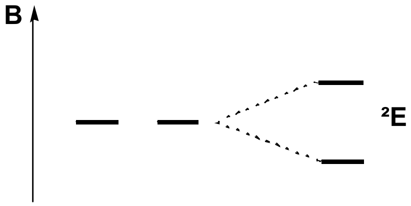
# 1. Introduction to NMR Spectroscopy

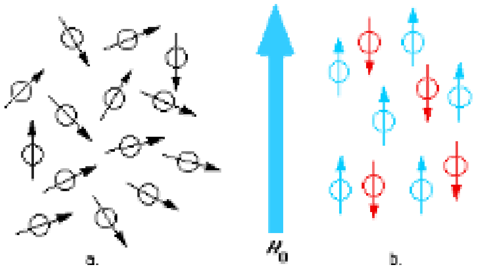
## 1.1. General

Nuclear Magnetic Resonance spectroscopy (NMR) is the most powerful technique for molecular characterisation. It can provide three-dimensional information on any type of molecule as long as the compound in question possesses NMR active nuclei – almost all do. In this workshop you will learn about the basic physics behind NMR spectroscopy followed by an introduction to the kind of structural information that can be extracted from an NMR spectrum. The workshop is limited to nuclei that possess a nuclear spin of 1/2 and within that subgroup focussing on the most widely used nuclei $^{1}H$, $^{13}C$, $^{19}F$ and $^{31}P$.

- $^{1}H$, $^{13}C$, $^{19}F$ and $^{31}P$ have a spin quantum number I = 1/2.
- In a magnetic field it each of these nuclei possesses 2I+1 spin states i.e. 2, +1/2 and -1/2. Only in a magnetic field is this degeneracy lifted (Zeeman effect)



**NMR spectroscopy measures this difference in energy.**



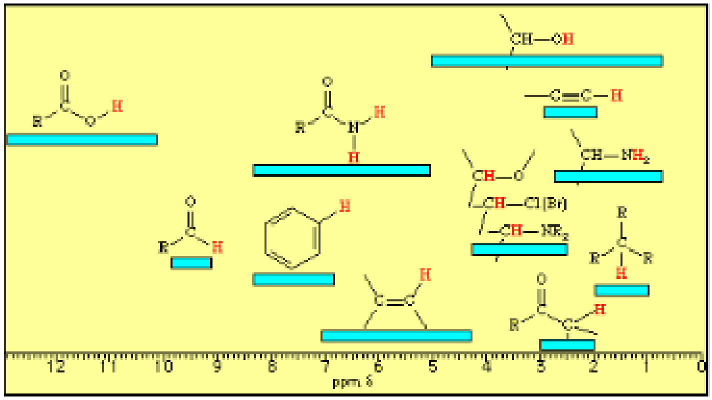
$$E = \gamma \frac{h}{2\pi} B_o$$

| nucleus | $I_N$ | γ | $S_{rel}$ | Nat. Abd. |
|---|---|---|---|---|
| | | $[10^{8}\ T^{-1}s^{-1}]$ | | [%] |
| $^{1}H$ | 1/2 | 2.675 | 1.00 | 99.98 |
| $^{13}C$ | 1/2 | 0.673 | $1.76\ 10^{-4}$ | 1.11 |
| $^{19}F$ | 1/2 | 2.517 | 0.83 | 100 |
| $^{15}N$ | 1/2 | -0.2712 | $3.85\ 10^{-6}$ | 0.37 |
| $^{31}P$ | 1/2 | 1.083 | 0.0665 | 100 |

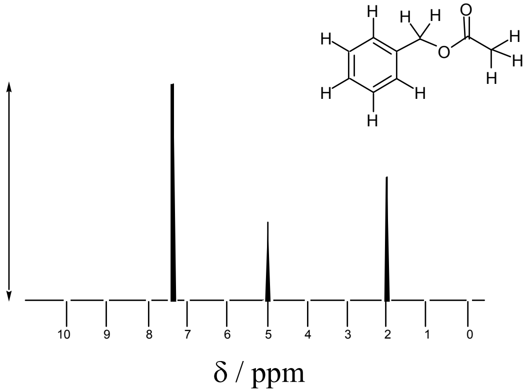
## 1.2. Salient Features of a $^{1}H$-NMR Spectrum

Let's start of with the case of $^{1}H$-NMR spectroscopy being the most common case. Everything you will come to learn about the interpretation of a $^{1}H$ NMR spectrum can be directly applied to other spin 1/2 nuclei.

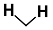
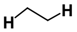
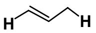
- Chemical shift
  - position in spectrum is determined by chemical environment



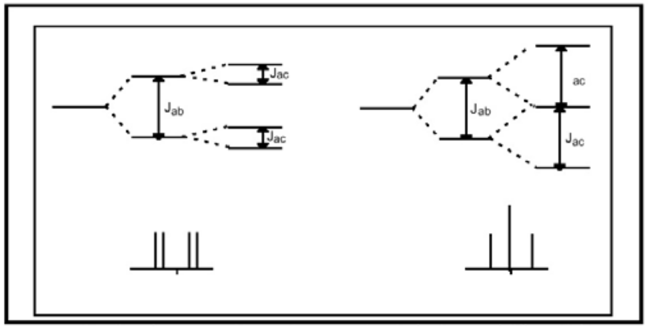
- Integration
  - peak intensities depend on the number of contributing nuclei.



- Coupling
  - peaks have a fine structure related to the presence of neighbouring nuclei

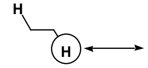
| | | |
|---|---|---|
| **$^2$J coupling (geminal)** |  | **J approx. 12Hz** |
| **$^3$J coupling (vicinal)** |  | **J depends on dihedral angle<br>approx. 7 Hz in alkyl groups** |
| **$^4$J coupling (allylic coupling)** |  | **J typically 1-2Hz** |

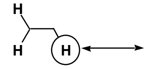
J = Coupling constant (measured in Hz)
Through bond coupling - scalar coupling

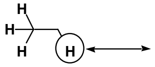


- **Rules for coupling**

(i) A nuclei which “sees” (interaction between magnetic fields) n equivalent spin 1/2 nuclei will appear as a series of n+1 lines where the separation of those lines is determined by the coupling constant J and the relative intensity of the lines are determined by Pascal’s triangle:


appears as a (1:1) doublet


appears as a (1:2:1) triplet


appears as a (1:3:3:1) quartet

- **The Simple Spin-Spin Coupling Rules**

**Consider only 3 J(H,H).** This is called **vicinal** coupling.

- observe H’-C-C-H”
- not observed H’-C-O-H” and H’-C-N-H” (fast proton exchange)

- **Splitting Pattern**

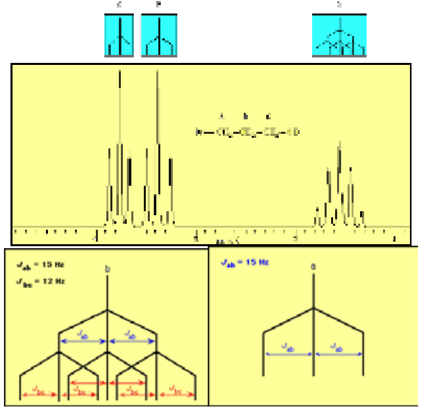
The chemically equivalent H-atoms do not cause a splitting.
The splitting pattern is a related to the number of equivalent H-atoms at the neigbouring atom.

- 0 H atoms as neighbour singlet
- 1 H atom as neighbour doublet (1:1) (e.g. -CH-CH-)
- 2 H atoms as neighbours triplet (1:2:1) (e.g. -CH-$CH_2$ -)
- 3 H atoms as neighbours quartet (1:3:3:1) (e.g. -CH –$CH_3$)
- 4 H atoms as neighbours quintet (1:4:6:4:1) (e.g. -$CH_2$-CH-$CH_2$-)
- 5 H atoms as neighbours sextet
- 6 H atoms as neighbours septet (e.g. $CH_3$-CH-$CH_3$)
- .... ...
- n H atoms as neighbors n+1 lines

**Intensity of the Multiplet Lines: Pascal's Triangle**

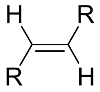
1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1

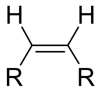
The intensity of all lines combined is proportional to the number of H-atoms responsible for the Resonance.**Rules for coupling.**

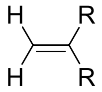


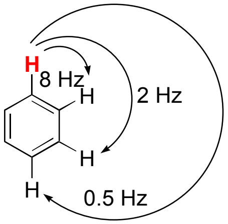
**Useful: $D_2O$ "shake"!!!**

### 1.3. Conformationally Rigid Systems

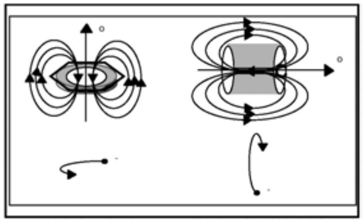


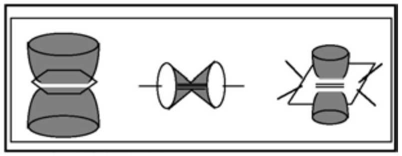


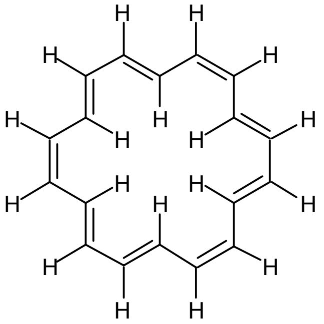




### 1.4. Chemical Anisotropy







## 2. Examples for $^{13}$C, $^{19}$F and $^{31}$P Spin Systems

Difference in nuclear sensitivity, the gyromagnetic ratio, and the abundance of the spin active isotope ($^{12}$C = 99% abundant with spin = 0 and $^{13}$C = 1 % abundant with spin = 1/2) may complicate the recording (sensitivity) and interpretation (abundance) of NMR spectra. However, as long as you stick to the advice of interpreting NMR spectra in the way in which it has been shown for $^{1}$H NMR spectroscopy (chemical shift, integration, splitting patterns, coupling constants; in this order) you should have no problem in the analysis of other spin 1/2 NMR spectra.

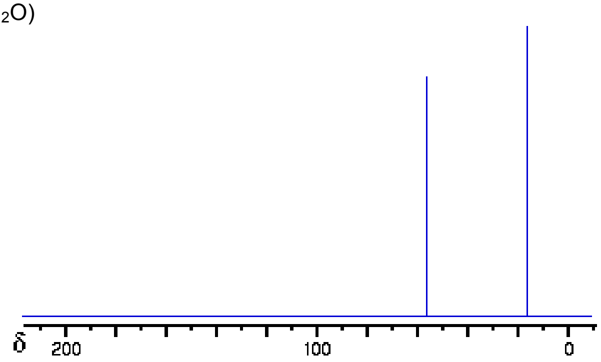
### 2.1. Decoupling

Since all nuclei in a molecule represent little magnets that interact with each other through bond and through space, a valuable technique to simplify NMR spectra is the use of decoupling techniques. The most commonly used approach is the heteronuclear decoupling, which removes all interactions between different types of nuclei ($^{1}$H and $^{13}$C) but not the coupling between any homonucleus. Thus a heterodecoupled $^{13}$C spectrum of hexane means that all the coupling between the protons and carbons have been removed but the coupling effects amongst the carbon-13 nuclei is still present. Although the coupling is still present it usually does not show in your spectrum because of the low abundance of the $^{13}$C nuclei. Statistically the chances of having to $^{13}$C nuclei being neighbours in hexane is 1:10000, which is below the detection limit of a NMR instrument.

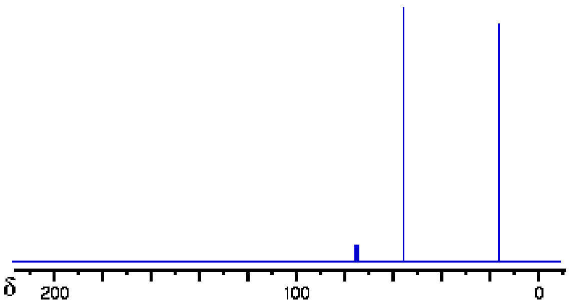
This situation is special for $^{13}$C. $^{19}$F and $^{31}$P nuclei are essentially 100% abundant, which means that homonuclear coupling will always produce the expected splitting patterns identical to those encountered in $^{1}$H NMR spectra already.

The following examples and tables have been taken from:
[http://www.cis.rit.edu/htbooks/nmr/bnmr.htm](http://www.cis.rit.edu/htbooks/nmr/bnmr.htm). Professor Hornak Department of Chemistry, Rochester Institute of Technology, Rochester, NY 14623-5603.

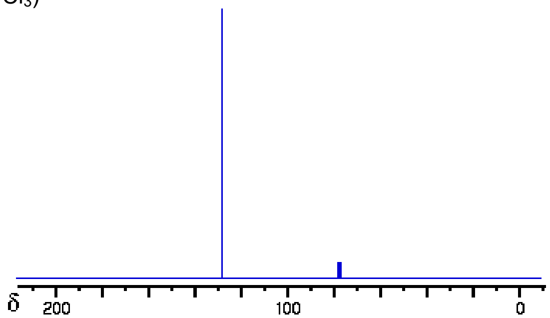
Ethanol (in $D_2O$)



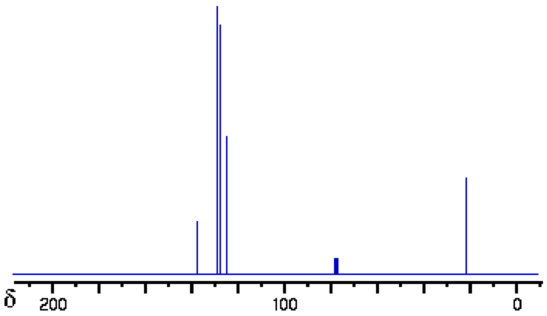
Ethanol (in $CDCl_3$)



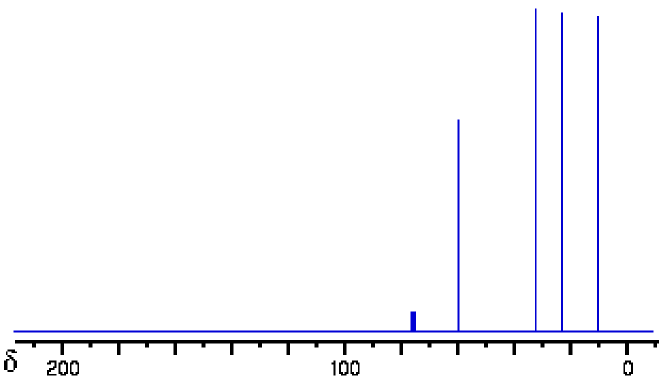
Benzene (in $CDCl_3$)



Toluene (in $CDCl_3$)

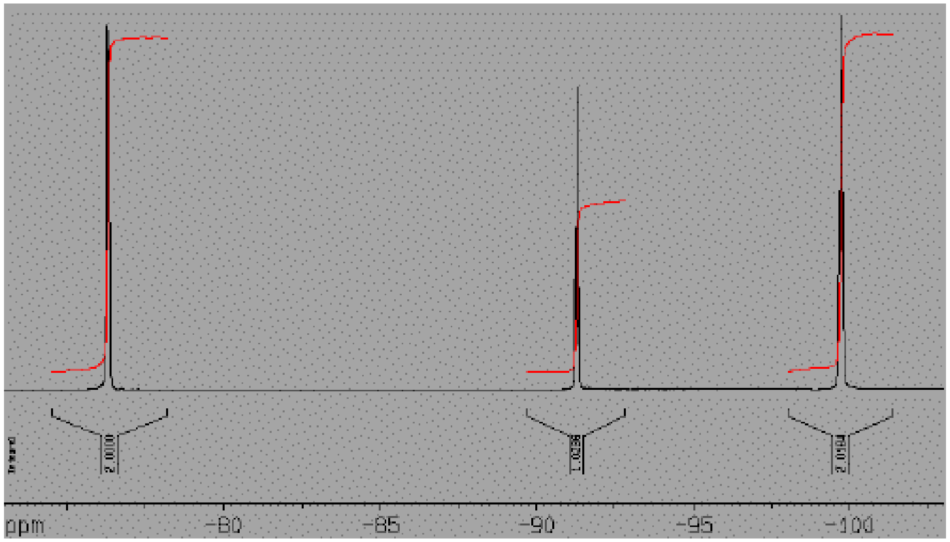


2-Butanol (in $CDCl_3$)

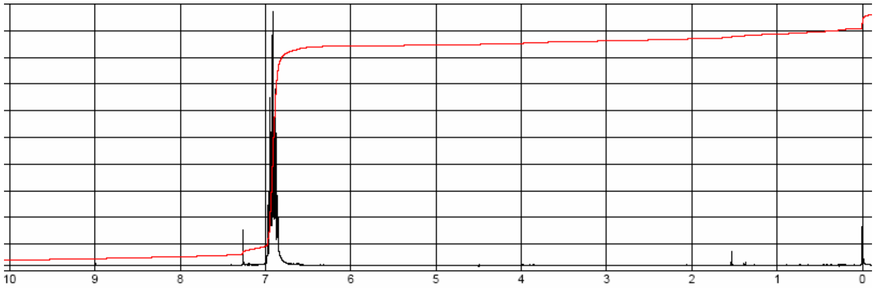


Fluorine-19 Chemical Shifts 🟩

| Fluorine-19 Environment | Chemical Shift Range (ppm) |
|---|---|
| $UF_6$ | -540 |
| FNO | -269 |
| $F_2$ | -210 |
| bare nucleus | 0 |
| $C(CF_3)_4$ | 284 |
| $CF_3(COOH)$ | 297 |
| fluorobenzene | 333 |
| F- | 338 |
| $BF_3$ | 345 |
| HF | 415 |



$^{19}F$ NMR of pentafluoro benzene



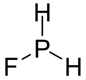
$^{1}H$ NMR of pentafluoro benzene

Phosphorous-31 Chemical Shifts R

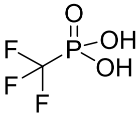
| **Phosphorous-31 Environment** | **Chemical Shift Range (ppm)** |
|---|---|
| $PBr_3$ | -228 |
| $(C_2H_5O)_3$ P | -137 |
| $PF_3$ | -97 |
| 85% phosphoric acid | 0 |
| $PCl_5$ | 80 |
| $PH_3$ | 238 |
| $P_4$ | 450 |

Stick spectra representations of all possible spin 1/2 NMR spectra (only consider relative chemical shifts and $^2J$ and $^3J$ couplings))

a)



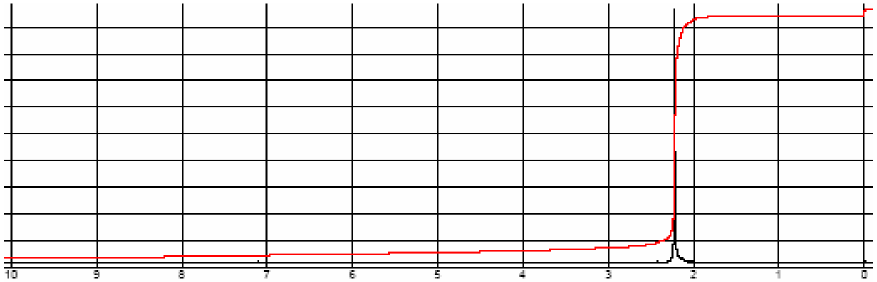
b)



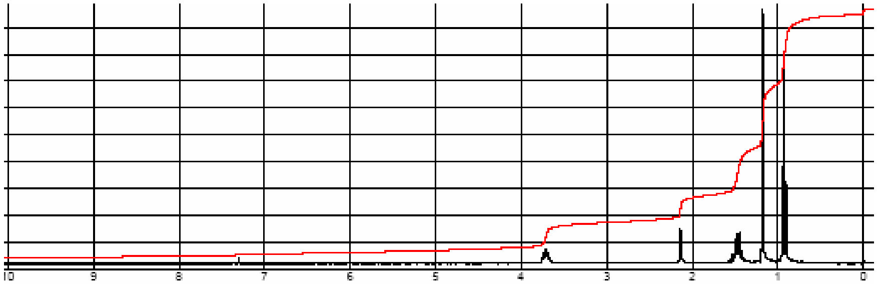
## NMR Workshop Group Exercise Sheet

1. Suggest a molecular structure consistent with the following data:

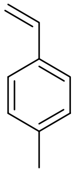
$C_{12}H_{18}$ , $UV_{max}$: approx. 250 nm

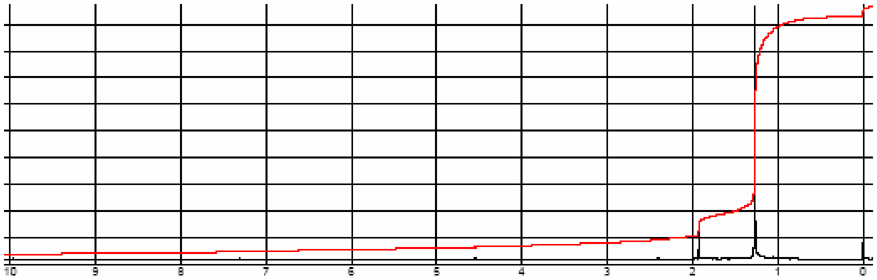


2. Explain why the shown NMR spectrum is consistent with only one of the possible isomers of butanol.

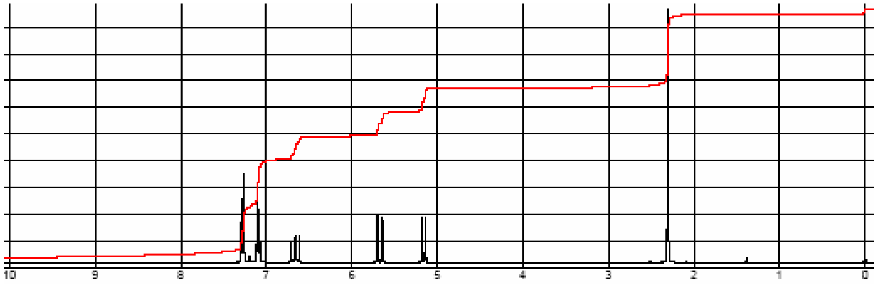


3. Draw a stick spectrum representation for the $^1H$ NMR spectrum of:
(Only consider $^3J_{H\text{-}H}$ couplings)

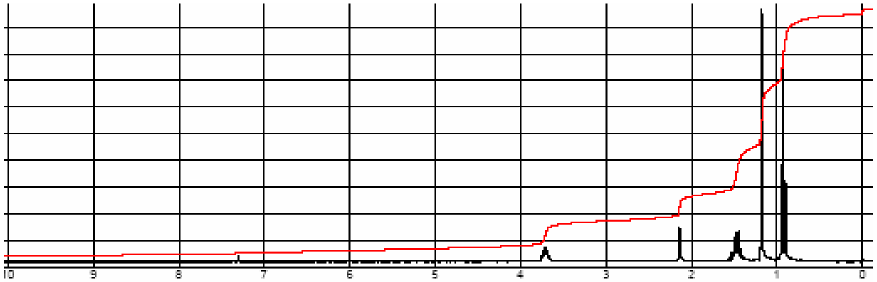




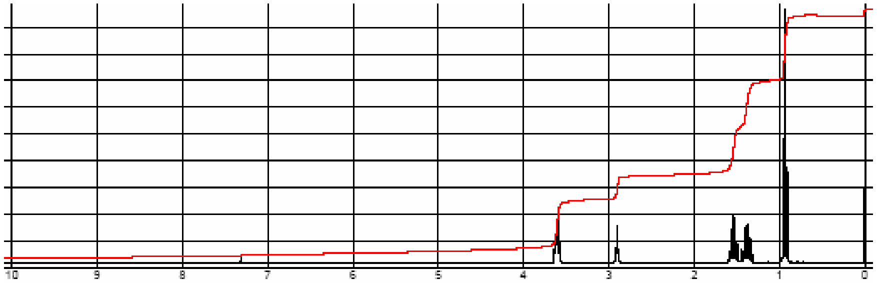
t-butanol (OH)



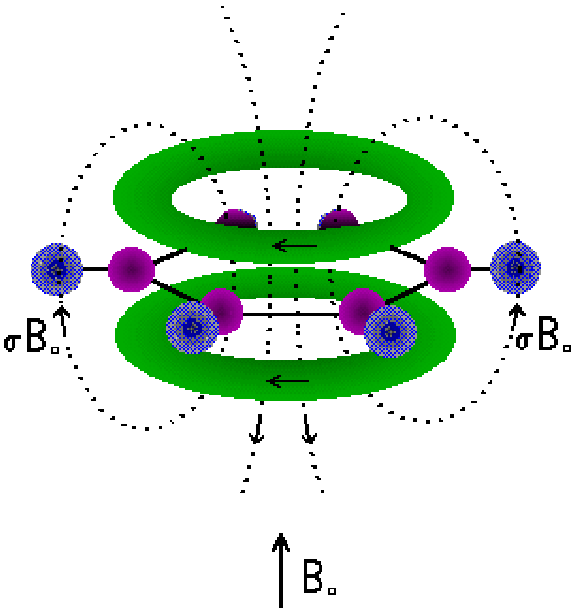
4-methyl styrene



2(=/-)-butanol (OH)



n-butanol (OH)


σB₀
σB₀
B₀