Molecular Properties

All Those Operators that *Aren't* Energy

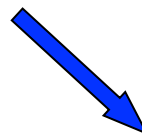## Video IV.viii

Winter School in Physical Organic Chemistry (WISPOC)
Bressanone, January 27–31, 2008

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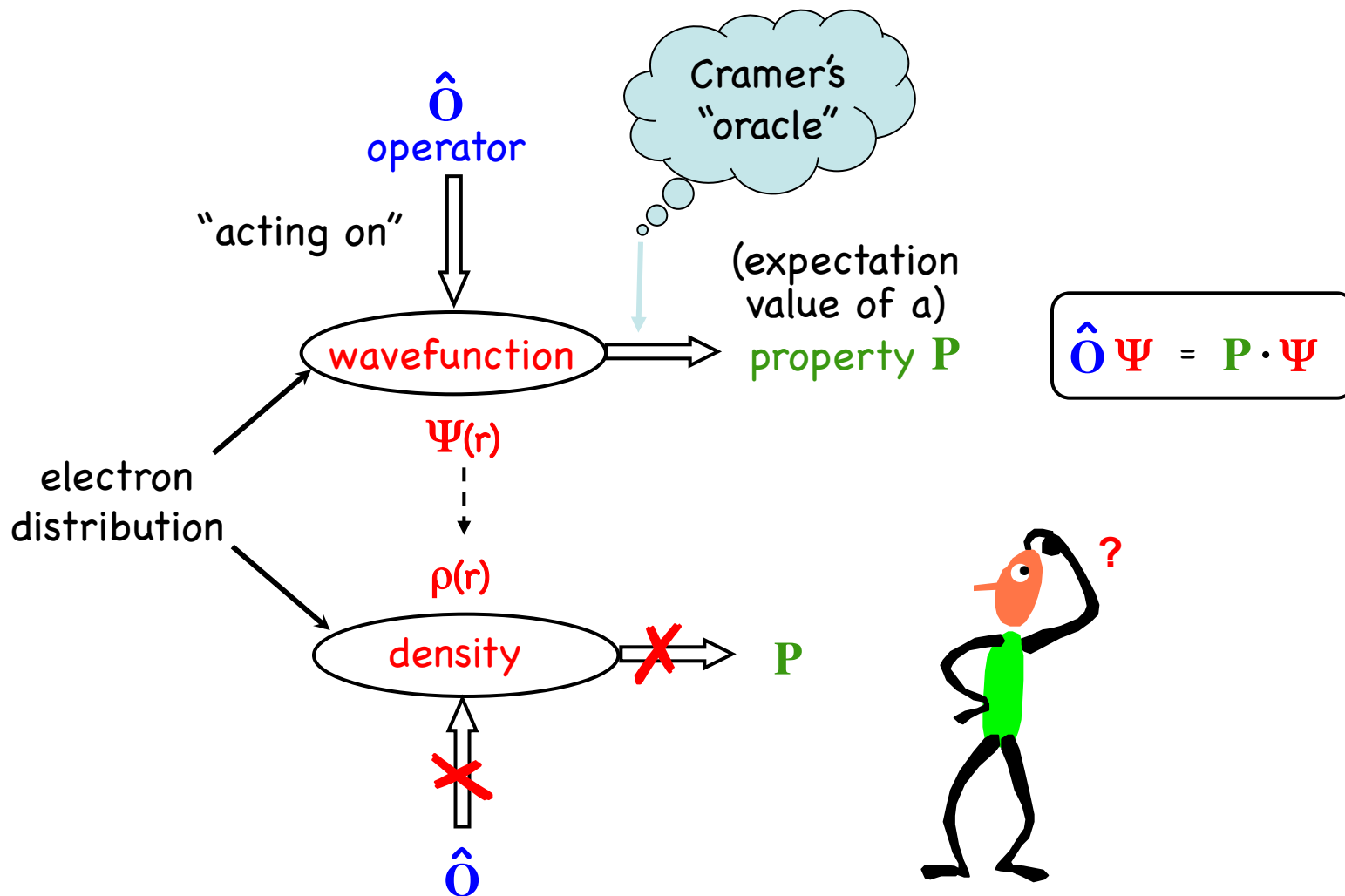Lecture 1:   • ground state properties

ground state properties

bulk properties

– density
– viscosity, hardness
– dielectric constant
– melting point
⋮

molecular properties

– dipole moment
– polarizability
– NMR chemical shift
– vibrational frequency
⋮

Molecular properties usually depend explicitly on the electron distribution

$\hat{O}$
operator

"acting on"

Cramer's "oracle"

wavefunction

Ψ(r)

(expectation value of a) property **P**

$$\hat{O}\,\Psi = \mathbf{P} \cdot \Psi$$

electron distribution

ρ(r)

density

P

$\hat{O}$

?

a more general approach

property = response of a molecule to a perturbation (λ)

change in energy

- change in geometry (R)
- external electric field (F)
- external magnetic field (M)
- nuclear magnetic field (I)

Taylor expansion: $E(\lambda) = E(0) + \dfrac{\partial E}{\partial \lambda}\lambda + \dfrac{1}{2}\dfrac{\partial^2 E}{\partial \lambda^2}\lambda^2 + \dfrac{1}{6}\dfrac{\partial^3 E}{\partial \lambda^3}\lambda^3 + \ldots$

$\underbrace{}$ $\underbrace{}$ $\underbrace{}$

first   second   third
order   order   order   **property**

λ is usually *directed,* i.e. represented by a *vector* (field)

$\Longrightarrow$ $\dfrac{\partial E}{\partial \lambda}$ = vector $\dfrac{\partial^2 E}{\partial \lambda^2}$ = matrix $\dfrac{\partial^3 E}{\partial \lambda^3}$ = tensor

properties that can be formulated (and calculated) as derivatives of the energy

nth derivative with regard to   change in geometry (R), external electric field (F)
external magnetic field (M, nuclear magnetic field (I)

n_R	n_F	n_B	n_I	Property

properties that can be formulated (and calculated) as derivatives of the energy

nth derivative with regard to

change in geometry (R), external electric field (F)
external magnetic field (M, nuclear magnetic field (I)

n_R	n_F	n_B	n_I	Property
1	0	0	0	Energy gradient **g**
2	0	0	0	Harmonic vibrational frequencies ω_i
3	0	0	0	(cubic) anharmonic corrections to vibrational frequecies $\omega_i x_i$

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0	1	0	0	Electric dipole moment μ
0	2	0	0	Electric polarizability α
0	3	0	0	(first electric) hyperpolarizability β

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0	0	1	0	Magetic (dipole) moment μ
0	0	2	0	magnetic susceptibility χ

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0	0	1	0	Magetic (dipole) moment μ
0	0	2	0	magnetic susceptibility χ
0	0	0	1	ESR hyperfine coupling constant a_i
0	0	0	2	Spin–spin coupling J_{ij} of different nuclei

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0	0	2	0	magnetic susceptibility χ
0	0	0	1	ESR hyperfine coupling constant a_i
0	0	0	2	Spin-spin coupling J_{ij} of different nuclei
1	1	0	0	Intensities of fundamental IR transitions
2	1	0	0	Intensities of overtones and combination bands in IR spectra

mixed derivatives

properties that can be formulated (and calculated) as derivatives of the energy

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0	0	2	0	magnetic susceptibility χ
0	0	0	1	ESR hyperfine coupling constant a_i
0	0	0	2	Spin-spin coupling J_{ij} of different nuclei
1	1	0	0	Intensities of fundamental IR transitions
2	1	0	0	Intensities of overtones and combination bands in IR spectra
1	2	0	0	Intensities of fundamental Raman transitions
2	2	0	0	Intensities of overtones and combination bands in Raman spectra

mixed derivatives
.
.

properties that can be formulated (and calculated) as derivatives of the energy

nth derivative with regard to   change in geometry (R), external electric field (F) external magnetic field (M, nuclear magnetic field (I)

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0	2	0	0	Electric polarizability α
0	3	0	0	(first electric) hyperpolarizability β
0	0	1	0	Magetic (dipole) moment μ
0	0	2	0	magnetic susceptibility χ
0	0	0	1	ESR hyperfine coupling constant a_i
0	0	0	2	Spin-spin coupling J_{ij} of different nuclei
1	1	0	0	Intensities of fundamental IR transitions
2	1	0	0	Intensities of overtones and combination bands in IR spectra
1	2	0	0	Intensities of fundamental Raman transitions
2	2	0	0	Intensities of overtones and combination bands in Raman spectra
0	1	1	0	Circular dichroism (CD)
0	2	1	0	Magnetic circular dichroism (MCD)

mixed derivatives
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properties that can be formulated (and calculated) as derivatives of the energy

nth derivative with regard to   change in geometry (R), external electric field (F) external magnetic field (M, nuclear magnetic field (I)

n_R	n_F	n_B	n_I	Property
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0	3	0	0	(first electric) hyperpolarizability β
0	0	1	0	Magetic (dipole) moment μ
0	0	2	0	magnetic susceptibility χ
0	0	0	1	ESR hyperfine coupling constant a_i
0	0	0	2	Spin-spin coupling J_{ij} of different nuclei
1	1	0	0	Intensities of fundamental IR transitions
2	1	0	0	Intensities of overtones and combination bands in IR spectra
1	2	0	0	Intensities of fundamental Raman transitions
2	2	0	0	Intensities of overtones and combination bands in Raman spectra
0	1	1	0	Circular dichroism (CD)
0	2	1	0	Magnetic circular dichroism (MCD)
0	0	1	1	Nuclear magnetic shielding ($\rightarrow$ chemical shift in NMR)

mixed derivatives
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1. perturbation = deviation from *equilibrium geometry* (Δq)

(molecule with ϕ = 3N–6 internal degrees of freedom)

$$E(\Delta q_i) = E(0) + \frac{\partial E}{\partial \Delta q_i}\Delta q_i + \frac{\partial^2 E}{\partial \Delta q_i \partial \Delta q_j}\Delta q_i \cdot \Delta q_j + \frac{\partial^3 E}{\partial "\Delta q_i^3"}"\Delta q_i^3" + \frac{\partial^4 E}{\partial "\Delta q_i^4"}"\Delta q_i^4" + \dots$$

= 0 at equilibrium

$\underbrace{}$ gradients g_i

$\underbrace{}$ harmonic force constants f_{ij}

$\underbrace{}$ cubic

$\underbrace{}$ quartic ......

force constants

Δq_i
- cartesian displacements
- bond strechings
- angle bendings ...

3N–6 normal modes $q_{n,i}$

IR– and Raman spectra

$$\begin{pmatrix} f_{11} & f_{12} & \cdots & f_{1\phi} \\ f_{21} & f_{22} & \cdots & f_{2\phi} \\ \vdots & \vdots & \ddots & \vdots \\ f_{\phi 1} & f_{\phi 2} & \cdots & f_{\phi\phi} \end{pmatrix}$$

matrix Λ

diagona-lization

$$\begin{pmatrix} n_{11} & 0 & \cdots & 0 \\ 0 & n_{22} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & n_{\phi\phi} \end{pmatrix}$$

atomic masses

3N–6 (harmonic!) vibrational frequencies

Intensities: calculated from mixed derivatives (see later)

prediction of vibrational spectra: some rules

1. calculation of vibrational spectra makes only physical sense *at potential energy minima*!

   always make sure that your structure is fully optimized, and that all frequecies are positive!

2. agreement between *individual* frequencies in calculated and measured vibrational spectra is *absolutely meaningless.*

   only a general agreement of the *entire spectral pattern* serves as an assignment tool. *All* important predicted bands should appear in the measured spectrum and vice versa!

3. big molecules (with no symmetry) have *very many* vibrational transitions

   the bigger your molecule, the more likely you will discern a general agreement between a calculated and a measured spectrum (if you kink your head and squint your eyes)

4. never use calculations as a substitute for chemical common sense.

   what you learned in analytical chemistry about *group frequencies* may be more useful than the results of quantum chemical calculations

5. never forget that what you calculate are always *fundamental harmonic* frequencies.
   - experimental spectra may contain *overtones, combination bands,* or *Fermi resonances*
   - deviations between theory and experiment may be due to anharmonicities

an example

UV-spectra in Ar/12K
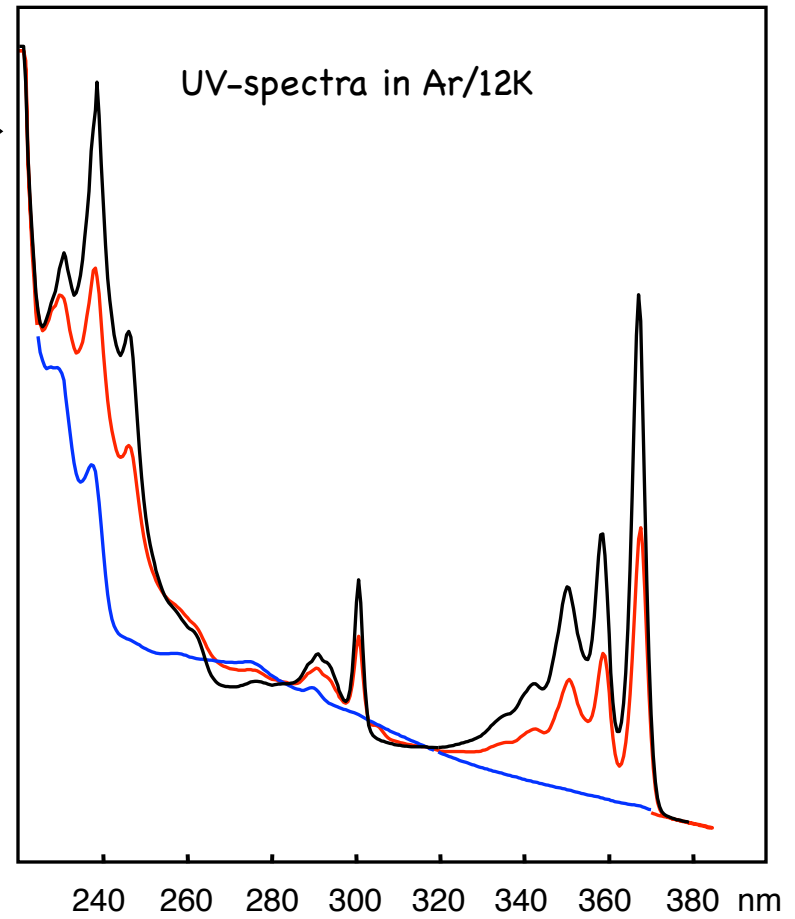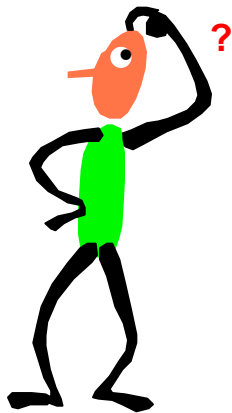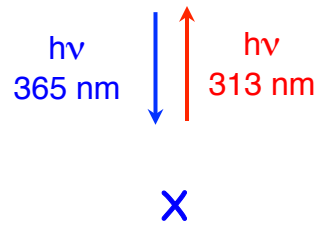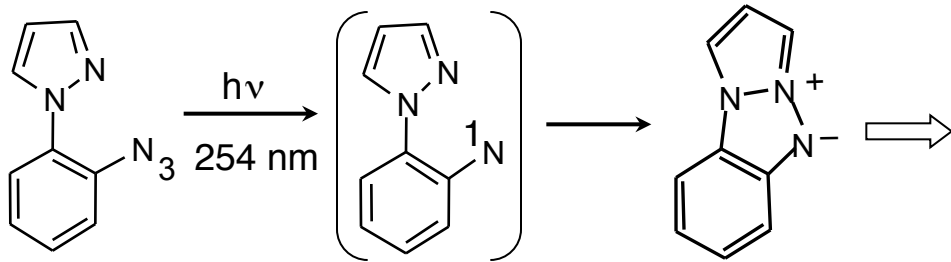
"pattern matching"
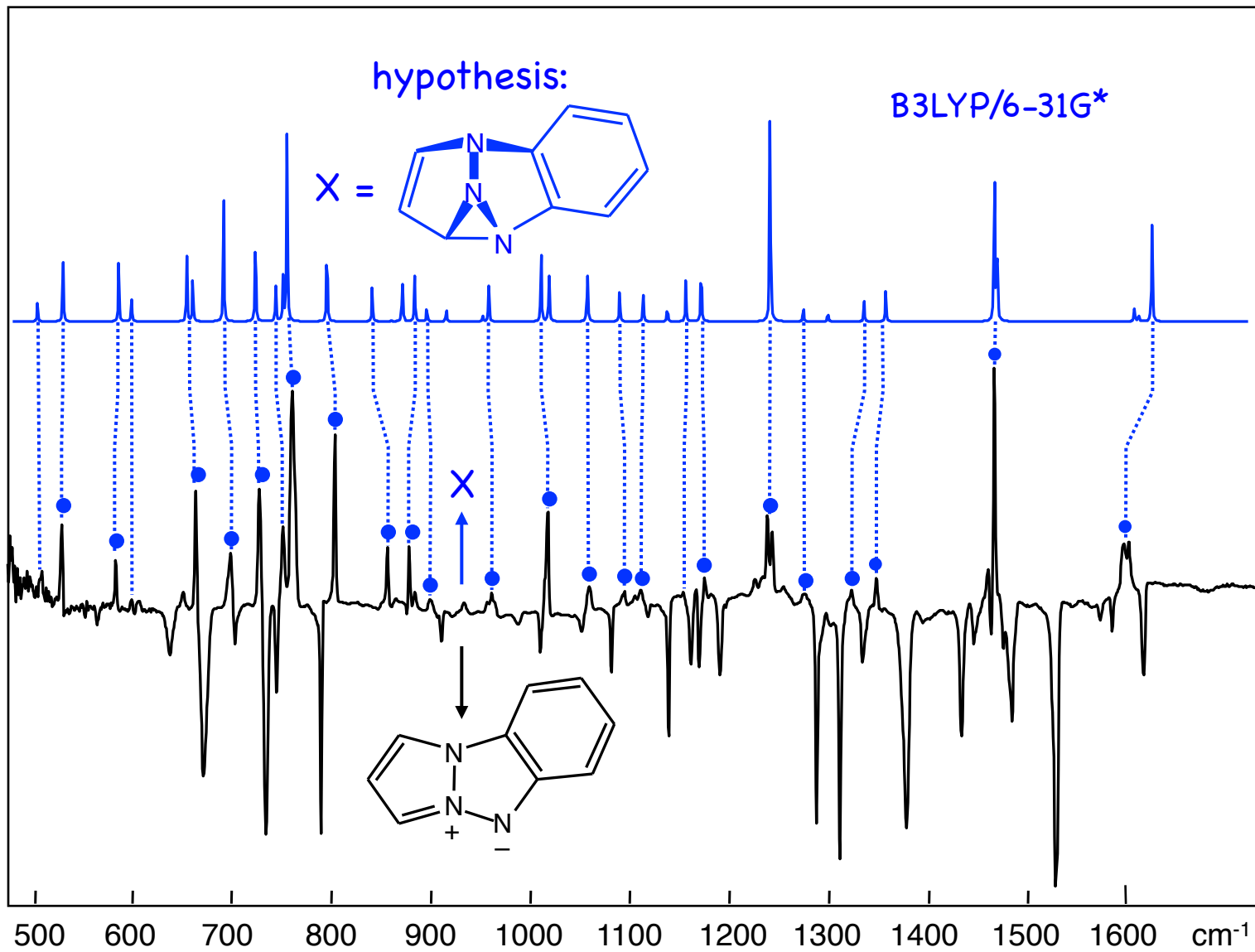
what method to use to calculate IR-spectra ?

see the large study by Scott and Radom, *J. Phys. Chem.* 100, 16502 (1996)
(122 molecules, 1066 fundamentals).

HF/6-31G*   large (100 cm^{-1}) systematic errors, many outliers

MP2/6-31G*   smaller (65 cm^{-1}) unsystematic errors, fewer outliers

BLYP/6-31G*   quite small (40 cm^{-1}) unsystematic errors, very few outliers

B3LYP/6-31G*   smaller (35 cm^{-1}) partially systematic errors, very few outliers

or other   no bigger   scale by a factor (ca 0.96)
hybrid   basis set
functionals   needed!

X-H stretching frequencies are usually off by more than the others, due to strong
anharmonicity. They are often not useful for identifying molecules, also because of
the presence of overtones and Fermi resonances in the region 2800-3300 cm^{-1}.

if your molecule is too big to run a frequency calculation with a hybrid DFT functional
and a DZP basis set, then it is probably too big to allow for a reliable comparison
between calculation and experiment.

2. perturbation = external electric field (F)

F = perturbation of the *potential energy term* V in the Hamiltonian
(quite simple to implement, as $\hat{V}$ is a simple multiplier)

$$E(F) = E(0) + \frac{\partial E}{\partial F} F + \frac{1}{2}\frac{\partial^2 E}{\partial F^2} F^2 + \frac{1}{6}\frac{\partial^3 E}{\partial F^3} F^3 + \ldots$$

μ_0	α	β	higher hyper-polarizabilities
dipole moment	polariz-ability	(first) hyperpol-arizability	

a) Dipole moments, μ_0/Debye

Molecule	exp	HF/ 6–31G*	MP2/ 6–31G*	B3LYP cc-pVTZ
CO	0.11	–0.26		
H_2O	1.85	2.20		
H_2S	0.97	1.41		
NH_3	1.47	1.92		
HF	1.83	1.98		

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H_2S	0.97	1.41	1.49	
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HF	1.8 3	1.9 8	1.9 8	

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H_2S	0.97	1.41	1.49	1.19
NH_3	1.47	1.92	1.92	1.59
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POL: Sadlei's pVTZ basis set, optimized for electrical properties

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H_2S	0.97	1.41	1.11	1.49	1.0 3	1.19
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H_2O	1.85	2.20	1.9 8	2.16	1.85	1.92	1.8 6
H_2S	0.97	1.41	1.11	1.49	1.0 3	1.19	1.01
NH_3	1.47	1.92	1.62	1.92	1.52	1.59	1.52
HF	1.8 3	1.98	1.92	1.9 8	1.80	1.8 3	1.80

POL: Sadlei's pVTZ basis set, optimized for electrical properties

$$\langle\alpha\rangle = 1/3\cdot(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$$

b) mean (static) polarizabilites, $\langle\alpha\rangle$/a.u.   (1 a.u.= 0.1482 Å³)

Molecule	exp	HF/ 6-31G*	HF/ POL	MP2/ 6-31G*	MP2/ POL	B3LYP cc-pVTZ	B3LYP POL
CO	13.08	9.25	12.23	9.54	13.09	11.11	13.18
H_2O	9.64	4.87	8.51	4.93	9.80	7.07	9.96
H_2S	24.71	14.45	23.77	14.20	24.70	18.54	25.24
NH_3	14.56	7.93	12.94	7.93	14.42	10.97	14.73
HF	5.60	2.68	4.88	2.73	5.67	1.95 (!)	5.83

Here, the POL basis set really helps!

$$\langle\beta\rangle = 3/5\cdot(\beta_{xxz}+\beta_{yyz}+\beta_{zzz})$$

c) mean (static) first hyperpolarizabilites, $\langle\beta\rangle$/a.u.

difficult to measure, comparisons can only be made to very good calculations

hybrid DFT methods do reasonably well, but *diffuse basis functions* are needed

3. perturbation = external magnetic field (B)

$$E(B) = E(0) + \underbrace{\frac{\partial E}{\partial B} B}_{m_0} + \underbrace{\frac{1}{2}\frac{\partial^2 E}{\partial B^2} B^2}_{\xi/\mu_0} + \ldots$$

m_0

(permanent)
magnetic
dipole moment

$\xi/\mu_0 \longrightarrow$ vacuum permeability

(relative)
magnetic
permeability

=0 for closed-shell compounds

related to the (macroscopic)
magnetic susceptibility

B interacts with the *magnetic moments* of the electrons caused by their *movement*, i.e. it is a perturbation to the *kinetic energy* or *momentum* term in the Hamiltonian. This perturbation is determined by the magnetic field's *vector potential* A(r).

Vector potentials are always defined relative to an *origin*, the "gauge" r_G.

➡ the results of calculations are origin or gauge-depenent!

Different solutions have been proposed to this problem. The two most popular are:

a) each basis function includes its own origin
(Gauge Including Atomic Orbitals, GIAO, London 1937

⬅ imlemented in the Gaussian program

b) MOs are localized such that they have their own origins
(Individual Gauge for Localized Orbitals, IGLO, Kutzlnigg 1982

3. perturbation = external magnetic field (B)

- rarely does one do calculations of magnetic susceptibilities.
- In practice, chemists use external magnetic fields as a means to let *other perturbations* manifest themselves (nuclear magnetic shielding, hyperfine coupling, MCD ...). such as:

4. perturbation = nuclear magnetic moments (I)

- nuclei j with nonzero spin (^1H, ^{13}C, ^{15}N ...) have magnetic moments I_j.
- These give rise to magnetic fields inside molecules.
- By analogy to the first three cases we write:

$$E(I_i, I_j \ldots) = E(0) \quad + \underbrace{\frac{\partial E}{\partial I_i} I_i}_{} \quad + \underbrace{\frac{\partial^2 E}{\partial I_i \partial I_j} I_i \cdot I_j}_{} + \ldots$$

ESR hyperfine coupling constant $\Longleftarrow a_i$

$h \cdot J_{ij} \Longrightarrow$ nuclear spin–spin coupling constant

5. two simultaneous perturbations

In the presence of two perturbation acting simultaneously, the energy is expanded in both perturbation, which leads to *mixed derivatives*, many of which are also related to molecular properties.

a) IR intensities: change in dipole moment μ for deformation along normal coordinate $q_{n,ii}$

in the "double harmonic approximation" (termination at first order):

$$\text{IR intensity } (q_{n,i}) \propto \left(\frac{\partial \mu}{\partial q_{n,i}} \right)^2 \propto \left(\frac{\partial^2 E}{\partial q_{n,i} \partial F} \right)^2$$

$$\text{dipole moment } \mu = \frac{\partial E}{\partial F}$$

b) Raman intensities: change in polarizability α for deformation along normal coordinate $q_{n,ii}$

in the "double harmonic approximation" (termination at first order):

$$\text{Raman intensity } (q_{n,i}) \propto \left(\frac{\partial \alpha}{\partial q_{n,i}} \right)^2 \propto \left(\frac{\partial^3 E}{\partial q_{n,i} \partial F^2} \right)^2$$

$$\text{polarizability } \alpha = \frac{\partial^2 E}{\partial F^2}$$

Note: IR- and Raman-intensities are proportional to derivatives of *electrical properties*. Remember that, to get those right, one needs special basis sets (e.g. Sadlej POL)

c) nuclear magnetic "shielding" (by the local magentic fields that arise from the circular movements of electrons induced by the external magnetic field B)

nuclear magnetic shielding constant σ (B) $\propto$ $\left(\dfrac{\partial\,^2 E}{\partial\,B\,\partial\,I_i} \right)^2$

$\Downarrow$

translates into NMR chemical shift

$\delta = 10^6 \times (\sigma - \sigma_0)(B)$

Finally, perturbations can also be *time dependent*.

In particular, electromagnetic radiation represents electric fields $F(t)$ and magnetic fields $B(t)$, oscillating with a frequency ω, which perturb the movements and the distribution of electrons in a molecule. See last lecture by Prof. Cramer

In particular electronic absorption spectra can be regarded (and calculated) as espressions of the *time-dependent polarizability* of a ground-state distribution of electrons (see last module by Prof. Cramer).

But now, back to applications!

Akorta et al. (Madrid)

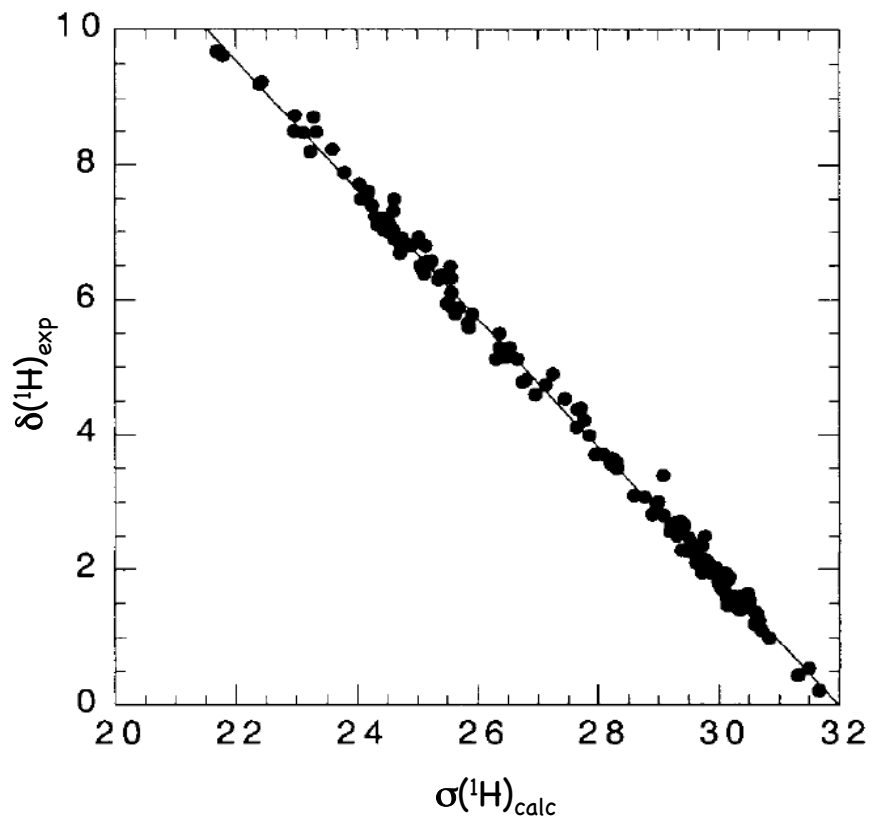461 ^{13}C chemical shifts calculated by GIAO/B3LYP/6-311++G(d,p)
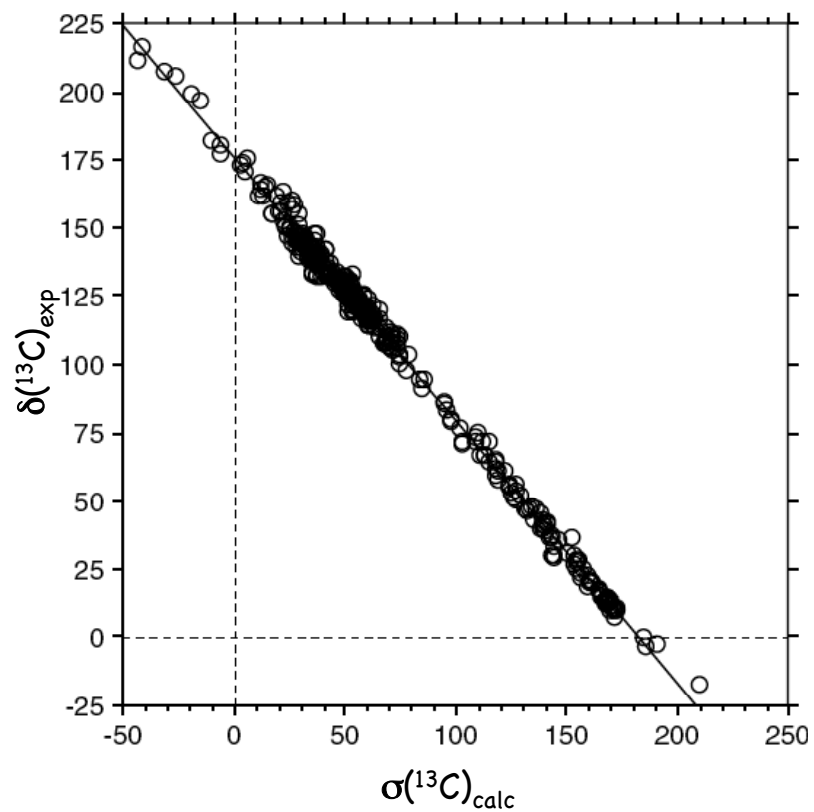
$$\delta(^{13}C)_{exp} = 175.7 - 0.963 \times \sigma(^{13}C)_{calc}$$

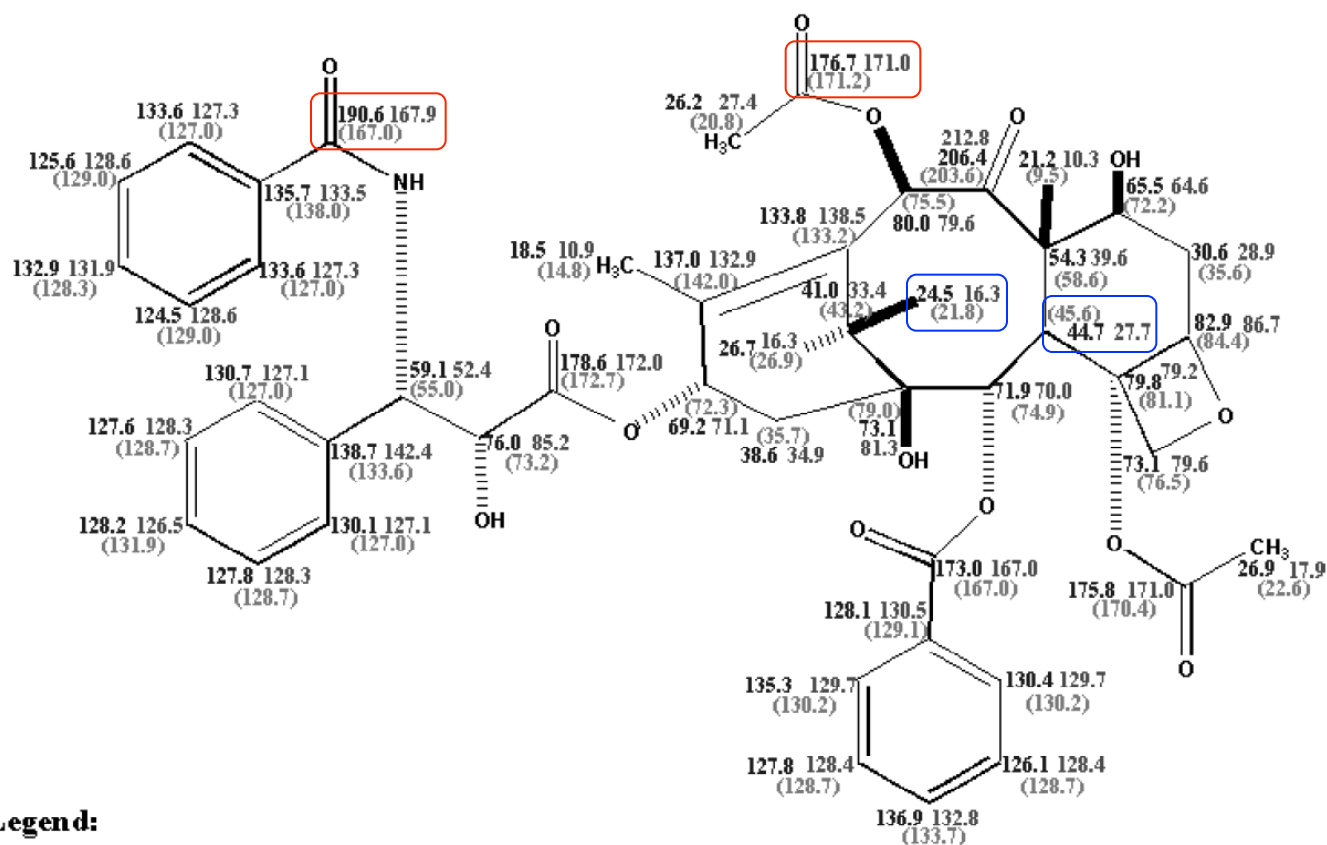$r^2 = 0.996$, rms error: 2.9 ppm

Rablen et al. (Swarthmore Coll.)

^{1}H chemical shifts of 80 organic compounds calculated by GIAO/B3LYP/6-311++G(d,p)

$$\delta(^1H)_{exp} = 30.6 - 0.957 \times \sigma(^1H)_{calc}$$

$r^2 = 0.996$, rms error: 0.15 ppm

Observed and Predicted ^{13}C Chemical Shifts for Taxol

Legend:

Gaussian 98 Shift   CS ChemNMR Pro Shift
    (Observed Shift)
Layout occasionally modified due to space constraints.

Chemical shifts are with respect to TMS.

b) nuclear spin-spin coupling constants J_{ij}

spin-spin coupling occurs by several mechanisms and, if computed quantum mechanically, is composed of several contributions (Fermi-contact, dipole-, spin-orbit coupling) which may be opposed. Errors in the prediction of some contributions may lead to large errors in J_{ij}.

	J_{ij} in Hz	B3LYP HIII	exp.
HF	$^1J_{FH}$	419.5	500 ± 20[f]
H_2O	$^1J_{OH}$	−71.8	−80.6[h]
	$^2J_{HH}$	−7.1	−7.11[h]
NH_3	$^1J_{NH}$	42.4	43.6[j]
	$^2J_{HH}$	−8.9	−10.0[j]
CH_4	$^1J_{CH}$	122.4	120.9[l]
	$^2J_{HH}$	−11.1	−12.0[l]
N_2	$^1J_{NN}$	1.6	1.8[n]
CO	$^1J_{CO}$	19.5	16.4[o]
C_2H_2	$^1J_{CC}$	200.8	184.5[t]
	$^1J_{CH}$	253.8	242.4[t]
	$^2J_{CH}$	52.2	53.8[t]
	$^3J_{HH}$	10.3	10.1[t]
C_2H_4	$^1J_{CC}$	70.1	67.5[v]
	$^1J_{CH}$	154.2	156.3[v]
	$^2J_{CH}$	−1.3	−2.4[v]
	$^2J_{HH}$	3.2	2.4[v]
	$^3J_{cis}$	11.0	11.7[v]
	$^3J_{trans}$	17.7	19.0[v]

[7s6p2d/4s2p]

↑

GIAO/B3LYP/HFIII basis set

Helgaker et al. *J. Chem. Phys.* 2000

⟹ seems to work quite well for rigid molecules

b) nuclear spin-spin coupling constants J_{ij}

how about conformationally flexible molecules ?

Karplus equation: $J_{HH} = C_0 + C_1 \cdot \cos(\omega) + C_2 \cdot \cos(2\omega)$

"exp": $C_0 = 7.8$, $C_1 = -1.0$, $C_2 = 5.6$

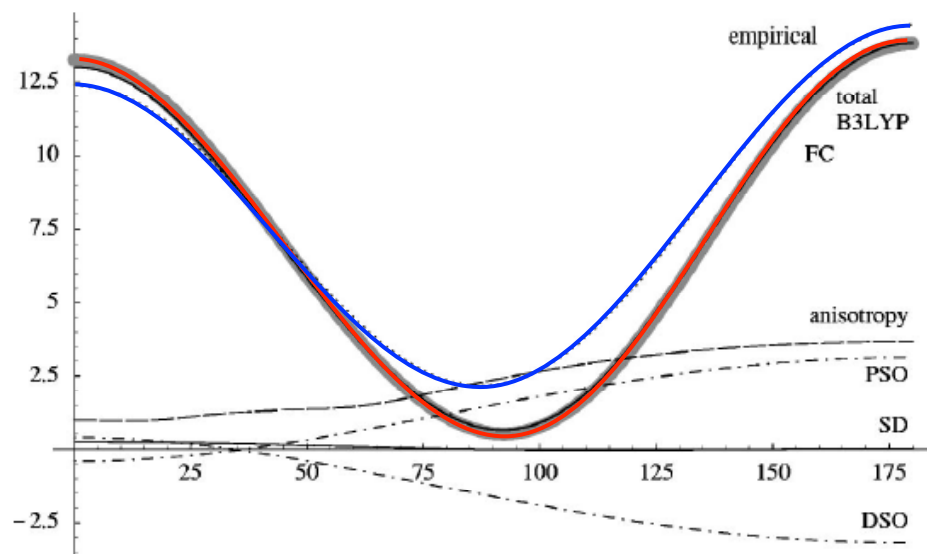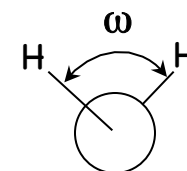calc: $C_0 = 7.0$, $C_1 = -0.1$, $C_2 = 6.5$

FIG. 2. The Karplus curve calculated at the B3LYP/HIII level compared with the empirical Durette–Horton curve. The Durette–Horton curve has been obtained by plotting (17); the B3LYP curves have been obtained by third-order polynomial fittings to successive calculated points for ϕ $= 0°, 10°, \ldots, 180°$.

[7s6p2d/4s2p]

GIAO/B3LYP/HFIII basis set