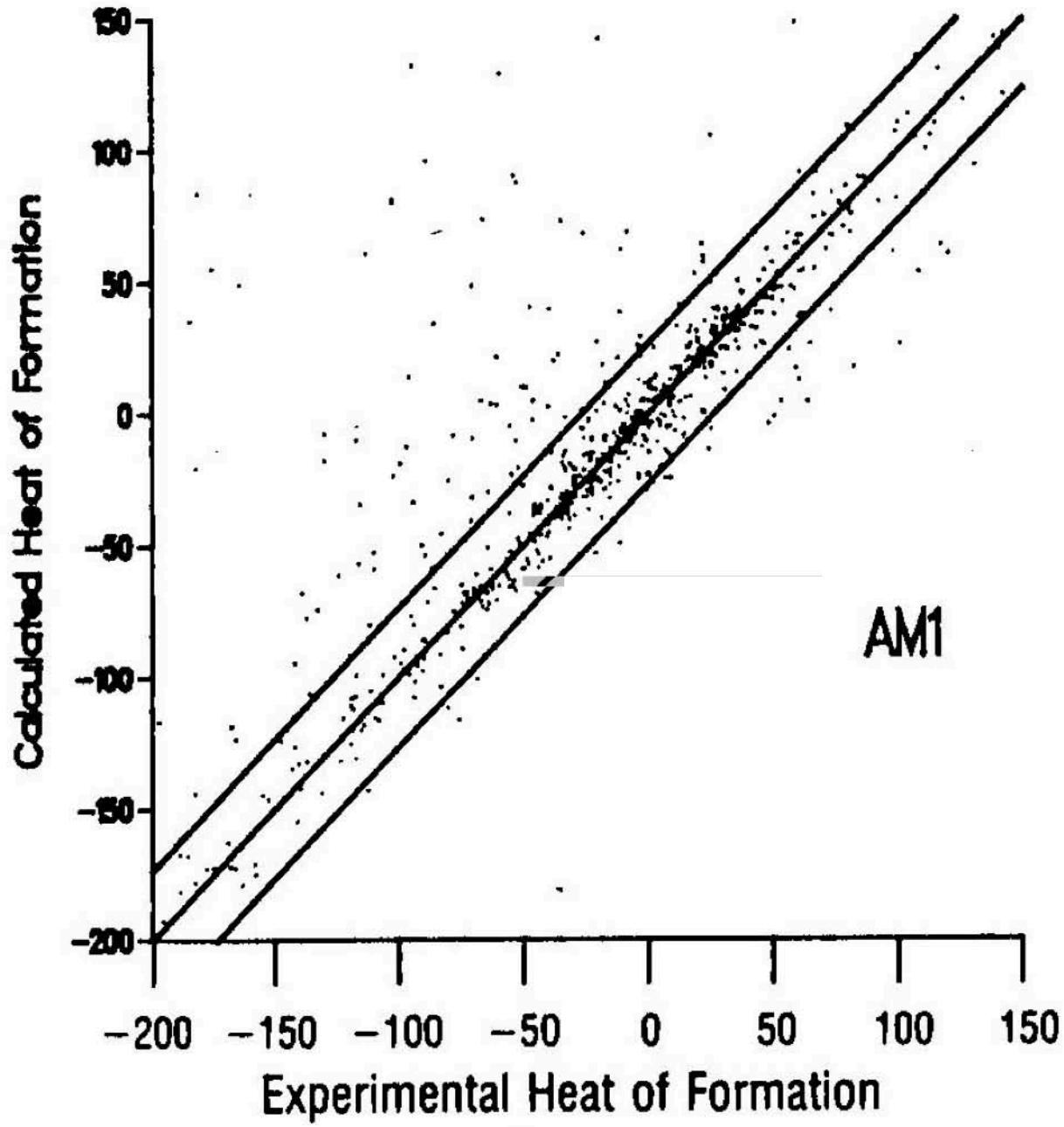
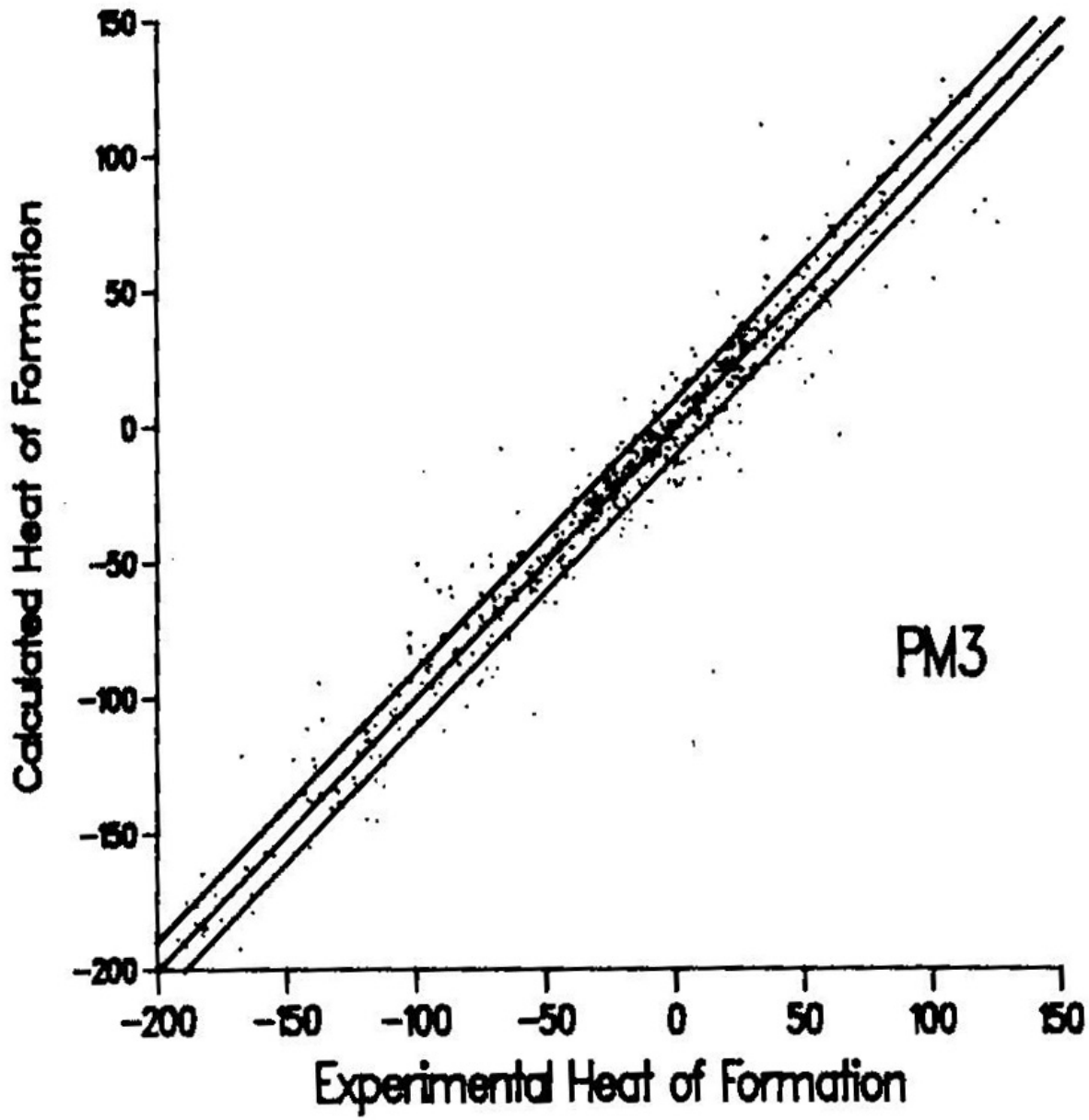
100
50
0
-50
-100
-150
-200
MNDO


150
100
50
0
-50
-100
-150
-200
Calculated Heat of Formation
AM1
-200
-150
-100
-50
0
50
100
150
Experimental Heat of Formation


PM3
Calculated Heat of Formation
Experimental Heat of Formation
150
100
50
0
-50
-100
-150
-200
-200
-150
-100
-50
0
50
100
150

Some Limitations of AM1

- predicts hydrogen bond strengths approximately correct (but geometry often wrong)
- activation energies much improved over MNDO
- hypervalent molecules improved over MNDO, but still significant errors
- alkyl groups systematically too stable by ca 2 kcal/mol per CH_2 group
- nitro groups too unstable
- peroxide bonds too short

Some Limitations of PM3

- hydrogen bonds are too short by 0.1 A
- almost all sp^3 nitrogens are pyramidal
- Si – halogen bonds too short
- structures for NH_2NH_2, ClF_3 wrong
- charge on nitrogens unrealistic