

Stacionární Schrödingerova rovnice $\hat{H}\Psi = E\Psi$

Metoda konfigurační interakce
Metoda vázaných klastrů
Poruchová teorie

Bornova-Oppenheimerova aproximace
Model nezávislých elektronů
Vlnová funkce ve tvaru Slaterova determinantu
MO LCAO + variační princip

Zahrnutí el.
korelace

Hartreeho-Fockova metoda (HF)

Separace σ - π

Zanedbání některých
integrálů
Empirické parametry

Neempirické
 π -elektronové
metody

Semiempirické metody
(NDO, AM1, PM3)

Zanedbání některých
integrálů
Empirické parametry

Zanedbání elektronové
repulse

Semiempirické
 π -elektronové
metody

Metoda EHT

Zanedbání elektronové
repulse

Separace σ - π

Hückelova metoda MO

Hartree-Fock-Roothaan

MO LCAO

$$\varphi_i = \sum_{\mu=1}^L c_{\mu i} \chi_{\mu}$$



FOCKOVY ROVNICE

$$\hat{\mathbf{F}}(i) \sum_{\mu=1}^L c_{\mu i} \chi_{\mu} = \varepsilon_i \sum_{\mu=1}^L c_{\mu i} \chi_{\mu}$$



$$\begin{aligned} \sum_{\mu=1}^L \langle \chi_{\nu} | \hat{\mathbf{f}}(i) | \chi_{\mu} \rangle c_{\mu i} &= \\ &= \varepsilon_i \sum_{\mu=1}^L \langle \chi_{\nu} | \chi_{\mu} \rangle c_{\mu i} \end{aligned}$$

SEKULÁRNÍ ROVNICE

$$\sum_{\mu=1}^L F_{\mu\nu} c_{\mu i} = \varepsilon_i \sum_{\mu=1}^L S_{\mu\nu} c_{\mu i} \Rightarrow \sum_{\mu=1}^L c_{\mu i} (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) = 0$$

$$F_{\mu\nu} = \langle \chi_{\mu} | \hat{\mathbf{f}}(i) | \chi_{\nu} \rangle = h_{\mu\nu}^{core} + \sum_{\kappa=1}^B \sum_{\lambda=1}^B P_{\kappa\lambda} \left[(\mu\nu | \kappa\lambda) - \frac{1}{2} (\mu\lambda | \kappa\nu) \right]$$

$$P_{\kappa\lambda} = 2 \sum_{j=1}^{n/2} c_{\kappa j}^* c_{\lambda j}$$

Semiempirické metody

- 1) Pouze valenční elektrony
- 2) Minimální báze (STO)
- 3) Zanedbání některých integrálů
- 4) Nahrazení některých integrálů empirickými parametry

CNDO

$$S_{\mu\nu} = \delta_{\mu\nu}$$

$$\sum_{\mu=1}^L F_{\mu\nu} c_{\mu i} = \varepsilon_i \sum_{\mu=1}^L S_{\mu\nu} c_{\mu i} \Rightarrow \sum_{\mu=1}^L c_{\mu i} (F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) = 0$$

$$F_{\mu\nu} = \langle \chi_{\mu} | \hat{\mathbf{f}}(i) | \chi_{\nu} \rangle = h_{\mu\nu}^{core} + \sum_{\kappa=1}^B \sum_{\lambda=1}^B P_{\kappa\lambda} \left[(\mu\nu | \kappa\lambda) - \frac{1}{2} (\mu\lambda | \kappa\nu) \right]$$

$$(\mu\nu | \kappa\lambda) = \delta_{\mu\nu} \delta_{\kappa\lambda} (\mu\mu | \lambda\lambda) = \gamma_{AB}$$

$$h_{\mu\mu}^{core} = U_{\mu}$$

$$h_{\mu\nu}^{core} = \frac{(\beta_A + \beta_B) S_{\mu\nu}}{2}$$

$$\gamma_{AA} = IP_A - EA_A$$

$$\gamma_{AB} = \frac{\gamma_{AA} + \gamma_{BB}}{2 + r_{AB} (\gamma_{AA} + \gamma_{BB})}$$

β – empirické parametry
Explicitně počítaný překryvový integrál

Může se explicitně počítat, obvykle se nahrazuje parametrem z IP_A a EA_A .
Nerozlišuje s, p, ... orbitaly !!!

INDO

$$(\mu\nu | \kappa\lambda) = \delta_{\mu\nu} \delta_{\kappa\lambda} (\mu\mu | \lambda\lambda) = \gamma_{AB}$$

Rozlišuje se typ AO v případě, že obě funkce jsou na stejném atomu:

$$(ss|ss) = G_{ss}$$

$$(ss|pp) = G_{pp}$$

.....

MINDO

$$h_{\mu\nu}^{core} \neq \frac{(\beta_A + \beta_B) S_{\mu\nu}}{2}$$

Explicitně se parametrizuje β_{AB} .

Rozsáhlejší parametrisace.

NDDO

$$(\mu\nu | \kappa\lambda) \neq 0 \leftarrow \mu, \nu \in A \wedge \kappa, \lambda \in B$$

AM1

NDDO typ, zavádí empirickou korekci na meziatomovou repulsi:
První z NDO metod schopná kvalitativně pospsat vodíkové vazby.

$$V_N(A, B) = Z_A Z_B (s_A s_A | s_B s_B) + \frac{Z_A Z_B}{r_{AB}} \sum_{i=1}^4 \left[a_{A,i} e^{-b_{A,i} (r_{AB} - c_{A,i})^2} + a_{B,i} e^{-b_{B,i} (r_{AB} - c_{B,i})^2} \right]$$

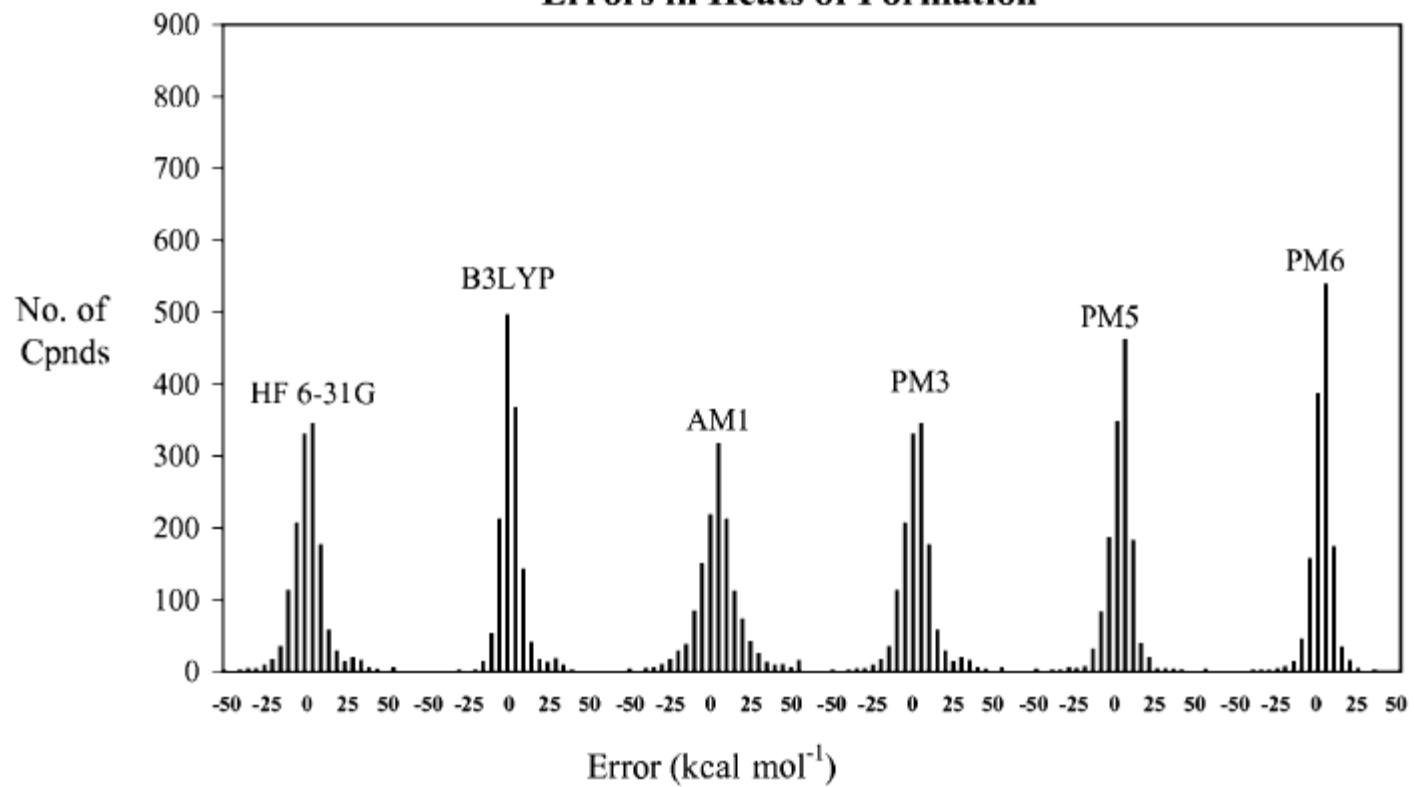
PM3

Postupná parametrizace nahrazena korektnější, matematicky stabilnější metodou

PM6

Liší se způsobem parametrizace – referenční set

Errors in Heats of Formation



Charge distribution

One-electron properties: $\hat{O}_1 = \sum_{i=1}^n \hat{o}(i)$ $\langle O_1 \rangle = \langle \Psi_0 | \hat{O}_1 | \Psi_0 \rangle = 2 \sum_i^{n/2} (\varphi_i | \hat{o} | \varphi_i) = \sum_{\mu\nu}^B P_{\mu\nu} (\chi_\mu | \hat{o} | \chi_\nu)$

Electric multipole moments:

$$\langle x^k y^l z^m \rangle = \sum_i^{\text{atoms}} Z_i x^k y^l z^m - \int \Psi_0(r) \left(\sum_j^{\text{electrons}} x^k y^l z^m \right) \Psi_0(r) dr$$

1. Mulliken population analysis:

(1955)

$$P_{\kappa\lambda} = 2 \sum_{j=1}^{n/2} c_{\kappa j}^* c_{\lambda j}$$

$$PM_{\mu\nu} = (PS)_{\mu\nu}$$

Population matrix

$$\sum_{\mu,\nu} PM_{\mu\nu} = N$$

$$GOP_\mu = \sum_\nu PM_{\mu\nu}$$

Gross orbital population

$$GAP_A = \sum_{\mu \in A} GOP_\mu$$

Gross atom population

$$q_A = Z_A - \sum_{\mu \in A} (PS)_{\mu\nu} \quad N = 2 \sum_i^{n/2} \int d\vec{r} |\varphi_i(\vec{r})|^2 = \sum_\mu^B \sum_\nu^B P_{\mu\nu} S_{\mu\nu} = \sum_\mu (PS)_{\mu\mu} = tr(PS)$$

Most common approach, however not very reliable

- charge due to overlap is equally distributed between two atoms
- strongly depends on the basis set
- use of diffuse function can lead to true nonsences

Diagonal elements –
Occupation of AO (GOA)

Charge distribu

One-electron propert

Electric multipole

$$\langle x^k y^l z^m \rangle = \sum_i^{atoms} Z_i x^k y^l z^m$$

	STO-3G	3-21G	6-31G	6-311G	6-31G*	6-31G**	cc- pVDZ	cc- pVTZ	cc- pVQZ
C ₁	0.343	0.830	0.688	0.667	0.771	0.752	0.290	0.397	0.572
O ₁	-0.287	-0.601	-0.528	-0.487	-0.561	-0.564	-0.358	-0.385	-0.464
O ₂	-0.321	-0.709	-0.693	-0.661	-0.731	-0.615	-0.282	-0.325	-0.411
H ₁	0.225	0.408	0.431	0.422	0.476	0.363	0.174	0.241	0.262
C	-0.214	-0.680	-0.513	-0.582	-0.587	-0.412	-0.017	-0.278	-0.272
H	0.084	0.251	0.205	0.215	0.209	0.156	0.065	0.112	0.094
H	0.084	0.251	0.205	0.215	0.209	0.156	0.065	0.112	0.094
H	0.085	0.249	0.204	0.214	0.215	0.162	0.062	0.125	0.124

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Population matrix

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$$GOP_{\mu} = \sum_{\nu} PM_{\mu\nu}$$

Gross orbitl population

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Gross atom population

$$q_A = Z_A - \sum_{\mu \in A} (PS)_{\mu\nu}$$

$$N = 2 \sum_i^{n/2} \int d\vec{r} |\varphi_i(\vec{r})|^2 = \sum_{\mu} \sum_{\nu} P_{\mu\nu} S_{\mu\nu} = \sum_{\mu} (PS)_{\mu\mu} = tr(PS)$$

Most common approach, however not very reliable

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- strongly depends on the basis set
- use of diffuse function can lead to true nonsences

Diagonal elements –
Occupation of AO (GOA)

Charge distribution

$$\text{One-electron properties: } \hat{O}_1 = \sum_{i=1}^n \hat{o}(i) \quad \langle O_1 \rangle = \langle \Psi_0 | \hat{O}_1 | \Psi_0 \rangle = \sum_i^{n/2} (\varphi_i | \hat{o} | \varphi_i) = \sum_{\mu\nu}^B P_{\mu\nu} (\chi_\mu | \hat{o} | \chi_\nu)$$

Electric multipole moments:

$$\langle x^k y^l z^m \rangle = \sum_i^{\text{atoms}} Z_i x^k y^l z^m - \int_V \Psi_0(r) \left(\sum_j^{\text{electrons}} x^k y^l z^m \right) \Psi_0(r) dr$$

1. Mulliken population analysis:

$$q_A = Z_A - \sum_{\mu \in A} (PS)_{\mu\nu}$$

$$P_{\kappa\lambda} = 2 \sum_{j=1}^{n/2} c_{\kappa j}^* c_{\lambda j}$$

Most common approach, however not very reliable

- charge due to overlap is equally distributed between two atoms
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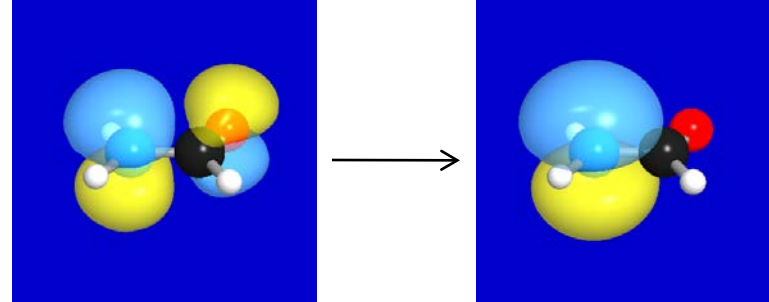
2. Lowdin population analysis

$$q_A = Z_A - \sum_{\mu \in A} (S^{1/2} P S^{1/2})_{\mu\nu}$$

Problem of MPA partially due to the use of nonorthogonal set of AO

=> transformation to orthogonal set of AO

=> contribution due to overlapping AO disappear (nondiagonal elements of **S** matrix are zero)



3. Natural Bond Orbital Analysis (NBO):

Defines atomic orbitals that are well adapted to the chemical environment of the atom.

Unitary transformation of canonical MO to “Lewis structure like” MO.

Partitioning the density matrix and overlap matrix over atomic blocks.

Natural atomic “preorbitals” are obtained by diagonalization of individual atomic blocks.

Preorbitals divided into two groups: (i) occupied orbitals form a Natural Minimal Basis and (ii) other orbitals form Natural Rydberg Basis.

Both blocks are then diagonalized, respecting the maximum occupancy => Natural Atomic Orbitals which give Natural Population (NAP).

Almost does not depend on the basis set.

Molecular electrostatic potentials are not reproduced too well.

4. Bader’s Topological Analysis

Charges derived by integration of electron density over the regions attributed to individual atoms.

The regions encompassing the atoms are delimited by surfaces that satisfy the “zero-flux” condition:

$$\nabla \rho(r) \cdot n(r) = 0 \quad N_{elec}(i) = \int_{\Omega_i} \rho(r) dr$$

$n(r)$ is a vector normal to the surface

The most “physical” approach.

Molecular electrostatic potential are not always described well

5. Potential Derived Charges

Calculating potentials on a grid of points (from the wavefunction)

Fitting the atomic charges to represent the potential on the grid

Electrostatic potential (ESP) - used for charges in several force field (Amber)

Good description of interaction between molecules

Using grid on the 1.8-2.5 times scaled VdW surface; multilayer grid

	Experiment	MP2 6-31G(d)	HF/6-31G(d)			
			[D]	$\langle\mu\rangle$	$\langle\mu\rangle$	Mulliken
water	1,85	2,16	2,20	2,39	2,25	2,63
methanol	1,70	1,77	1,87	2,68	1,85	3,00
formaldehyde	2,33	2,17	2,67	3,15	2,67	3,97
acetone	2,88	2,64	3,11	3,80	3,15	4,65
cyclopropanone	2,67	2,58	3,15	3,65	3,19	2,43
acetic acid	1,70	1,46	1,79	2,00	1,83	2,37
furan	0,66	0,60	0,77	1,96	0,74	1,75
methanethiol	1,52	1,78	1,79	-0,86	1,75	0,71
RMS error		0,21	0,31	0,93	0,33	1,05

Gaussian input/output

Keyword: Pop (Population)

Options:

Minimal, Regular, Full - do MPA for a given subset of orbitals

NO (NaturalOrbitals) - do NBO analysis

MK - do ESP charge fitting

Molecular structures

Table 8-2. Effect of gradient corrections on computed bond lengths for different bonding situations [\AA].

Bond		SVWN ^a	BLYP ^a	SVWN ^b	BLYP ^b	BP86 ^b	BPW91 ^b	Experiment
H-H	$R_{\text{H-H}}$	0.765	0.748	0.765	0.748	0.752	0.749	0.741
H ₃ C-CH ₃	$R_{\text{C-C}}$	1.513	1.541	1.510	1.542	1.535	1.533	1.526
	$R_{\text{C-H}}$	1.105	1.104	1.101	1.100	1.102	1.100	1.088
H ₂ C=CH ₂	$R_{\text{C-C}}$	1.331	1.341	1.327	1.339	1.337	1.336	1.339
	$R_{\text{C-H}}$	1.098	1.095	1.094	1.092	1.094	1.092	1.085
HC≡CH	$R_{\text{C-C}}$	1.212	1.215	1.203	1.209	1.210	1.209	1.203
	$R_{\text{C-H}}$	1.078	1.073	1.073	1.068	1.072	1.070	1.061

^a 6-31G(d) basis set; ^b 6-311++G(d,p) basis set.

H-X ... too long
 C-C ... too short
 C=C ... O.K.
 C≡C ... too long

Hybrid functional (B3LYP) – reasonable geometries

Table 8-4. Compilation of mean absolute deviations for bond lengths [\AA] / bond angles [degrees] for small main group molecules from different sources.

32 1st row species, 6-31G(d) basis, Johnson, Gill, and Pople, 1993			
HF	0.020 / 2.0	SVWN	0.021 / 1.9
MP2	0.014 / 1.8	BLYP	0.020 / 2.3
QCISD	0.013 / 1.8		
33 1st row species, TZ2P basis, Laming, Termath, and Handy, 1993			
SVWN	0.090 / 1.9	CAM(A)LYP	0.007 / 1.7
BLYP	0.013 / 1.7	CAM(B)LYP	0.009 / 1.5
13 species, Martin, El-Yazal, and François, 1995a			
CCSD(T)/cc-pVDZ	0.018 / 2.2	B3LYP/cc-pVDZ	0.009 / 1.7
CCSD(T)/cc-pVTZ	0.014 / 0.6	B3LYP/cc-pVTZ	0.004 / 0.3
CCSD(T)/cc-pVQZ	0.002 / 0.4	B3LYP/cc-pVQZ	0.004 / 0.3
20 organic molecules, Rauhut and Pulay, 1995			
BLYP/6-31G(d)	0.012 / 0.6	B3LYP/6-31G(d)	0.003 / 0.5

Vibrational frequency

Table 8-7. Frequency scaling factors, rms deviation, proportion outside a 10 % error range and listings of problematic cases [cm^{-1}] for several methods employing the 6-31G(d) basis set. Taken from Scott and Radom, 1996.

Method	f^a	RMS ^b	10 % ^c	Problematic Cases (Deviations larger than 100 cm^{-1})
HF	0.8953	50	10	233(O ₂), 221(O ₃ , F ₂), 180(¹ A ₁ -CH ₂), 164(F ₂ O), 139(N ₂), 120(N ₂ F ₂), 115(HOF, NF ₃), 103(NCIF ₂)
MP2	0.9434	63	10	660(O ₃), 304(NO ₂), 277(N ₂), 225(O ₂), 150(HF), 149(¹ A ₁ -CH ₂), 142(HC ₂ H), 136(HC ₄ H), 131(CINS), 120(CIC ₂ H), 117(H ₂), 115(³ B ₂ -CH ₂), 111(C ₂ N ₂), 101(FCN)
QCISD	0.9537	37	6	202(¹ A ₁ -CH ₂), 129(HF), 117(C ₂ H ₂), 101(O ₃)
BLYP	0.9945	45	10	224(¹ A ₁ -CH ₂), 189(H ₂), 165(HF), 116(OH), 113(SO ₃), 112(³ B ₁ -CH ₂), 111(SO ₂), 109(C ₂ H ₂)
BP86	0.9914	41	6	229(¹ A ₁ -CH ₂), 142(H ₂), 115(HF), 114(³ B ₂ -CH ₂), 106(F ₂)
B3LYP	0.9614	34	6	204(¹ A ₁ -CH ₂), 132(HF), 125(F ₂), 121(H ₂), 110(O ₃)
B3P86	0.9558	38	4	204(¹ A ₁ -CH ₂), 146(F ₂), 139(O ₃)
B3PW91	0.9573	34	4	204(¹ A ₁ -CH ₂), 140(F ₂), 137(O ₃)

^a Scale factor; ^b root mean square error after scaling in cm^{-1} ; ^c percentage of frequencies that fall outside by more than 10 % of the experimentally observed fundamentals.

Infrared intensities:

Intensity is related to the square of the infinitesimal change of the electric dipole moment with respect to the normal coordinate q :

$$I_a = C \left| \frac{\partial \mu}{\partial q_a} \right|^2 = -C \left| \frac{\partial^2 E}{\partial F \partial q_a} \right|^2$$

(C ... numerical constant, includes degeneracy)

“Double harmonic approximation” - brings about 10% error.

Electron correlation important.

Flexible basis set required.

Molecule	Vibration	exp.	CCSD(T)	QCISD	SVWN	SVWN	SVWN	BP86	BLYP	BLYP	B3LYP	B3LYP	B3LYP	
(<i>symm.</i>)	(<i>irrep</i>)		TZ2Pf ^a	Basis L ^b	6-31G(d)	TZP	Basis L	TZP	6-31G(d)	Basis L	6-31(d)	cc-pVTZ	Basis L	
HCN	ω_1 (σ)	54	64	65.5	61.1				76.6	46.2	58.6	52.5	60.7	67.4
(C _{∞v})	ω_2 (π)	46	71	69.4	71.2				73.8	65.8	75.6	71.0	72.6	72.8
	ω_3 (σ)	0.1	0.1	0.66	0.8				0.7	0.3	0.2	2.0	1.3	1.4
CO ₂	ω_2 (π_u)	48	59	68.0	47.4				51.8	43.2	48.1	61.4	63.7	64.1
(D _{∞h})	ω_3 (σ_u)	548	634	708.4	442.5				563	428.1	562.3	545.8	629.2	677.1
H ₂ O	ω_1 (a_1)	2.2	4.7	4.8	2.1	3.8	5.3	0.7	0.0	1.6	1.7	3.2	4.5	
(C _{2v})	ω_2 (a_1)	63.9	69.5	68.0	79.1	79.5	72.2	68.6	62.7	63.6	75.8	69.5	72.1	
	ω_3 (b_2)	48.2	48.4	56.1	28.0	65.9	72.3	42.0	8.0	45.4	19.4	40.8	60.2	
H ₂ CO	ω_1 (a_1)	75.5±7	59.4	62.6	57.5	70.7	72.4	79.5	63.1	81.1	55.9	69.2	72.3	
(C _{2v})	ω_2 (a_1)	74±5	74.5	88.7	91.7	110.9	106.6	107.	87.1	102.6	98.7	107.1	112.5	
								0						
	ω_3 (a_1)	11.2±1	10.6	12.4	4.7	9.6	9.3	10.4	6.6	11.1	6.4	9.9	12.0	
	ω_4 (b_1)	6.5±0.6	4.4	5.8	2.9	6.1	7.1	4.9	1.5	5.8	1.4	3.2	5.7	
	ω_5 (b_2)	87.6±8	108.4	91.5	170.7	117.5	115.7	145.	195.4	137.3	164.7	145.1	114.2	
								1						
	ω_6 (b_2)	9.9±1	12.0	11.8	7.9	8.3	8.4	9.4	9.9	9.4	12.6	12.8	11.7	
NH ₃	ω_1 (a_1)	7.6±0.9	2.3	3.8	0.3	4.1	3.2	7.4	3.6	7.3	0.8	2.4	4.0	
(C _{3v})	ω_2 (a_1)	138±6	147	141.4	218.1	139.5	156.8	120.	120.8	131.3	156.1	146.7	150.0	
								6						
	ω_3 (e)	3.8±0.8	3.8	6.6	1.2	17.6	23.1	5.1	7.0	4.2	1.0	1.1	9.2	
	ω_4 (e)	28.2±0.5	31	27.6	39.8	36.7	38.8	33.4	23.2	29.4	30.6	33.6	32.8	

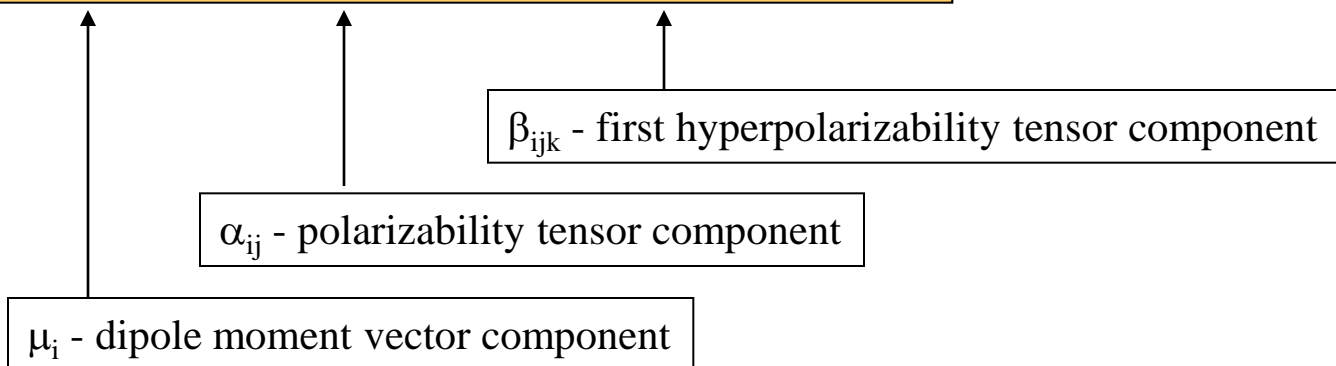
Electric properties

Molecule in electric field F - charge density is modified.

Derivatives of energy taken at zero field - static response properties of the molecule.

Energy can be described in terms of a Taylor expansion:

$$E(\vec{F}) = E(\vec{0}) + \sum_i \left(\frac{\partial E}{\partial F_i} \right)_0 F_i + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 E}{\partial F_i \partial F_j} \right)_0 F_i F_j + \frac{1}{6} \sum_{i,j,k} \left(\frac{\partial^3 E}{\partial F_i \partial F_j \partial F_k} \right)_0 F_i F_j F_k + \dots$$



Polarizability - measure of the ease with which the charge density of a system will get distorted by an external field

Polarizability is related to excitation energy: $\alpha \propto \sum_{n=1} \frac{1}{E_0 - E_n}$

E_n - energy of n th excited state

Calculations require large basis sets including diffuse and polarization function

Table 10-2: Average Polarizabilities $\langle\alpha\rangle$ for selected molecules [in a.u., 1 a.u. = 0.1482 Å³]

Molecule	HF POL ^a	MP2 POL ^a	SVWN numerical ^b	SVWN POL ^a	SVWN TZVP-FIP ^c	BLYP POL ^a	BLYP TZVP-FIP ^c	B3LYP POL ^a	B3LYP d-augTZ ^d	HCTH(AC) POL ^e	PBE1PBE POL ^f	Exp. ^{a,d}
HF	4.88	5.67	6.23	6.17	5.94	6.26	6.00	5.83	5.79	5.60	5.67	5.60
HCl	16.67	17.37		18.43		18.54		17.90	17.99	17.77	17.58	17.39
F ₂	8.58	8.22		8.82		8.96		8.69	8.46	8.43	8.37	8.38
Cl ₂	29.89	30.56		31.70		31.97		31.16	31.27	30.84	31.05	30.35
CH ₄	15.91	16.54	17.70	18.01		17.59		17.03	17.25	16.51	16.86	17.27
SiH ₄	29.97	31.04		34.28		33.14		32.25	32.13			31.90
NH ₃	12.94	14.42	15.54	15.57	14.96	15.62	14.94	14.73	14.73	14.25	14.34	14.56
PH ₃	29.93	30.69		32.52		32.13		31.35	31.32	31.07	31.03	30.93
H ₂ O	8.51	9.80	10.60	10.54	10.20	10.64	10.26	9.96	10.01	9.67	9.69	9.64
H ₂ S	23.77	24.70		26.13	24.95	26.07	24.72	25.24	25.19	24.99	24.60	24.71
CO	12.23	13.09	13.70	13.62	13.39	13.66	13.43	13.18		13.03		13.08

^a taken from Cohen and Tantirungrotechai, 1999 and McDowell, Amos and Handy, 1995; ^b taken from Dickson and Becke, 1996; ^c taken from Calaminici, Jug and Köster, 1998; ^d taken from van Caillie and Amos, 1998; taken from Tozer and Handy, 1998; taken from Adamo et al., 1999.

- DFT (LDA and GGA) systematically overestimate polarizabilities
- problem of incorrect asymptotic decay
- hybrid functionals and functionals with correct decay - performs better

FIP – field induced polarization

Hyperpolarizability - mostly determined by electron density in long range
 Calculations require even larger basis sets including diffuse and polarization function.
 Problems related to incorrect asymptotic behavior becomes more serious.

Table 10-4: Average first hyperpolarizabilities $\langle\beta\rangle$ for selected molecules [in a.u.]

Molecule	accurate ab initio ^a	SVWN numerical ^b	SVWN aug- POL ^c	SVWN TZVP- FIP ^d	SVWN aug-STO- VTZP ^e	BLYP aug- POL ^c	BLYP TZVP- FIP ^d	BLYP aug-STO- VTZP ^e	B3LYP aug- POL ^c	B77-1 aug- POL ^c	HCTH(AC) aug-POL ^c	LB94 aug-STO- VTZP ^e
HF	-7.3	-9.2	-8.9	-9.6	-9.2	-8.7	-9.9	-9.5	-7.4	-7.2	-7.4	-6.9
H ₂ O	-18.0	-24.8	-24.8	-22.4	-25.7	-24.4	-22.3	-27.1	-19.2	-18.7	-18.3	-16.7
H ₂ S	-7.7		-14.7	-9.1		-10.5	-9.8		-7.2	-7.4	-10.2	
NH ₃	-34.3	-55.6	-55.7	-34.1	-55.4	-58.6	-34.9	-64.6	-41.0	-38.9	-33.3	-30.5
H ₂ CO	40.3		90.7			90.9			67.1	64.1	43.1	
CH ₃ F	40.3		63.7			62.3			50.6	49.7	34.3	
CH ₃ CN	-40.4		-61.6			-64.2			-52.9	-46.3	-145.5	
CO	23.5, 26.6	30.5	29.5	22.9	30.5	29.3	22.0	31.1	26.9	26.3	22.6	20.6

^a from different sources, quoted in Cohen, Handy and Tozer, 1999 and van Gisbergen, Snijders and Baerends, 1998b; ^b taken from Dickson and Becke, 1996; ^c taken from Cohen, Handy and Tozer, 1999; ^d taken from Calaminici, Jug, and Köster, 1998; ^e taken from Gisbergen, Snijders and Baerends, 1998b.

Magnetic properties

Presence of external magnetic fields => interaction with nuclear or electron spin (NMR, EPR).

Electron correlation important, flexible basis set required.

Second order properties:

$$\sigma_{st} \propto \left. \frac{\partial^2 E}{\partial X_s \partial Y_t} \right|_{\bar{X}=\bar{Y}=0}$$

X ~ B (magnetic field) AND Y ~ nuclear magnetic moment	=> nuclear shielding tensor
X ~ B (magnetic field) AND Y ~ electronic spin	=> ESR g-tensor
X AND Y - two different nuclear magnetic moments	=> spin-spin coupling constant

Exchange-correlation functional should depend on current density j induced by the magnetic field.

$$E_{xc}[\rho(\vec{r}), j(\vec{r})] \quad \text{Usually omitted.}$$

Gauge-problem:

Normal straightforward implementation - results depends on the choice of coordination system.

Gauge-invariance - accomplished with the use of

IGLO - individual gauges for localized orbitals

GIAO - gauge-invariant atomic orbitals

Chemical shifts

Problem case: O₃

Table 11-2: Absolute ¹⁷O NMR chemical shifts [in ppm] for ozone

Nucleus	HF ^a	MP2 ^a	CCSD(T) ^b	LDA ^a	BLYP ^a	B3LYP ^a	PBE0 ^c	Exp.
O _{terminal}	-2793	+1055	-1208	-1520	-1454	-1673	-1453	-1290 ^b , -1254 ^c
O _{central}	-2717	+2675	-754	-914	-892	-1115	-1040	-724 ^b , -688 ^c

Table 11-1: Absolute and relative (in parentheses, with respect to CH₄, NH₃, and H₂O)
¹³C, ¹⁵N, and ¹⁷O NMR chemical shifts [in ppm].

Molecule	Nucl.	HF ^a	MP2 ^a	LDA ^a	BLYP ^a	B3LYP ^a	PBE0 ^b	Exp. ^a
CH ₄	C	195.7	201.5	193.7	187.5	189.6	194.0	195.1
NH ₃	N	262.6	276.2	266.1	259.2	260.3	263.1	264.5
H ₂ O	O	326.9	344.8	332.3	326.4	325.7	328.9	344.0
C ₂ H ₆	C	184.0	188.0	176.7	169.7	173.6	179.7	180.9
		[11.7]	[13.5]	[17.0]	[17.8]	[16.0]	[14.3]	[14.2]
C ₂ H ₄	C	59.9	71.2	42.3	47.1	48.7	58.4	64.5
		[135.8]	[130.3]	[151.4]	[140.4]	[140.9]	[135.6]	[130.6]
C ₂ H ₂	C	113.9	123.3	100.0	105.7	106.3	114.0	117.2
		[81.8]	[78.2]	[93.7]	[81.8]	[83.3]	[80.0]	[77.9]
CH ₃ F	C	124.5	121.8	103.2	101.2	106.6	116.5	116.8
		[71.2]	[79.7]	[90.5]	[86.3]	[83.0]	[77.5]	[78.3]
CH ₃ CN	C _{term}	190.9	193.6	182.3	177.1	180.4	187.7	187.7
		[4.8]	[7.9]	[11.4]	[10.4]	[9.2]	[6.3]	[7.4]
	C _{centr}	60.6	76.1	54.7	57.8	57.4	68.2	73.8
		[135.1]	[125.4]	[139.0]	[129.7]	[132.2]	[125.8]	[121.3]
	N	-46.6	-13.2	-44.7	-36.5	-40.7	-24.4	-8.1
		[309.2]	[289.4]	[310.8]	[295.7]	[301.0]	[287.5]	[272.6]
CH ₃ OH	C	143.7	142.2	126.1	122.0	127.4	136.5	136.6
		[52.0]	[59.3]	[67.6]	[65.5]	[62.2]	[57.5]	[58.5]
	O	274.7	350.6	334.5	313.9	321.6	334.7	
		[52.2]	[-5.8]	[2.2]	[10.9]	[4.1]	[-5.8]	
CO ₂	C	47.8	63.5	47.2	47.9	46.9	56.8	58.5
		[147.9]	[138.0]	[146.5]	[139.6]	[142.7]	[137.2]	[136.6]
	O	214.8	241.0	203.3	206.5	206.9	220.0	243.4
		[112.1]	[103.8]	[129.0]	[118.3]	[118.8]	[108.9]	[100.6]
Mean abs.	C	8.5	5.6	15.2	15.0	13.0	3.1	
Deviation		[8.1]	[1.6]	[14.4]	[7.8]	[7.9]	[2.5]	

- LDA fails
- GGA and hybrid functionals give reasonable results, better than HF
- MP2 is generally better than GGA but it may completely fail

Hyperfine coupling constants:

anisotropic term - interaction between the magnetic moments of the electrons and the nuclei

isotropic term - interaction between the nuclear spin and the spin of the unpaired electron

$$A_I^{iso} = C \sum_{\mu}^K \sum_{\nu}^K P_{\mu\nu}^{\alpha-\beta} \int \eta_{\mu} \delta(\vec{r}_I) \eta_{\nu} d\vec{r}$$

C ... constant, depends on the nucleus I

P ... difference between the density matrices of electrons with up and down spins

δ ... Dirac delta function which ensures that only the density at the position of the nucleus I is taken

Sensitive to the molecular geometry.

Requires electron correlation and flexible basis set.

Table 11-5: Isotropic hyperfine structures [Gauss]

Molecule	Parameter	PW86 ^a	B3LYP ^b	PBE0 ^b	Exp. ^{a,b}
CH ₃	A _H	-20.8	-23.3	-26.1	-23, -25.1
	A _C	32.8	29.8	29.2	≈38, 28.4
CH ₂ O ⁺	A _H	133.3	130.3	134.2	133
	A _C	-31.8	-33.5	-34.6	-39
	A _O	-12.6	-15.4	-14.5	

Taken from ^aEriksson et al., 1994 and ^bAdamo, Cossi and Barone, 1999.