Theoretical Chemistry

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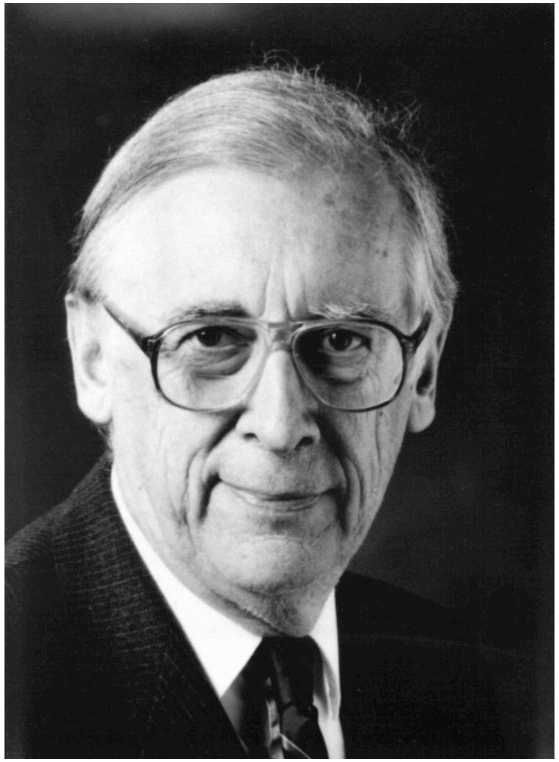
Summary

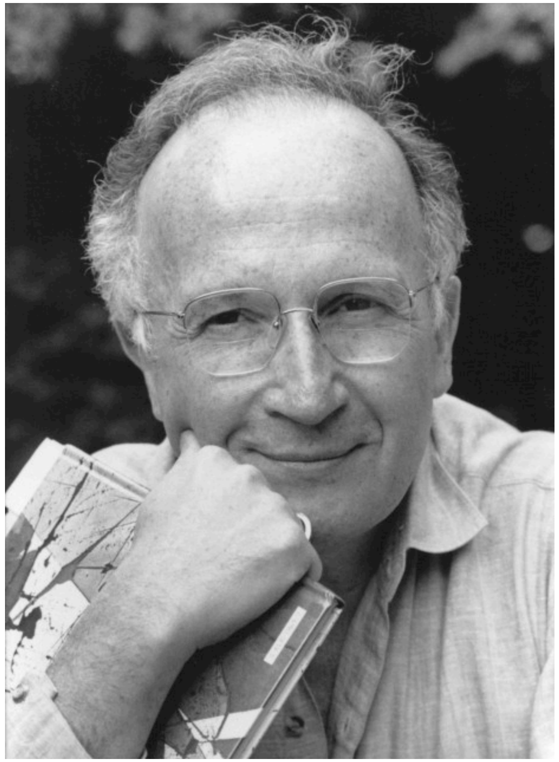
- The Hartree-Fock-Roothaan method
- Pople and Dunning basis sets
- **Semiempirical models**
- Configuration interaction
- Möller-Plesset perturbation theory
- Density functional theory
- Time-dependent DFT

SEMIEMPIRICAL MODELS

Erich Hückel
(1896-1980)



John Pople
(1925-2004)



Roald Hoffman
(1937-)

Practical Limitation of the Ab Initio Implementation Of Hartree-Fock-Roothaan Method

Total electronic energy

$$\langle E \rangle = \sum_{i=1}^{N} 2I_i + \sum_{i=1}^{N}\sum_{j=1}^{N}\left(2J_{ij} - K_{ij}\right)$$

Roothaan linear expansion of MOs

$$\phi_i(\mathbf{r}) = \sum_{p=1}^{M} C_{pi}\chi_p(\mathbf{r})$$

Inventory of the integrals to be computed

$$I_i = \int \phi_i^*(\mathbf{r}_\mu)\hat{h}\phi_i(\mathbf{r}_\mu)d\mathbf{r}_\mu = \sum_{p=1}^{M}\sum_{q=1}^{M} C_{pi}C_{qi}h_{pq}$$

$$h_{pq} = \int \chi_p(\mathbf{r}_\mu)\hat{h}\chi_q(\mathbf{r}_\mu)d\mathbf{r}_\mu \Longrightarrow \text{M}^2 \textit{ integrals}$$

$$J_{ij} = \int \frac{\phi_i^*(\mathbf{r}_\mu)\phi_i(\mathbf{r}_\mu)\phi_j^*(\mathbf{r}_\nu)\phi_j(\mathbf{r}_\nu)}{r_{\mu\nu}} d\mathbf{r}_\mu d\mathbf{r}_\nu = \sum_{p=1}^{M}\sum_{q=1}^{M}\sum_{r=1}^{M}\sum_{s=1}^{M} C_{pi}C_{qi}C_{rj}C_{sj}\left(pq|rs\right)$$

$$\left(pq|rs\right) = \int \frac{\chi_p(\mathbf{r}_\mu)\chi_q(\mathbf{r}_\mu)\chi_r(\mathbf{r}_\nu)\chi_s(\mathbf{r}_\nu)}{r_{\mu\nu}} d\mathbf{r}_\mu\, d\mathbf{r}_\nu \Longrightarrow \text{M}^4 \textit{ integrals}$$

A HF calculation on the acetonitrile molecule using the 6-311+G(d,p) basis set requires calculating about $81^4/8 = 5.10^6$ (pq|rs) integrals

SEMI-EMPIRICAL MODELS: BASIC PRINCIPLES

Approximations on the integrals

a priori weak integrals are neglected in the HF equations

Empirical corrections

The integrals considered in the calculations are parameterized to reproduce either experimental results or results obtained using more sophisticated *ab initio* methods

Several families of methods

We can distinguish methods that are:

- **Restricted to all valence electrons**
  - Extended Hückel method, proposed by R. Hoffman
  - CNDO, INDO, <u>NDDO</u>, first introduced by J. Pople

  For an historical overview, see: Pople and Beveridge, *Approximate molecular orbital theory*, McGraw Hill, New York (1970)
  - INDO/S (ZINDO) dedicated to the simulation of electronic spectra
- **Restricted to π electrons**
  - Pariser-Parr-Pople (PPP) … Hubbard for physicists
  - Hückel … Tight-Binding for physicists

Parameterization

*All these methods include **empirical parameters** that have to be properly adjusted*

VALENCE-ELECTRON SEMI-EMPIRICAL MODELS

The core/valence separation

The HF energy of a closed-shell molecule

$$\langle E \rangle = \sum_{i=1} 2I_i + \sum_{i=1} \sum_{j=1} (2J_{ij} - K_{ij})$$

can be decomposed so as to explicitly use terms involving core orbitals and valence orbitals:

$$\langle E \rangle = \underbrace{\sum_{i=1}^{\text{core}} 2I_i + \sum_{i=1}^{\text{core}} \sum_{j=1}^{\text{core}} (2J_{ij} - K_{ij})}_{\text{core shell orbitals}} + \underbrace{\sum_{i=1}^{\text{valence}} 2I_i + \sum_{i=1}^{\text{valence}} \sum_{j=1}^{\text{valence}} (2J_{ij} - K_{ij})}_{\text{valence orbitals}} + \underbrace{\sum_{i=1}^{\text{valence}} \sum_{j=1}^{\text{core}} (2J_{ij} - K_{ij})}_{\text{core/valence interaction}}$$

One assumes that modifying the valence part of the electronic cloud hardly impacts the core orbitals. The core-shell energy E^{core} can thus be considered as constant. Moreover, with:

$$I'_i = I_i + \sum_{j=1}^{\text{core}} (2J_{ij} - K_{ij})$$

the total HF energy yields:

$$\langle E \rangle = E^{\text{core}} + \sum_{i=1}^{\text{valence}} 2I'_i + \sum_{i=1}^{\text{valence}} \sum_{j=1}^{\text{valence}} (2J_{ij} - K_{ij})$$

which is a similar, up to the constant term E^{core}, to the HF energy expression, where sums run over valence orbitals only. The 1-electron integrals I' describe the interactions between the valence electron i and the nuclei, and account for the electrostatic screening due to the inner shell electrons.

VALENCE-ELECTRON SEMI-EMPIRICAL MODELS

Common features of valence-electron semiempirical methods

MOs expansion

$$\phi_i = \sum_p C_{pi}\,\chi_p$$

*The MOs are linear combination of **valence** AOs*
*AOs are described using a **minimal basis set of Slater functions***

The core electrons are considered to be a part of the nuclei

ZDO (Zero Differential Overlap) approximation

The overlap integrals

$$S_{pq} = \int \chi_p(\nu)\chi_q(\nu)dV_\nu$$

are neglected when solving the Fock equations

$$\mathbf{FC} = \varepsilon\mathbf{SC} \;\Rightarrow\; \mathbf{FC} = \varepsilon\mathbf{IC}$$

VALENCE-ELECTRON SEMI-EMPIRICAL MODELS

CNDO, INDO and NDDO methods
differ in the way the 2-electron integrals are treated

$$(pq|rs) = \int \frac{\chi_p(\mathbf{r}_\mu)\chi_q(\mathbf{r}_\mu)\chi_r(\mathbf{r}_\nu)\chi_s(\mathbf{r}_\nu)}{r_{\mu\nu}} d\mathbf{r}_\mu \, d\mathbf{r}_\nu$$

CNDO (Complete Neglect of Differential Overlap)

- One-center Coulomb integrals $\gamma_{AA}=(p^A p^A | p^A p^A)$ are determined from experimental ionization potentials

- Two-center electronic repulsion integrals $\gamma_{AB}=(p^A p^A | q^B q^B)$ are evaluated by using a function of the distance between atoms A and B

- p-type orbitals are replaced by s-type orbitals in the $(p^A p^A | q^B q^B)$ integrals, so that:

$$\gamma_{AB} = \left(p_s^A p_s^A \middle| q_s^B q_s^B\right) = \left(p_s^A p_s^A \middle| q_p^B q_p^B\right) = \left(p_p^A p_p^A \middle| q_p^B q_p^B\right)$$

- Consequently, all one-center 2-electron integrals γ_{AA} are equal, independently on which type of orbital they are built

VALENCE-ELECTRON SEMI-EMPIRICAL MODELS

INDO (Intermediate Neglect of Differential Overlap)

Fixes some shortcomings of CNDO

- All the one-center 2-integrals are calculated
- Two-center electronic repulsion integrals $\gamma_{AB}=(p^A p^A | q^B q^B)$ are evaluated in the same way as in CNDO, by using a function of the distance between atoms A and B
- This method takes into account the differences of spin distributions, and allows distinguishing between singlet and triplet states

INDO/S (INDO for Spectroscopy)

- Coupled with a CIS (Configuration Interaction with Single excitations) calculation scheme to evaluate the excitation energies
- Parameters have been fitted to reproduce the UV/Vis. spectra of organic molecules
- ZINDO (Zerner's INDO) uses a different set of parameters

VALENCE-ELECTRON SEMI-EMPIRICAL MODELS

NDDO (Neglect of Diatomic Differential Overlap)

The most recent and complete level of semiempirical approximation

- All 2-electron integrals except those based on the differential overlap of two orbitals centered on different atoms are considered

one-center integrals $\left(p^A q^A \middle| r^A s^A\right)$

two-center integrals $\left(p^A q^A \middle| r^B s^B\right)$

three- and four-center integrals are neglected

Different methods have been developped on the basis of the NDDO approximation by using more and more precise parameterizations

MNDO (Dewar 1977), **AM1** (Dewar 1985), **PM3** (Stewart 1989), **PM6** (Stewart 2007)
PM7 (Stewart, under development)… *and many others!*

Most popular semiempirical codes:
MOPAC (http://openmopac.net)
AMPAC (http://www.semichem.co.uk)

GENERAL PHILOSOPHY OF NDDO PARAMETERIZATION

M. Dewar (1918-1997)

Experimental data from a **small group of representative molecules** (*molecular basis set for parameterization*, MBSP) is used to derive the parameters values

The items of data used are **heats of formation, ionization potential, dipole moments, molecular geometries, heats of reaction, rotational and inversion barriers** (all gas phase)

Extensive experience has shown that the set of parameters values is **extendible beyond the limit of those molecules** in the MBSP

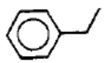
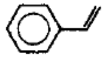
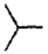
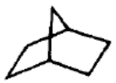
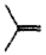
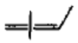
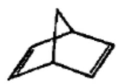
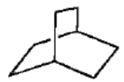
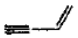
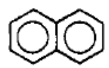
The different parameterizations depend on:

- The parameterization algorithm
- The molecules selected in the MBSP
- The targeted physico-chemical properties

Molecular Basis Set For Parameterization

Parameterization algorithms optimize the parameters in such a way that the statistical error with respect to reference experimental data is minimized

Table II. Heats of Formation ΔH_f for Closed Shell Molecules

Molecule	ΔH_f, kcal/mol			Ref	Molecule	ΔH_f, kcal/mol			Ref
	Calcd	Exptl	Error			Calcd	Exptl	Error	
H_2	0.7	0.0	+0.7						
CH4	−11.9	−17.9	+6.0	*a*		8.6	7.2	+1.4	*a*
C_2H_6	−19.7	−20.2	+0.5	*a*					
C_2H_4	15.3	12.5	+2.8	*a*		37.5	35.3	+2.2	*a*
C_2H_2	57.3	54.3	+3.0	*a*					
$CH_3CH_2CH_3$	−24.9	−24.8	−0.1	*a*					
$CH_3CH{=}CH_2$	4.9	4.9	0.0	*a*		33.6	43.9	−10.3	*a*
$CH_3C{\equiv}CH$	40.9	44.4	−3.5	*a*					
$CH_2{=}C{=}CH_2$	43.8	45.6	−1.8	*a*		69.1	51.9	+17.2	*a*
	−29.7	−30.4	+0.7	*a*					
						33.7	44.3	−10.6	*a*
	−26.8	−32.4	+5.6	*a*					
						28.6	30.9	−2.3	*a*
	0.3	−0.2	+0.5	*a*					
	−5.1	−3.0	−2.1	*a*		30.2	37.3	−7.1	*c*
	−4.0	−1.9	−2.1	*a*					
						−10.3	−12.4	+2.1	*e*
	−2.1	−4.3	+2.2	*a*					
	33.4	38.8	−5.4	*a*		62.6	59.7	+2.9	*c*
	28.9	26.0	+2.9	*a*					
	35.6	39.5	−3.9	*a*		−26.3	−24.1	−2.2	*e*
	24.4	34.7	−10.3	*a*					
	65.0	72.8	−7.8	*b*		38.1	36.1	+2.0	*a*
	102.2	113.0	−10.8	*b*					

M. J. S. Dewar and W. Thiel, *Journal of the American Chemical Society*, **1977**, *99*, 4907.

SEMIEMPIRICAL NDDO CALCULATION OF HEATS OF FORMATION

The Heats of Formation resulting from semiempirical calculations are calculated using empirical atomic Heats of Atomization

Example : $N + 3H \rightarrow NH_3$

1) The total AM1 energy of the system is first calculated. The **atomization energy** is then computed by subtracting the total energies of the atoms (as predicted by the model being used) in their stoichiometric ratios.

$$\Delta E^{atom}_{AM1} = \underbrace{E^{AM1}_{TOT}(NH_3)}_{\text{total AM1 energy}} - \underbrace{3E^{AM1}_{TOT}(H) - E^{AM1}_{TOT}(N)}_{\substack{\text{empirical parameters depending} \\ \text{on the parametrization}}}$$

($E^{AM1}(H) = -11.396$ eV !!)

2) The Heat of Formation ΔH_f of the system is then calculated using the **enthalpies of atomization of the atoms** and the atomization energy.

$$\Delta H^{atom}_{298K} = \underbrace{3 \times \Delta H^{atom}_{298}(H) + \Delta H^{atom}_{298}(N)}_{\substack{\text{experimental parameters} \\ \text{not dependent on the parametrization}}}$$

Then : $$\boxed{\Delta H_f = \Delta E^{atom}_{AM1} + \Delta H^{atom}_{298}}$$

Semi-Empirical NDDO Parameters

1-electron integrals

$$\hat{h}_\mu = -\frac{1}{2}\Delta_\mu - \sum_{a=1}^{P}\frac{Z_a}{r_\mu} = -\frac{1}{2}\Delta_\mu - \frac{Z_A^*}{r_\mu} - \sum_{a\neq A}^{P}\frac{Z_a^*}{r_\mu} = -\frac{1}{2}\Delta_\mu - V_A - \sum_{a\neq A} V_a$$

$$h_{pq} = \int \chi_p(\nu)\hat{h}(\nu)\chi_q(\nu)\,d\mathbf{r}_\nu = (p\,|\,q)$$

- ***one-center 1-electron integrals***

$$\left(p^A\,|\,q^A\right) = (p^A\,|-\frac{1}{2}\Delta - V_A\,|\,q^A) - \sum_{a\neq A}\underbrace{(p^A\,|\,V_a\,|\,q^A)}_{V_{pq,a}}$$

nuclear attraction between atom a (plus its core electrons) and the charge distribution pq centered on A

$$\left(p^A\,|\,q^A\right) = \delta_{pq}U_p - V_{pq,a}$$

$$U_p = (p^A\,|-\frac{1}{2}\Delta - V_A\,|\,p^A) \qquad V_{pq,a} = \sum_{a\neq A} Z_a^*(p^A q^A\,|\,s^a s^a) + f_1(R_{Aa})$$

- ***two-center 1-electron integrals***

$$\left(p^A\,|\,q^B\right) = (p^A\,|-\frac{1}{2}\Delta - V_A\,|\,q^B) - \sum_{a\neq A}\underbrace{(p^A\,|\,V_a\,|\,q^B)}_{\neq 0 \text{ only if } a=B}$$

$$\left(p^A\,|\,q^B\right) = (p^A\,|-\frac{1}{2}\Delta - V_A - V_B\,|\,q^B)$$

$$\left(p^A\,|\,q^B\right) = \frac{1}{2}\left(\beta_A\left(\chi_p\right) + \beta_B\left(\chi_q\right)\right)S_{pq}$$

not consistent with the ZDO approximation!
… at the origin of the "Modified" label

SEMI-EMPIRICAL NDDO PARAMETERS

2-electron integrals

$$(pq|rs) = \int \frac{\chi_p(\mathbf{r}_\mu)\chi_q(\mathbf{r}_\mu)\chi_r(\mathbf{r}_\nu)\chi_s(\mathbf{r}_\nu)}{r_{\mu\nu}} d\mathbf{r}_\mu \, d\mathbf{r}_\nu$$

- ***one-center 2-electron integrals***

$$J_{pq} = (p^A p^A \,|\, q^A q^A)$$

$$K_{pq} = (p^A q^A \,|\, p^A q^A)$$

All one-center integrals (***U_p, J_{pq}, K_{pq}***) are parameterized to reproduce the corresponding ionization energies and electron affinities

- ***two-center 2-electron integrals***

$$(p^A q^A \,|\, r^B s^B) = \sum_{\ell 1} \sum_{\ell 1} \sum_{m} \left[M^m_{\ell 1}(A) \middle| M^m_{\ell 2}(B) \right]$$

M = *multipole moments associated with the charge distributions*

$\ell(\ell_1, \ell_2)$ = order of the multipole

m = its orientation

Point charge approximation:

M_ℓ is represented by ℓ charges of $1/2^\ell$ amplitude separated by a distance D_ℓ

$$\left[M^m_{\ell 1}(A) \middle| M^m_{\ell 2}(B) \right] = \frac{e^2}{2^{\ell 1 + \ell 2}} \sum_{i=1}^{2^{\ell 1}} \sum_{j=1}^{2^{\ell 2}} f_2(R_{ij})$$

*If **p=q=s-type** orbital, electron 1 is a **monopole***

*If **p=s-type** and **q=p-type**, electron 1 is a **dipole***

*If **p=p-type** and **q=p-type**, electron 1 is a **quadrupole***

Semi-Empirical Parameters

MNDO and AM1 *differ only in the way the core-core repulsion is treated, and how the parameters are assigned*

MNDO

$$V_{AB} = Z_A^* Z_B^* (s^A s^A \mid s^B s^B)(1 + e^{-\alpha_A R_{AB}} + e^{-\alpha_B R_{AB}})$$

$$\text{if B=H: } V_{AH} = Z_A^* Z_H (s^A s^A \mid s^H s^H)\left(1 + \frac{e^{-\alpha_A R_{AH}}}{R_{AH}} + e^{-\alpha_H R_{AH}}\right)$$

Overstimation of the repulsion between nuclei at large distances

→ ***Weak interactions are unreliale (e.g. it does not predict hydrogen bonds)***

AM1

$$V_{AB} = Z_A^* Z_B^* (s^A s^A \mid s^B s^B)\left(1 + \exp(-\alpha_A R_{AB}) + \exp(-\alpha_B R_{AB})\right)$$
$$+ Z_A^* Z_B^* (s^A s^A \mid s^B s^B)\left(\sum_i K_{Ai} \exp\left(L_{Ai}(R_{AB} - M_{Bi}\right)^2 + \sum_j K_{Bj} \exp\left(L_{Bj}(R_{AB} - M_{Bj}\right)^2\right)$$

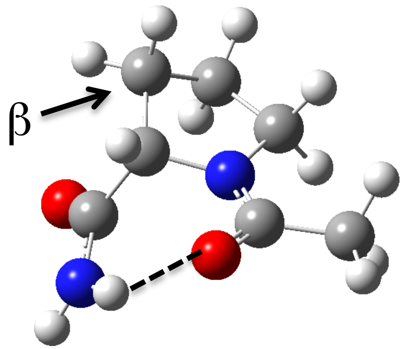
Use of “attractive” Gaussian functions at large distance

→ ***AM1 predicts hydrogen bonds with correct strengths***
(however the geometry can be wrong)

PM3: *Complete reparameterization of AM1 using an automatic process and a significantly larger MBSP*

PM6: *further modifications in core-core repulsion terms, and extension to transition metals (see J. Mol. Model. 2007, 1173.)*

A Representative Example: the N-Acetyl Proline Amide

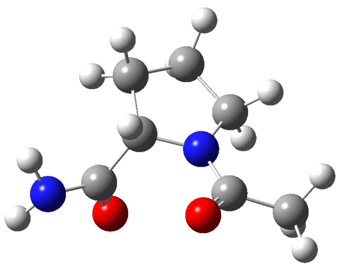


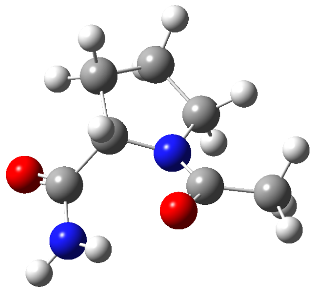
HF/6-31G(d,p)

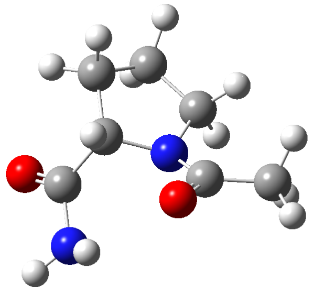
H bond = 2.09 Å

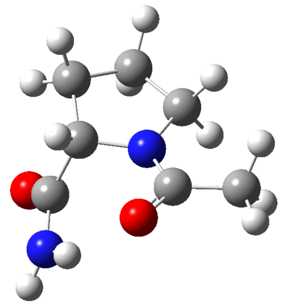
Five membered proline ring in the envelope form, with atoms C-N-C-C approximately in one plane and the β carbon atom out of this plane (N-C-C-C_β = 29°)

Planar amide group









MNDO

✗ No H bond

✗ N-C-C-C_β = -1°

✗ Non-planar amide group

AM1

✓ H bond = 2.14 Å

✗ N-C-C-C_β = 1°

✓ Planar amide group

PM3

✓✗ H bond = 2.59 Å

✗ N-C-C-C_β = 0°

✗ Non-planar amide group

PM6

✓ H bond = 2.01 Å

✓ N-C-C-C_β = 11°

✓ Planar amide group

Electron Density Within the NDDO Approximation

Mulliken AO populations

$$Q_p = \sum_i n_i \left(C_{pi}\right)^2$$

Occupation number of MO ϕ_i (n_i = 0, 1 or 2)

LCAO coefficient

Average number of electrons around atom A within the molecule:

$$n_A = \sum_{p \in A} Q_p = \sum_{p \in A} \sum_i n_i \left(C_{pi}\right)^2$$

Net atomic charges

$$\delta_A = Z_A - n_A$$

Number of valence electrons in atom A isolated

Electron Density Within the NDDO Approximation

Dipole moment

$$\vec{\mu}_0 = \left\langle \Psi_0 \middle| \hat{\vec{\mu}} \middle| \Psi_0 \right\rangle \qquad \hat{\vec{\mu}} = \sum_{i}^{\text{electrons}} -|e|\mathbf{r}_i + \sum_{A}^{\text{nuclei}} Z_A |e| \mathbf{R}_A$$

Rearranging the above expressions for a closed-shell system:

$$\vec{\mu} = 2\sum_{i}^{\text{occ}} \left\langle \phi_i \middle| -e\mathbf{r} \middle| \phi_i \right\rangle + \sum_{A}^{\text{nuclei}} eZ_A R_A$$

Developing the MOs over the AOs:

$$\vec{\mu} = -e\sum_{p,q}^{\text{occ}} D_{pq} \left\langle \chi_p \middle| \mathbf{r} \middle| \chi_q \right\rangle + e\sum_{A}^{\text{nuclei}} Z_A \mathbf{R}_A$$

with D_{pq} the elements of the first order density matrix in the AOs basis.

Dipole integrals in the NDDO approximation

$$\left\langle \chi_p^A \middle| \mathbf{r} \middle| \chi_q^B \right\rangle = 0 \qquad \left\langle \chi_p^A \middle| \mathbf{r} \middle| \chi_p^A \right\rangle = \mathbf{R}_A$$

The two-center dipole integrals are ignored. Only the integrals in which p and q are centered on the same atom are non zero

$$\left\langle \chi_p^A \middle| \vec{r} \middle| \chi_q^A \right\rangle = \frac{2n+1}{\sqrt{3}} \times \sqrt{2\alpha_p} \times \sqrt{2\alpha_q} \times \frac{\left(4\alpha_p\alpha_q\right)^n}{\left(\alpha_p + \alpha_q\right)^{2n+2}}$$

where n, α_p and α_q are the quantum number and the Slater exponents of the AOs χ_p and χ_q

Dipole moment expression

$$\vec{\mu} = \underbrace{e\sum_{A}^{\text{nuclei}} q_A R_A}_{\text{point charge contribution}} \underbrace{- 2e\sum_{A}^{\text{nuclei}} \sum_{p<q}^{p,q\in A} D_{pq} \left\langle \chi_p^A \middle| \mathbf{r} \middle| \chi_q^A \right\rangle}_{\text{hybrid contribution}}$$

with q_A the net charge of atom A

Electron Density Within the NDDO Approximation

Exercise: dipole moment of the LiH molecule

1. Optimize the bond length at the MNDO level
2. Write the LCAO expansion of the occupied orbital ϕ
3. Calculate by hand the atomic charges and check your results wrt to computations
4. Starting from the general expression of the dipole moment, prove that:

$$\vec{\mu}_0 = -2|e|\langle\phi|\vec{r}|\phi\rangle + |e|Z_{Li}\vec{R}_{Li} + |e|Z_H\vec{R}_H$$

5. Using the LCAO expansion of ϕ, show that μ can be written as the sum of two contributions, referred to as the *point charge* and the *hybrid* contributions

$$\vec{\mu}_0 = \vec{\mu}_{charge} + \vec{\mu}_{hybrid} = |e|\delta\vec{\ell}_{Li-H} - 2|e|D_{2s/2px}\langle 2s_{Li}|\vec{r}|2p_{Li}\rangle$$

6. Calculate the point charge contribution.
7. Calculate the hybrid contribution, using n = 2 and $\alpha_{2s(Li)} = \alpha_{2p(Li)}$ = 0,70238 in the dipole integral expression.
8. Convert into Debye and check your results wrt to computations

Atomic units of length: 1 Bohr = 5.2918.10^{-11} m.
Atomic units of energy: 1 Hartree = 27.21 eV.
e = 1.602.10^{-19} m.
1 D = 3.3356.10^{-30} C.m.

Example of NDDO Calculations: The Water Molecule

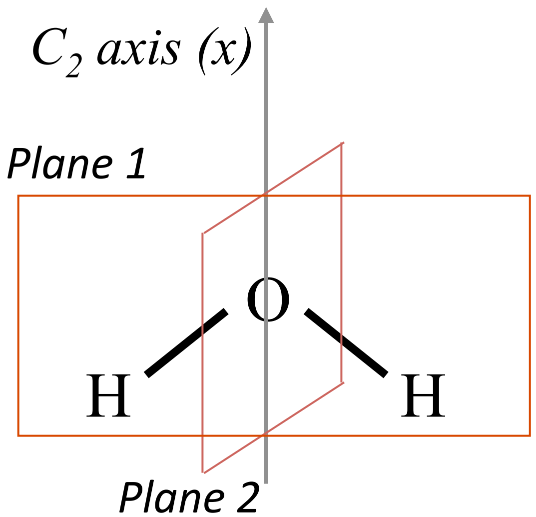
$$\phi_i = \sum_p C_{pi}\,\chi_p$$

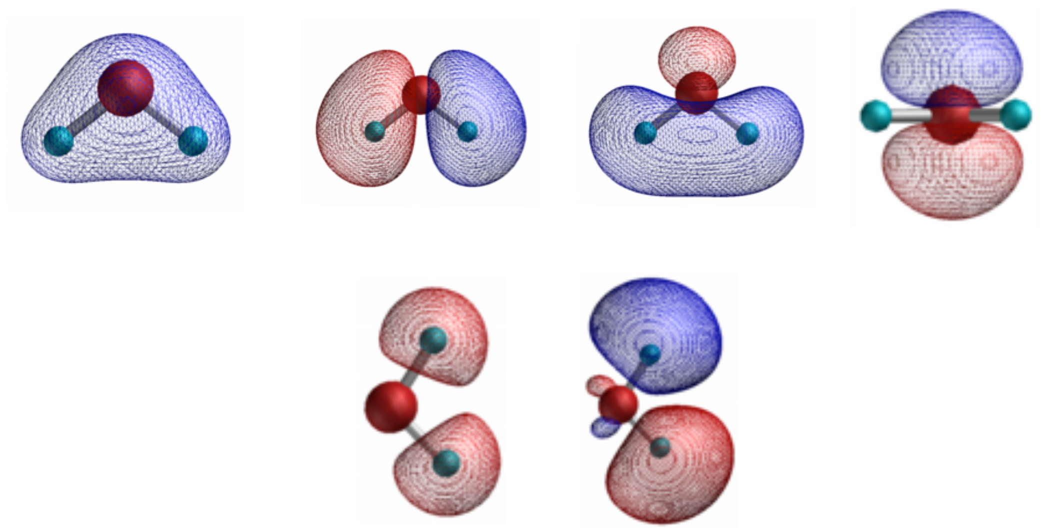
O : $1s^2\,2s^2\,2p^4$: 4 AOs, 6 valence electrons

H : $1s^1$: 1 AO, 1 valence electron

AM1 RHF EIGENVECTORS AND EIGENVALUES

ROOT NO.		1	2	3	4	5	6
		-36.425	-18.199	-14.954	-12.464	4.419	6.191
		1 A1	**1 B2**	**2 A1**	**1 B1**	**3 A1**	**2 B2**
s O	1	.8955	.0000	.3599	.0000	-.2620	.0000
Px O	1	.0950	-.6049	-.4965	.0000	-.3573	-.5009
Py O	1	.1205	.4768	-.6299	.0000	-.4534	.3948
Pz O	1	.0000	.0000	.0000	1.0000	.0000	.0000
s H	2	.2955	-.4510	-.3371	.0000	.5469	.5446
s H	3	.2955	.4510	-.3371	.0000	.5469	-.5446





Example of NDDO Calculations: The Water Molecule

MNDO

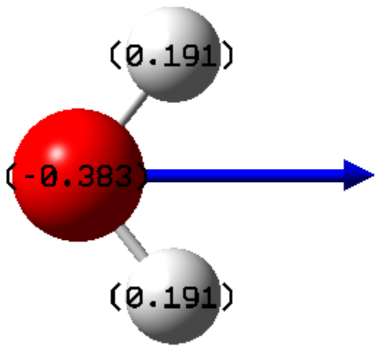
```
NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS
ATOM NO.   TYPE          CHARGE        ATOM ELECTRON DENSITY
  1 O          -0.3255  }           6.3255  }
  2 H           0.1628  } δA        0.8372  } nA
  3 H           0.1628  }           0.8372  }

DIPOLE (DEBYE)    X         Y         Z       TOTAL
POINT-CHG.      0.524     0.706     0.000     0.879
HYBRID          0.539     0.725     0.000     0.904
SUM             1.063     1.431     0.000     1.783
```

AM1

```
NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS
ATOM NO.   TYPE          CHARGE        ATOM ELECTRON DENSITY
  1 O          -0.3826              6.3826
  2 H           0.1913              0.8087
  3 H           0.1913              0.8087

DIPOLE (DEBYE)    X         Y         Z       TOTAL
POINT-CHG.      0.677     0.859     0.000     1.094
HYBRID          0.475     0.602     0.000     0.767
SUM             1.152     1.461     0.000     1.861
```



Experimental dipole value: 1.847 D (*J. Chem. Phys.* **1973**, *59*, 2254)

How Accurate is a Semiempirical Calculation?

Overall performance of MNDO, AM1 and PM3

Reported average errors (From *Introduction to Computational Chemistry* - Frank Jensen)

Table 3.1 Average heat of formation error in kcal/mol (number of compounds)

Compounds:	MNDO	AM1	PM3
H, C, N, O (276)	18.5	10.5	7.9
F (133)	84.2	49.5	11.2
Si (78)	22.9	20.8	14.2
All normal valent (607)	24.3	14.8	11.2
Hypervalent (106)	104.5	62.3	17.3
All (713)	46.2	27.6	11.6

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

Angles (degrees)

MNDO	4.3
AM1	3.3
PM3	3.9

Ionization potentials (eV)

MNDO	0.78
AM1	0.61
PM3	0.57

Dipole moments (D)

MNDO	0.45
AM1	0.35
PM3	0.38

AM1 contains more adjustable parameters than MNDO
All parameters are fully optimized in PM3
→ **Errors decrease in the order MNDO > AM1 > PM3**

***Caution! Considering average errors can be misleading*.**
For specific (classes of) compounds the ordering may be different.
A semiempirical method should always be validated before use.

SOME GENERAL CONCLUSIONS ON SEMIEMPIRICAL METHODS

Semiempirical methods can provide results accurate enough to be useful, particularly for organic molecules with computation requirements low enough to make them convenient on personal computers.

These methods are generally good for predicting molecular geometry and energetics.

Semiempirical methods can be used for predicting vibrational modes and transition structures, but perform less reliably than *ab initio* methods.

Semiempirical calculations generally give poor results for van der Waals, dispersion intermolecular forces and polarisabilities, due to the lack of diffuse basis functions.

Semiempirical calculations generally give poor results for metal-containing compounds.

Computational Chemistry: A Practical Guide for Applying Techniques to Real-World Problems.
David C. Young, 2001, John Wiley & Sons, Inc.

How to Build an Input File for AMPAC?

Build your molecule using the Ampac Graphical User Interface (AGUI) and save the input file using the .dat extension.
The builder contains predefined molecular fragments and chemical functions, with possibility to create your own fragments. Complex molecules can be built in few clicks.

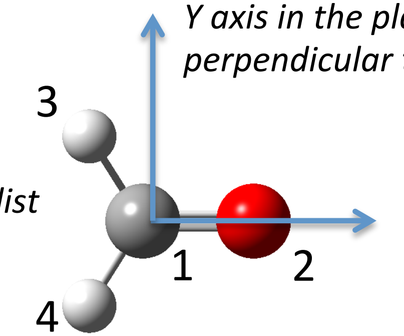
Example of input file: formaldehyde molecule

```
am1 rhf singlet truste t=auto
Formaldehyde
Input for a geometry optimization
 C              0.000000  0     0.000000  0     0.000000  0
 O              1.227317  1     0.000000  0     0.000000  0
 H             -0.592145  1     0.939404  1     0.000000  0
 H             -0.592145  1    -0.939404  1     0.000039  1
 0              0.000000  0     0.000000  0     0.000000  0
```

Keywords
Title section
Comment section

Cartesian coordinates and optimization flags

Default Cartesian axis



Y axis in the plane of the 3 first atoms, perpendicular to X

First atom in the list at the origin

X axis defined by the Atom1-Atom2 direction

How to Build an Input File for AMPAC?

The spatial arrangement of the nuclei can be specified either by **Cartesian or internal coordinates**, arranged in a standard ***z*-matrix** fashion.

Example: formaldehyde molecule. Input file using internal coordinates

```
am1 rhf singlet truste t=auto                                      Keywords
Formaldehyde                                                       Title section
Input for a geometry optimization                                  Comment section
 C              0.000000  0     0.000000  0     0.000000  0     0     0     0
 O              1.227317  1     0.000000  0     0.000000  0     1     0     0
 H              1.110457  1   122.224918  1     0.000000  0     1     2     0
 H              1.110457  1   122.224918  1  -179.997621  1     1     2     3
 0              0.000000  0     0.000000  0     0.000000  0     0     0     0
```

distances *angles* *dihedrals* *connectivities*

Atom 2 (O) is distant from atom 1 (C) by 1.227 Å

Atom 3 (H) is distant from atom 1 (C) by 1.110 Å and the angle H3-C1-O2 is of 122.22°

Atom 4 (H) is distant from atom 1 (C) by 1.110 Å, the angle H4-C1-O2 is of 122.22°, and the dihedral angle H4-C1-O2-H3 is equal to -179.99°

Note that, though of common usage, the term z-matrix is incorrect for AMPAC, since the actual form of the matrix is an x-matrix: the first atom is located at the origin and the first bond is along the x-axis of the Cartesian frame.