Extended Hückel Molecular Orbitals and Oscillator Strength Calculations

ICON-EDiT

Manual written by

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ICON-EDiT

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1 Introduction

ICON-EDiT is a FORTRAN program package that performs extended-Hückel molecular orbital and oscillator strength calculations on molecules.

s,p,d orbitals, a two-body repulsive energy term, options for different Wolfsberg-Helmholz formulas, charge iteration procedures, population analysis, FMO (fragment molecular orbitals), geometry variation, energy minimization and oscillator strength calculations are included.

ICON-EDiT consists of four parts, **INPUTC, ICONC, EDiT** and **GOP.**

The **INPUTC** part of the program is a self-explanatory input program. It reads the necessary input parameters from the ASCII data files ATOMDEF.DAT, VOI.DAT and FOI.DAT that can be extended and/or adapted to meet the requirements of the user.

ICONC performs extended-Hückel calculations on files created by **INPUTC**.

EDiT allows to calculate oscillator strengths of **e**lectronic **d**ipole-**i**nduced **t**ransitions (EDiTs) based on Slater-type extended-Hückel wave functions.

GOP searches for a minimum in an energy hyper surface using **INPUTC** and **ICONC** with files created by **INPUTC** for input.

ICON-EDiT runs under Windows NT, however, no machine specific specialties have been included.

2   Package

The extended-Hückel part of ICON-EDiT is an updated version of ICONC&INPUTC.[1] ICON8,[2] FMO,[3] GENINS and CONVERT provided by the ROALD HOFFMANN group have been used as bases for ICON-EDiT which includes among other new features an ASED procedure.[4] EDiT is a program to calculate oscillator strengths of electronic dipole-induced transitions (EDiTs) based on the EHMO Slater-type wave functions generated by ICONC&INPUTC.[5]

2.1 Contents

The package consists of the FORTRAN sources *FILENAME*.F, the corresponding *FILENAME*.EXE files, the data files *FILENAME*.DAT and some examples *FILENAME*.GEN, *FILENAME*.MO and *FILENAME*.KAR. The 32-bit extender programs DOSXMSF.EXE and DOSXNT386.EXE are included for those wishing to run the binaries under DOS and/or Windows 3.x.

2.1.1 Source files

The source codes of INPUTC, ICONC and EDiT are split into their subroutines, the source code of GOP is distributed in modules. All sources are located in the respective subdirectories of the directory SOURCES.

With the exception of GOP, the programs have already been compiled on different platforms such as VAX/VMS, IBM RS/6000, DEC/ALPHA, LINUX, DOS/WINDOWS and many more. No problems have been reported so far. However, a few points should be noted:

- If you wish to compile the programs with the VAX FORTRAN make sure to change the carriage control character „\" to „$" in the FORMAT statements.

- The Machine constants used in the Eigenvalue solve engine GIVENS.FOR should be adapted to the requirement of your computer. The correct machine constants for MSDOS, VAX and IBM RS/6000 are included in the respective file. The user only has to unmark the corresponding lines in this subroutine.

- All three programs have been designed to contain the user changeable parameters in their proper parameter files which are *ICONPARA*.FOR, *INPUPARA*.FOR and *EDPARA*.FOR. The parameters listed therein should be adaptable to the requirements of the user and/or the available resources, such as computer memory. The maximum number of atoms (variable MXATOM) has been tested for up to 999. We do not guarantee correct results, if you push this limit beyond.

- GOP uses a compiler-specific routine to access the operating system. You will have to change the file 'INPUTC_ICONC.f90' to compile the program with your own compiler.

The program-package is available at no charge. As a consequence no responsibility and no support can be provided by the authors..

2.1.2 Executables

INPUTC.EXE reads the data files *ATOMDEF*.DAT, *VOI*.DAT and *FOI*.DAT which must be located in the same directory as the binary itself. Its purpose is to output either a cartesian coordinate file (*FILENAME*.KAR) or an internal coordinate file (*FILENAME*.GEN) depending on the choice you have made (cf. Chapter 2.2). As ICONC is designed to work with cartesian coordinates only, the .gen files can be converted to the temporary files *TEMP*.VAR and *TEMP*.KAR. The memory requirement is rather small (» 180 kBytes).

The *FILENAME*.GEN and the *TEMP*.KAR files are the input files for ICONC.

ICONC.EXE is the actual extended-Hückel molecular orbital (EHMO) program. The memory requirement is » 6.5 MBytes for a DOS/Windows 3.x binary compiled for 100 atoms (cf. variable MXATOM in *ICONPARA*.FOR).

EDiT.EXE calculates electronic dipole-induced transitions between an initial molecular orbital Ψ_i and a final MO Ψ_f. Besides the files *FILENAME*.MO and *FILENAME*.GEN that are related to the ICONC program, EDiT needs an input file *FILENAME*.EDI that has to be created seperately in an ASCII editor of your choice. A binary dimensioned for 100 atoms (and up to 400 AOs) uses about 4.5 MBytes of RAM.

GOP.EXE searches for a minimum on an energy hyper surface of a molecule specified in a .gen file. The user may choose which properties of the molecule to include in a calculation and which not. GOP itself uses practically no resources, but it makes calls on INPUTC and ICONC, so the memory requirement is the same as for them.

DOS/Windows 3.x specialties:

- The DOS/Windows 3.x binaries have been created using the Microsoft FORTRAN PowerStation compiler. In order for the 32-bit binaries to run on a 16-bit operating system the respective 32-bit extender programs are included in this distribution. These are DOSXMSF.EXE and DOSXNT.386, respectively (DOSXMSF.EXE being the proper extender program). If you intend to use these programs under DOS only, you can forget about DOSXNT.386. DOSXMSF.EXE should be copied to a location stated in your PATH environment (i.e. to the current working directory). If you plan to run the programs under Windows 3.x in a DOS shell you should add the line

      DEVICE=X:\SOMEPATH\DOSXNT.386

  to the [Enh386] section of your SYSTEM.INI file.

- The program consuming the most memory is ICONC. Depending on the configuration of your PC (different drivers, SMARTDRIVE, RAMDISK, etc.) 8 or 16 MBytes of RAM should allow to run ICONC without needing to access virtual memory. If you have less built-in physical memory you can still run the programs by allowing the programs to page out parts of its image to the hard disk. Virtual memory will be accessed on the drive where DOSXMSF.EXE is located. This will NOT work on a compressed drive. Therefore, if you have DriveSpace installed you may want to relocate the swap space by adding something like

      SET DOSX = SWAPDIR X:\MYSWAP

  to your *AUTOEXEC*.BAT file. However, if you run the programs under Windows 3.x in a DOS shell, Windows will take care of your virtual memory. Size and properties can then be adjusted by starting the control panel application and selecting the 386 Enhanced icon. Do NOT run ICON-EDiT under Windows 3.x unless you are sure to have enough free RAM.

2.1.3 Data Files

ATOMDEF.DAT is needed by INPUTC. It contains the atomic symbols, the number of valence electrons, the quantum numbers of the orbitals, the corresponding Slater exponents and the Coulomb integrals. For most of the main group elements the quantum number ND has been chosen equal to 0. A quantum number of 0 means that the corresponding atomic orbital is skipped. To include *d* orbitals ND = 0 has to be substituted with ND = 3, 4 or 5 depending on the period to which the atom belongs.

Special notation: atomic symbols followed by M, -, 1, 2 or 3 have the meanings: metal, anion, cation, higher oxidation states.

Be careful! It is wise to check whether the parameters are well suited to your problem.

ATOMDEF.DAT can easily be changed or extended according to the special needs of the user. Be careful not to change the format. The number of atoms that can be defined is limited to 150.
FOI.DAT is needed by INPUTC. It contains the charge iteration parameters of the transition elements.
VOI.DAT is needed by INPUTC. It contains the charge iteration parameters of the main group elements.

2.1.4 Contents of the distribution

The .zip files (also available as .tar.gz files) can be downloaded from the following website:
http://iacrs1.unibe.ch/members/iconedit.html

NT-bin.zip	sources.zip	examples.zip	q-tools.zip
INPUTC.EXE	INPUTC (DIR)	2-H2O_GOP.GEN	Q-TOOLS.EXE
ICONC.EXE	ICONC (DIR)	2H2OAG_ANGLE.GEN	SAMPLES(DIR)
EDiT.EXE	EDiT (DIR)	2H2OAG_DISTANCE.GEN	Containing some examples.
GOP.EXE	GOP (DIR)	BENZENE.GEN	Refer to the description of
ATOMDEF.DAT	containing the sources	BENZENE.OUT	Q-TOOLS
FOI.DAT		BENZENE1.PGR.GOP	
VOI.DAT		BENZENE1.E_MIN.OUT	
		BIPY.KAR	
		BIPY.OUT	
		C2H2.GEN	
		C2H4.GEN	
		C60.GEN	
		CH4.GEN	
		CH4.MO	
		CH4.OUT	
		GLYCIN.KAR	
		GLYCIN.OUT	
		H2.GEN	
		H2.OUT	
		H2O.KAR	
		H2O.OUT	
		H2O_GOP.GEN	
		MNO4-.EDI	
		MNO4-.EDO	
		MNO4-.EDS	
		MNO4-.GEN	
		MNO4-.MO	
		MNO4-.OUT	
		NICO4IT.KAR	
		NICO4IT.OUT	
		PROPEN_F.GEN	
		PROPEN_F.OUT	

2.2 INPUTC

INPUTC is a self-explanatory FORTRAN program which produces files used as input for the EHMO program *ICONC*.EXE. You may select between different coordinate types for the input of molecules as well as between different options for the EHMO calculation.

ICONC accepts only input files with atom positions in cartesian coordinates. INPUTC converts internal coordinates to cartesian coordinates.

INPUTC needs the parameter files *ATOMDEF*.DAT, *VOI*.DAT and *FOI*.DAT. These files must be in the current working directory.

To start the program type **INPUTC** at the command line prompt.

The program will then ask for the type of input you want to make. The questions are:

```
1   Cartesian coordinates
2   Internal coordinates (with variations)
3   Conversion of a file from #2 (.GEN file)
0   End
```

Option 1 asks for input of the atomic positions in Cartesian coordinates. A file with the extension .KAR is then written to the hard disk. Input files in Cartesian coordinates (e.g. *name*.KAR files) can be used for ICONC calculations without conversion.

Option 2 asks for the atomic positions in internal coordinates. Besides the fact that internal coordinates are often useful and allow a much easier setup of molecular geometries from known data such as bond angles and bond lengths, INPUTC supports automatic geometry variation for this type of coordinates. In a first step INPUTC dumps an internal coordinate file with the extension .GEN to the hard disk. It then varies the geometries and writes its output to the temporary files *TEMP*.VAR and *TEMP*.KAR. These files are temporary in the sense that they will be overwritten the next time you choose either option 2 or 3. As the .GEN files contain variation information in a condensed form you may wish to keep these files only. The *TEMP*.KAR files needed as input for ICONC can be generated from the respective .GEN file at any time by choosing option 3. The *TEMP*.VAR files contain the varied internal coordinates what is handy to check the success of geometry variation. We now briefly discuss the setup of internal coordinate geometries.

The first atom **1** in Figure 1 defines the origin. If you choose an angle α of $\pm 180^o$ the second atom **2** lies on the *Z*-axis in positive direction. **For a dihedral angle of 0° or 180° the third atom is in the XZ-plane.** To set up the coordinate system and/or any reference point the user can create dummy atoms. Dummy atoms are automatically removed from calculation; they have to be given the highest numbers. Hence, if you consider a molecule consisting of *N* atoms the first dummy atom has to be labeled with *N+1*. Sequencing of atoms for counting is determined by only the real (excluding dummy) atoms. **You can only point once to the same atom** but you can point from a selected atom to other atoms as often as you like. The bond angle is the angle between the vector **b** and the connection between the two atoms **1** and **2**. The dihedral angle ξ is the angle between the last defined plane and

the new vector to be defined. At the beginning the *XZ*-plane is defined by the vectors **a** and **b**. Please note that the dihedral angle is associated with the vector **K - L**.

We further explain the use of the above definitions by adding a few examples.
If atom 1 is located at position (x=0, y=0, z=0) the input in internal coordinates (r,α,ξ) must be (0,0,0).
If then atom 2 is located at (x=0, y=1, z=0) the input must be (1,180,0) and so on.
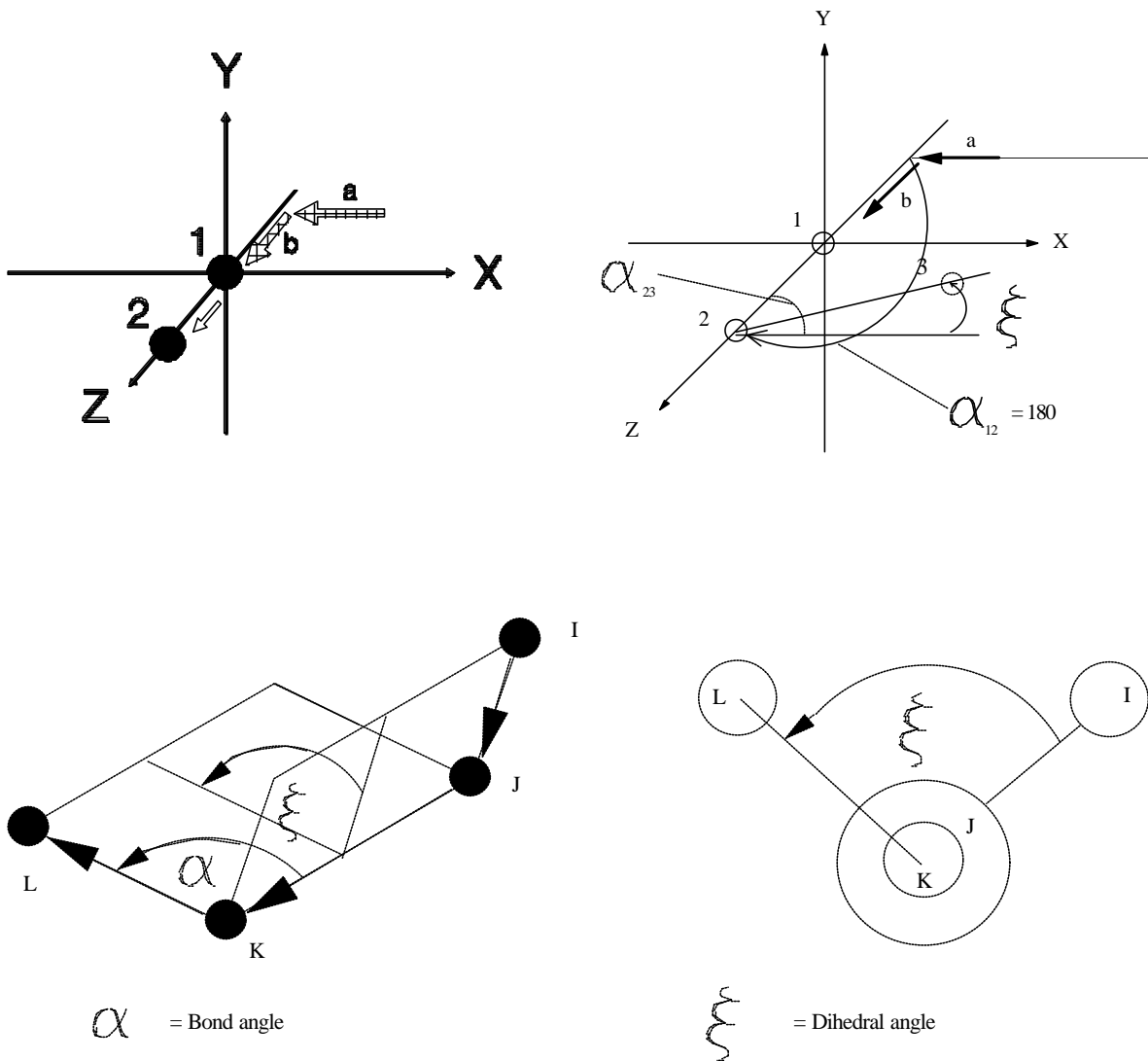
Figure 1: Definition of the bond angle α and the dihedral angle ξ. In case of atoms 1 and 2 in the upper scheme **K** corresponds to atom 1.

Figure 2: EXAMPLE 1, D_{2h} H_4

number of atoms	4
number of dummy atoms	0
number of vectors	3

D2h point group; e.g. D2h H4

4 atoms and three connections
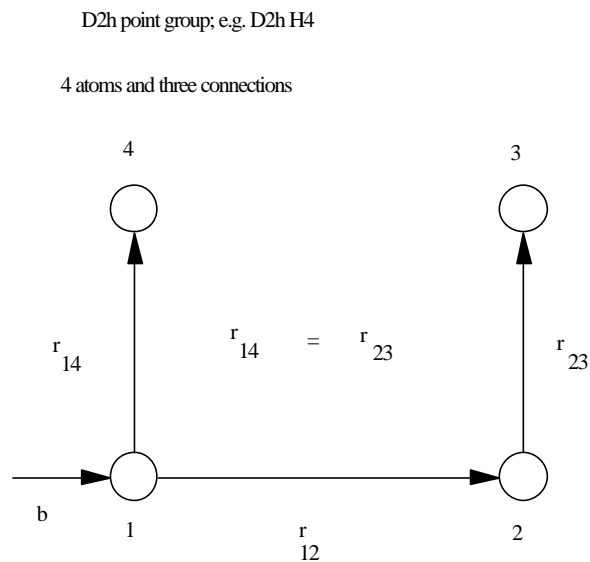
vector	distance	α	ξ
1 2	2	180	0
2 3	2	90	0
1 4	2	90	0

If we want to place the four atoms in the x,y plane, so that the z axis coincides with the C_4 axis, the following input will do it:
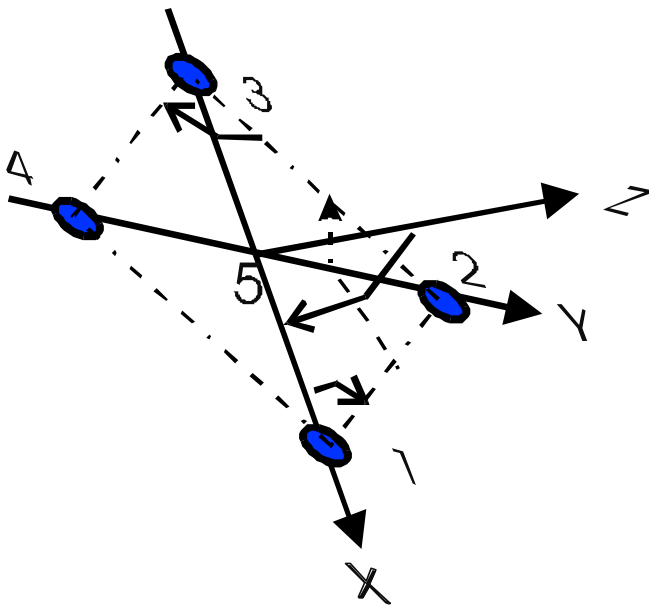
vector	distance	α	ξ
5 1	0,707107	90	0
1 2	1	45	90
2 3	1	90	0
3 4	1	90	0

atom	x	y	z
1	0,7071	0	0
2	0	0,7071	0
3	-0,7071	0	0
4	0	-0,7071	0
5=dummy	0	0	0

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The following input places the four atoms into the y,z plane, so that the x axis coincides with the C_4 axis:

vector	distance	α	ξ
5 1	0,707107	180	0
1 2	1	45	0
2 3	1	90	0
3 4	1	90	0
atom	x	y	z
1	0	0	0,7071
2	0,7071	0	0
3	0	0	-0,7071
4	-0,7071	0	0
5=dummy	0	0	0

Figure 3: EXAMPLE 2, T_d CH_4

number of atoms	5
number of dummy atoms	0
number of vectors	4
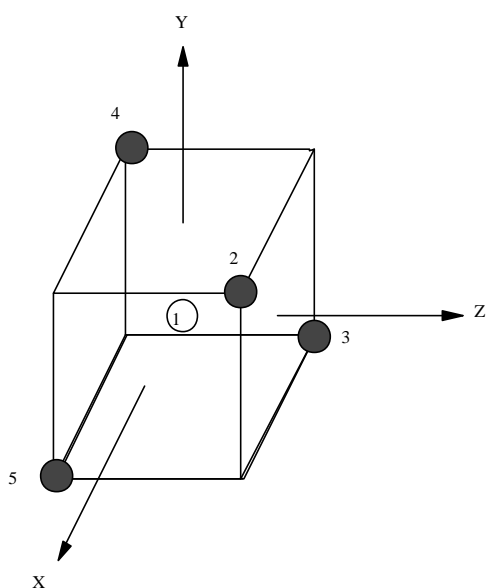
vector	distance	α	ξ
1 2	1.090	125.2644	45.0
1 3	1.090	125.2644	225.0
1 4	1.090	54.7356	135.0
1 5	1.090	54.7356	315.0
Atom	x	y	z
1	0	0	0
2	a	a	a
3	-a	-a	a
4	-a	a	-a
5	a	-a	-a
		a=0.6293	

<u>Figure 4:</u> EXAMPLE 3, D_{6h}-benzene

This example illustrates how to place the z-axis perpendicular to the plane of a molecule with D_{nh} symmetry, so that the C_n axis coincides with the z-axis. If you choose the coordinate system in this way, ICONC will deliver symmetry adapted wave functions.

number of atoms	12
number of dummy atoms	1
number of vectors	12

Internal coordinates, number 13 is the dummy atom:

```
13   1   1.40  90.0     .0 places atom 1 on the x axis at position 1.4
 1   2   1.40  60.0   90.0 rotation from the (x,z) plane to to(x,y) plane
 2   3   1.40 120.0     .0
 3   4   1.40 120.0     .0
 4   5   1.40 120.0     .0
 5   6   1.40 120.0     .0
 1   7   1.06 180.0     .0
 2   8   1.06 240.0     .0
 3   9   1.06 240.0     .0
 4  10   1.06 240.0     .0
 5  11   1.06 240.0     .0
 6  12   1.06 240.0     .0
 * C C C C C * H H H H H
```

Resulting cartesian coordinates:

```
 1    1.400000        .000000        .000000
 2     .700000       1.212436        .000000
 3    -.700000       1.212436        .000000
 4   -1.400000        .000000        .000000
 5    -.700000      -1.212436        .000000
 6     .700000      -1.212436        .000000
 7    2.460000        .000000        .000000
 8    1.230000       2.130422        .000000
 9   -1.230000       2.130423        .000000
10   -2.460000        .000000        .000000
11   -1.230000      -2.130422        .000000
12    1.230000      -2.130423        .000000
 * C C C C C * H H H H H
```

Figure 5: EXAMPLE 4, Zeise-Salt $((H_2C = CH_2) PtCl_3)$, try ZEISE.GEN.
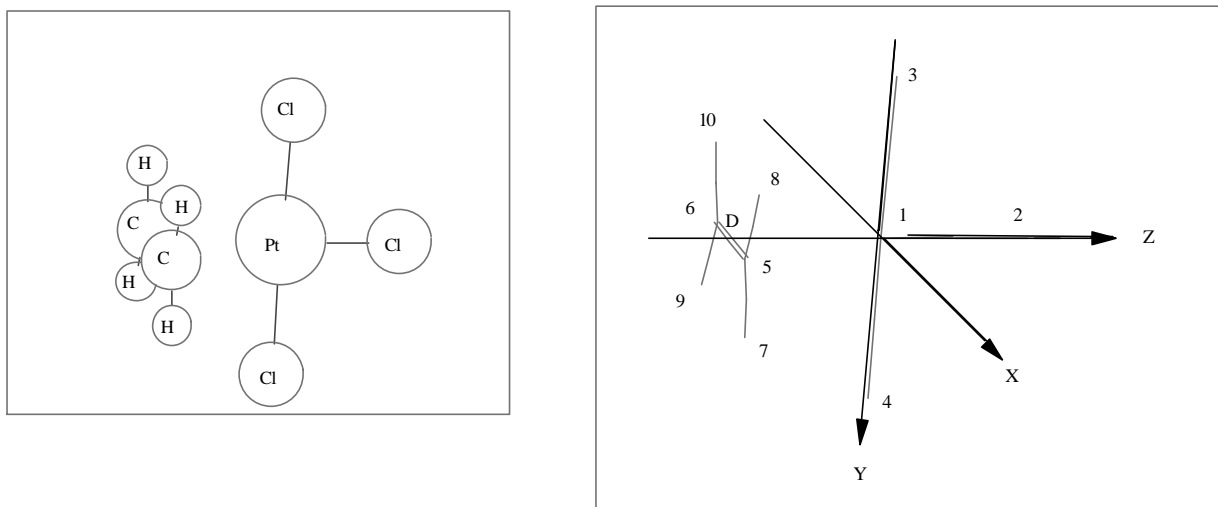

```
number of atoms            10
number of dummy atoms D     1
number of vssectors        10
```

vector number	vector		distance	α	ξ
1	11	1	2.090	180.0	0.0
2	1	2	2.300	180.0	0.0
3	1	3	2.300	90.5	270.0
4	1	4	2.300	90.5	90.0
5	11	5	0.735	90.0	0.0
6	11	6	0.735	270.0	0.0
7	5	7	1.080	109.5	90.0
8	5	8	1.080	109.5	270.0
9	6	9	1.080	109.5	90.0
10	6	10	1.080	109.5	270.0

Figure 6: EXAMPLE 5, $(H_2C = CH_2) PtCl_2N(CH_3)_2$, try CHNCLPT.GEN.
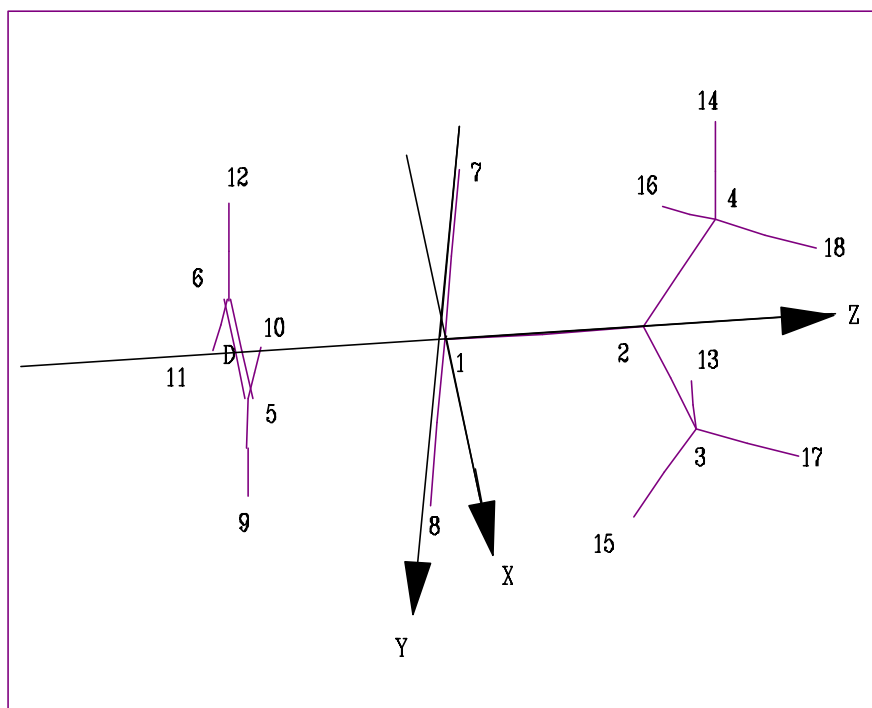
number of atoms	18
number of dummy atoms D	1
number of vectors	18

vector number	vector		distance	α	ξ
1	19	1	2.090	180.0	0.0
2	1	2	2.020	180.0	0.0
3	2	3	1.580	114.0	90.0
4	2	4	1.580	114.0	270.0
5	19	5	0.735	90.0	0.0
6	19	6	0.735	270.0	0.0
7	1	7	2.300	90.5	270.0
8	1	8	2.300	90.5	90.0
9	5	9	1.080	109.5	90.0
10	5	10	1.080	109.5	270.0
11	6	11	1.080	109.5	90.0
12	6	12	1.080	109.5	270.0
13	3	13	1.080	109.5	270.0
14	4	14	1.080	109.5	90.0
15	3	15	1.080	109.5	150.0
16	4	16	1.080	109.5	330.0
17	3	17	1.080	109.5	30.0
18	4	18	1.080	109.5	210.0

Figure 7: EXAMPLE 6, 4' -Phenylterpyridine, try PTPY.GEN.
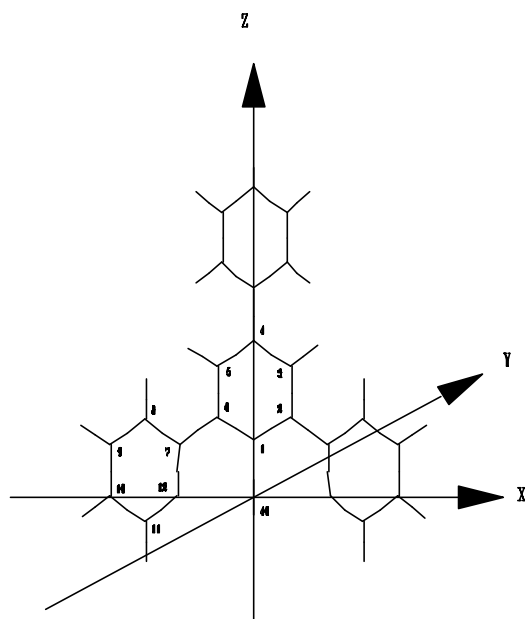
number of atoms   = 39
number of vectors = 39
number of dummy atoms = 1

D = dummy atom. The dummy atom(s) must have the last number(s).

vector number	vector		distance	α	ξ
1	40	1	2.000	180.000	0.0
2	1	2	1.352	243.325	0.0
3	2	3	1.395	116.675	0.0
4	3	4	1.395	120.000	0.0
5	4	5	1.395	120.000	0.0
6	5	6	1.395	120.000	0.0
7	6	7	1.489	240.000	0.0
8	7	8	1.395	240.000	0.0
9	8	9	1.395	120.000	0.0
10	9	10	1.395	120.000	0.0
11	10	11	1.395	120.000	0.0
12	11	12	1.352	116.675	0.0
13	2	13	1.489	236.675	0.0
14	13	14	1.395	120.000	0.0
15	14	15	1.395	240.000	0.0
16	15	16	1.395	240.000	0.0
17	16	17	1.395	240.000	0.0
18	17	18	1.352	243.325	0.0
19	4	19	1.489	240.000	0.0
20	19	20	1.395	240.000	0.0
21	20	21	1.395	120.000	0.0
22	21	22	1.395	120.000	0.0
23	22	23	1.395	120.000	0.0
24	23	24	1.395	120.000	0.0
25	22	25	1.084	240.000	0.0
26	20	27	1.084	240.000	0.0
27	21	26	1.084	240.000	0.0
28	3	28	1.084	240.000	0.0
29	5	35	1.084	240.000	0.0
30	8	36	1.084	240.000	0.0
31	9	37	1.084	240.000	0.0
32	10	38	1.084	240.000	0.0
33	11	39	1.084	240.000	0.0
34	14	29	1.084	120.000	0.0
35	15	30	1.084	120.000	0.0
36	16	31	1.084	120.000	0.0
37	17	32	1.084	120.000	0.0
38	23	33	1.084	240.000	0.0
39	24	34	1.084	240.000	0.0
40	24	24	1.084	240.000	0.0

Figure 8: EXAMPLE 7, $H_8 Si_8 O_{12}$, try H8SI8O12.GEN.
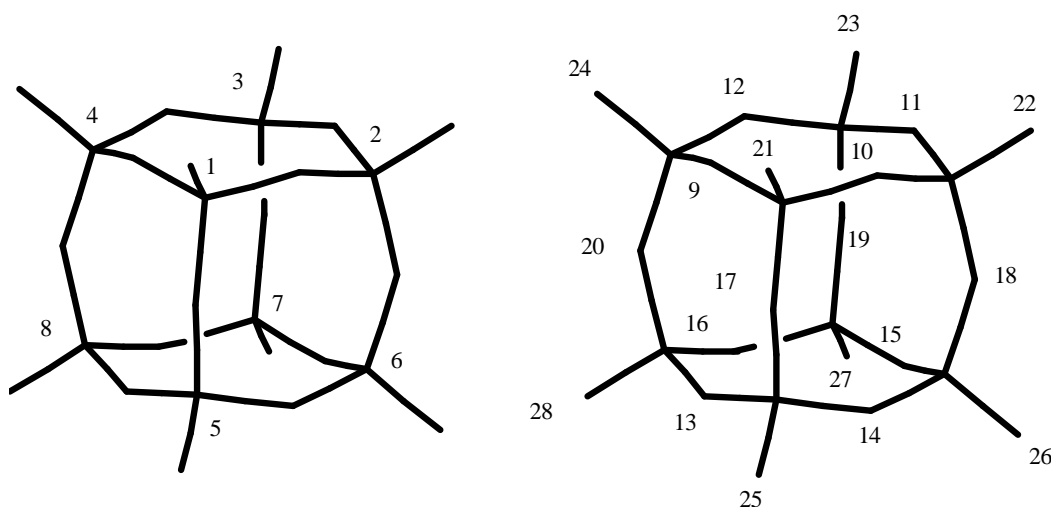
number of atoms	28
number of dummy atoms D	1
number of vectors	28

D is number 29 in the centre of the cage.

vector number	vector		distance	α	ξ
1	29	9	2.64428	135.0	0.0
2	29	10	2.64428	135.0	90.0
3	29	11	2.64428	135.0	180.0
4	29	12	2.64428	135.0	270.0
5	29	13	2.64428	45.0	0.0
6	29	14	2.64428	45.0	90.0
7	29	15	2.64428	45.0	180.0
8	29	16	2.64428	45.0	270.0
9	29	17	2.64428	90.0	45.0
10	29	18	2.64428	90.0	135.0
11	29	19	2.64428	90.0	225.0
12	29	20	2.64428	90.0	315.0
13	29	1	2.69795	125.2644	45.0
14	29	2	2.69795	125.2644	135.0
15	29	3	2.69795	125.2644	225.0
16	29	4	2.69795	125.2644	315.0
17	29	5	2.69795	54.73561	45.0
18	29	6	2.69795	54.73561	135.0
19	29	7	2.69795	54.73561	225.0
20	29	8	2.69795	54.73561	315.0
21	1	21	1.45	180.0	0.0
22	2	22	1.45	180.0	0.0
23	3	23	1.45	180.0	0.0
24	4	24	1.45	180.0	0.0
25	5	25	1.45	180.0	0.0
26	6	26	1.45	180.0	0.0
27	7	27	1.45	180.0	0.0
28	8	28	1.45	180.0	0.0

After this you will be asked: „Do you want to define additional parameters?" Answering **Y** will show you the next menu:

---

1 Charge iteration
2 Controlling output options
3 Orbital occupation
4 Individual 1+k, d parameters
5 Weighted Wolfsberg-Helmholz formula
6 Simple Wolfsberg-Helmholz formula
7 FMO (Fragment Molecular Orbital) Calculation
8 Omit atoms from repulsion energy calculation
9 Exit

REMARK 1   The default option for calculating the off-diagonal elements is the distance dependent formula:

$$K = 1 + \kappa \cdot \frac{\exp(-\delta(R-d_0))}{q} \text{ with } \kappa = 1 \text{ and } \delta = 0.35$$

$$q = 1 + ([(R-d_0) - |R-d_0|] \cdot \delta)^2$$

Option 4 allows to define other κ, δ parameters.
It also allows to define individual κ, δ values for specified atom pairs.

REMARK 2   Charge iteration can be carried out at a single atom, at a few atoms or at all atoms.

The experience shows that it is in general not necessary to carry out charge iteration for organic molecules, but in some cases it is important.

As a rule charge iteration should be applied at approximately the equilibrium geometry only. The thus obtained parameters can then be used for all the other calculations, see e.g. refs [6-7] and [9].

In general it is not necessary to carry out charge iteration at different geometries, a procedure which is usually time consuming.

In some cases it is, however, important to carry out charge iteration at each geometry investigated; see e.g. ref. [6-7].

REMARK 3   Option 2 includes the following possibilities for controlling the output of ICONC:

    1 Coordinates and parameters
    3 Distance matrix
    4 Overlap matrix
    5 Madelung parameters
    6 Hückel matrix
    8 Energy levels
    9 Total energy
  10 Wave functions
  11 Density matrix
  12 Overlap population matrix
  13 Reduced overlap population matrix
  14 Complete charge matrix
  15 Reduced charge matrix
  16 Net charges and populations
  17 Energy matrix
  18 Reduced energy matrix
  19 Energy partitioning
  20 Reduced energy partitioning
  21 Core-core repulsion energy matrix
  22 Moby output
  25 Exit

REMARK 4   If calculations are performed for varying geometries, MOBY output is only generated for the last geometry. MOBY output generates connectivity information that has to be regarded as a proposal only and may have to be changed by the user. MOBY output files have the extension .mo. They serve as input files for the programs MOBY and EDiT.

REMARK 5   To calculate the sum

$$\sum_s b_s^0 E_s^0 \quad \text{and} \quad E_{Rep}$$

by means of eqs. (3) and (51) respectively, the valence electrons of the atoms are filled into the energetically lowest levels according to the Aufbau principle. The thus resulting electron configuration does in general not correspond to the electron configuration of the free atoms in case of transition elements. You can change this by choosing the corresponding switch in *Option 2*. If charge iteration is used, we recommend to apply the default option.

REMARK 6   The easiest way to get familiarized with the program is to try the different options and to study the results. Perhaps you may also want to try some of the examples included.

REMARK 7　　The charge iteration parameters are split up in two files; VOI.DAT containing the parameters for main group elements and FOI.DAT comprising the respective parameters for transition metals. If you intend to perform charge iteration on both types of elements you have to choose method B „VSIE-parameters (for d-elements)" .You will then be asked whether you want to do charge iteration on all atoms or on selected atoms only. The latter option allows you to specify the elements you want to charge iterate. In order to have charge iteration on selected atoms you may want to give the atoms occupying different symmetry positions different names. You do this by copying the respective rows in ATOMDEF.DAT, VOI.DAT and/or FOI.DAT and giving the elements different names (eg. *O1* and *O2*, for two symmetrically distinguishable types of oxygen atoms, the name must not contain more than 2 letters). Consider for example *CO_2*. As the needed parameters are already included in VOI.DAT you will choose method A. If you then choose charge iteration on selected atoms you will be asked on how many atoms you want to charge iterate. The program proposes 3. As you only have two types of (symmetrically) distinguishable atoms, select **2**! The program then lists the atoms. The oxygen is listed twice as the program does not know about symmetry. The proposed succession of the atoms has to be obeyed. Hence, if the program prints the list „O C O", you will have to select *O* and **then** *C*. Otherwise the oxygen atoms will be charge iteratated with the carbon parameters, which is of course wrong!

Option 3 converts a previously generated internal coordinate file with the extension .GEN (cf. Option 2) into a Cartesian file named *TEMP*.KAR.

2.3 ICONC

ICONC is a FORTRAN program. It performs extended-Hückel calculations on molecules.

s, p, d orbitals are accepted.

A two-body repulsive energy term is included.

A distance-dependent Wolfsberg-Helmholz constant is used by default. Other options can be chosen.

ICONC can perform FMO calculations.

ICONC accepts input files with atom positions in Cartesian coordinates only. The easiest way to use the programs is to first apply INPUTC which creates the *.KAR files that ICONC accepts as its input.

To start the program type   **ICONC** < *filename*.KAR > *filename*.OUT

The „<" and „>" signs are essential. They redirect standart input and standard output of ICONC. The standard input will be read from *filename*.KAR while the standard output will be written to *filename*.OUT.

REMARK: The calculated wave functions are usually not symmetry adapted. For the degenerate orbitals of highly symmetric molecules this may cause the wave functions difficult to interpret. To get symmetry adapted wave functions, appropriate rotation has to be carried out. It is always possible, however, to solve the problem by inducing a small appropriate antisymmetric distortion. Appropriate distortions are distortions which remove specific or all C_3 axis of rotation.

In addition to the *filename*.OUT ICONC creates the two temporary files *ENERNI*.DAT and *ENERTOT*.DAT. *ENERNI*.DAT contains the number of orbitals and the orbital energies. *ENERTOT*.DAT contains the VARIED BOND LENGTHS OR BOND ANGLES, the SUM OF ONE-ELECTRON ENERGIES, the ORBITAL STABILIZATION ENERGY, the TWO-BODY REPULSION ENERGY and the STABILIZATION + REPULSION ENERGY. These files are often very useful. If for example you want to draw an energy hypersurface, all the needed information is contained in *ENERTOT*.DAT.

The output option MOBY creates in addition a file *filename*.MO. The *.MO files were originally introduced to meet the requirements of the molecular modeling package MOBY by Udo Höweler, Springer Verlag Berlin, 1993. We then found these files convenient for the EDiT program as well.

2.4 EDiT

EDiT is a FORTRAN program that performs oscillator strength calculations of electronic dipole-induced transitions (EDiTs) based on EHMO wave functions generated by ICONC.

To start the program type

<div align="center">EDiT.bat filename</div>

The *filename*(.EDI) is the EDiT input file, that will be created by the ICONC program (Output control parameter #23 → False) and has to be modified with an ASCII text editor of your choice. The different options that determine the run-time behaviour of EDiT can be chosen by stating the respective KEYWORDs in *filename*.EDI. The text below written in Courier is a sample input file set up to calculate the first electronic transition in permanganate. Please refer to this file which is also included in the distribution to get a brief overview of the possible keywords.

```
!%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
!
! mno4-.edi  - Input file for oscillator strength calculations with EDiT
!
! %%Creator: ICONC
!
! %%Usage: EDiT < mno4-.edi > mno4-.log
!
! %%Keywords:
!  OUTFILE=???  - Output file is mno4-.eds.
!  SPECFILE=??? - Corrected line spectrum file for smoothing is mno4-.eds.
!  OSCILLOUT    - Print the oscillator strengths.
!  DIPLENOUT    - Print the transition dipole lengths.
!  MATOUT       - Print the transition dipole matrices.
!  FITONLY      - Do Gaussian smoothing only.
!  MATRICE=ALL  - ALL transition matrix elements are taken into account.
!  CUTOFF=xx.x  - Cutoff length for off block diagonal elements is 10.0 A.
!  POL = XYZ    - X, Y, and Z transitions considered.
!  CORRECT      - Correction for degeneracies is done with TOL = 0.0001 eV.
!  VERBOSE      - Print verbose output to log file.
!
!%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
!
TITLE Electronic Transitions in Mno4-
!
! The files
KEYWRD OUTFILE=mno4-.edo
KEYWRD SPECFILE=mno4-.eds
!
! Output
KEYWRD OSCILLOUT
KEYWRD DIPLENOUT
!KEYWRD MATOUT
!
!KEYWRD FITONLY
!
! Method
KEYWRD MATRICE=ALL
!KEYWRD CUTOFF=10.0
!
! Polarization
KEYWRD POL = XYZ
KEYWRD CORRECT, TOLERANCE=0.0001
!
! Verbose output to log file
KEYWRD VERBOSE
!
[WAVERANGE]
! Change these numbers to something more reasonable :-)
```

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```
START 4711, 4711
END 4711, 4711
!
[FIT_SPEC]
E_RANGE 20000.0, 40000.0
H_WIDTH 750.0
POINTS 20000
SPECS X, Y, Z, XYZ*
!
![DOT]
!E_RANGE 20000.0, 40000.0
!DELTA_E 10.0
!
!
! No changes should be necessary below here.
!-------------------------------------------------------------------------
[ATOMS]
MN    .0000    .0000    .0000
 O    9180    .9180    .9180
 O   -.9180   -.9180    .9180
 O   -.9180    .9180   -.9180
 O    .9180   -.9180   -.9180
[ATOMS_END]

[STO]
MN 4s. 4p. 3d.
  1.6500 1.0000 .0000 .0000
  1.1500 1.0000 .0000 .0000
  5.1500 .5470 2.1000 .6050
 O 2s. 2p.
  2.5750 1.0000 .0000 .0000
  2.2750 1.0000 .0000 .0000
 O 2s. 2p.
  2.5750 1.0000 .0000 .0000
  2.2750 1.0000 .0000 .0000
 O 2s. 2p.
  2.5750 1.0000 .0000 .0000
  2.2750 1.0000 .0000 .0000
 O 2s. 2p.
  2.5750 1.0000 .0000 .0000
  2.2750 1.0000 .0000 .0000
[STO_END]

[WAVE_FUNCTIONS]
  21.994005   1
  1.277633 .000000 .000000 .000000 .000000 .000000 .000000 .000000
   .000000 -.458772 .141484 .141484 .141484 -.458772 -.141484 -.141484
   .141484 -.458772 -.141484 .141484 -.141484 -.458772 .141484 -.141484
  -.141484
  .
  .
  .
  .
  .
  .
  .
```

To calculate the electronic dipole-induced transitions the program needs the Slater exponents, the geometry information and the final and initial wave functions. All these data is stored in the *.EDI file and is written on request by ICONC (Output control parameter #23 → False). After running the ICONC calculation you should make sure that the *filename*.EDI was written. Then you can modify the parameters and options directly in the file. Especially you have to define the waverange in which the electronic dipole-induced transitions should be calculated.

REMARK: As MS-DOS does not distinguish between capital and lower case letters the EDiT program may conflict with the proper MS-DOS editor *EDIT*.COM in the sense that EDiT will be called first. EDiT will then show its heading information and wait for input which it probably won't get as one usually does not start a full screen editor by redirecting a file to it. If this should happen just press CTRL-C to abort EDiT. If this should be a stumbling-block you have the choice of either renaming *EDiT*.EXE to *EDiTOr*.EXE (Electronic Dipole-induced Transitions by the use of Slater-type Orbitals) or starting the DOS editor by typing *EDIT*.COM *somefile*.*.

2.5 G O P

The Graphic Optimization Program (*GOP*) is a FORTRAN 90 program which searches for a minimum in an energy hyper surface using INPUTC and ICONC. In the current version, a simplex algorithm is being used (see 'Algorithm used' for detail).

In contrast to the other programs in this package, GOP is NOT portable, because it needs to make calls to INPUTC and ICONC using the operating system. If you want to compile the program yourself, you may have to change the source file INPUTC_ICONC.f90 (all other source files conform to the FORTRAN 90 ANSI standard).

Input for GOP is provided through a .gen file which must be created using INPUTC before running GOP. It lets you specify which angles and distances of the molecule specified in the .gen file you want to include in the optimization process.

GOP needs ICONC and INPUTC with all their needed parameter files. These files must be in the current working directory.

To start the program type GOP at the command line prompt.

The program will ask for the name of the .gen file you want to use for calculation. You can enter an entire path, up to 45 characters, including the filename, but leave away the extension .gen. If GOP can't locate or access the specified file, it will exit with an error message.
Note that GOP won't make any changes to your .gen file, but uses a temporary .gen file, named 'temp$1.gen' or similar.

After you have specified the .gen file, the **main menu** will appear:

```
*****************************************
*    simplex search for energy minimum   *
*                                         *
* 1 use variations in .gen file to        *
*      choose the parameters              *
* 2 choose parameters individually        *
* 0 exit                                  *
*****************************************
```

Option 1:
GOP will take the parameter for the energy hyper surface from the variations in the specified .gen file. Take the following .gen file as example:

```
   2   3   2   2
   2   0   2   0
water-corrected values
 0 3 0 0 0 1FFFFFFTFF 1.95 .000 .000FFFFFFFFFFFFFFFFFFFFFF
        .400000
  1   2    .95700    .00000    .00000
  1   3    .95700 104.60000    .00000
 * * H
 O 6 22.5750-28.87 22.2750-13.00
 H 1 11.3000-15.79
  1
   2   3   1.10000    .40000
111    2 2   1.000000
111    2 1   1.000000
111    1 1   1.000000
```

It contains three variations, the first changing the bonding angle (H-O-H), the second and third changing the two distances between O and H. Therefore GOP will optimize a three-dimensional energy hyper surface, $E(\alpha(H-O-H), d(OH_1), d(OH_2))$.

Please note that GOP will uncouple all coupled variations! If the variations in the above .gen file should look like

```
111    2 2   1.000000
111    2 1   1.000000
111 *  1 1   1.000000
```

meaning that the two distances are varied together, the hyper surface optimized by GOP will still be three-dimensional.

The number of variations and the increment are ignored by GOP.

If you choose this option, you will get to the menu 'settings for simplex algorithm' (described below).

Option 2:

With this option, GOP lets you specify which properties of which vectors in your .gen file to use as parameters for the energy hyper surface.

First you will be asked to enter the number of parameters you want to optimize. If you type in a number < 1, no calculation will be performed.

Then GOP will ask you to specify the vector and the type of change for each parameter (distance, bond angle, dihedral angle).

Note that GOP will accept impossible inputs (like -1 for a vector), but this may lead to exceptional program termination, endless calculation or strange results.

Then you will get to the menu '**settings for simplex algorithm**':

```
*****************************************
*    settings for simplex algorithm     *
*                                       *
* 1 use default settings                *
* 2 choose individual settings          *
*****************************************
```

Option 1 will leave the following default settings:
- starting values for parameters: taken from the specified .gen file
- initial step sizes: 0.05 for distances, 1.0 for angles
- stopping criterion: 1.e-4
- maximum number of function evaluations: 500
- name of output file: E_MIN.OUT
- progress report is disabled

Option 2 will let you change all of these settings.

Note that all inputs you make must conform to FORTRAN:
- decimal numbers must be written with a point (not comma)
- if you want to type a decimal with an exponent, you <u>must</u> write a decimal point:
   1.e-4 means 0.0001; 2.3e3 means 2300 etc., but 1e2 is illegal.

Explanation of the settings:

starting value for parameters: These determine where the optimization routine starts the search for the minimum. If you have a more or less vague idea where the minimum could be, set the starting values accordingly. The number of calculations GOP has to make to find a minimum depends strongly on them. Different starting values can lead to different minimums or to no minimum at all.

initial step sizes: These determine how far off the starting point the first few calculations will be made. The default values should be quite reasonable in most cases. But if you start close to a minimum you may want to choose smaller step sizes to ensure you don't go away from it with the first few steps. Also, if you are close to the minimum with just one parameter, you may make its step size small. Example: You may know that in a water molecule the distances (O-H) are about .958 Å, but have no idea about the bonding angle. So you will set the initial value for the distances to .958 and choose a step size of .0005, and for the angle start at 90° with a step size of 2 or even 5.

stopping criterion: This determines to what precision the minimum is searched. It should not be smaller than about 1.e-10 to make sure no rounding errors are made. Note that the maximum precision for distances and angles provided by INPUTC is five decimals. A too high precision of the energy value may not be sensible.

maximum number of function evaluations: The program stops after it has calculated more points than specified by this number, even if no minimum is found.

name of output file: specifies the file in which to store the results of calculation.

progress report: There are three settings for the progress report: 1) negative integer: no report (default); 2) zero: report after initial evidence of convergence; 3) positive integer: report after every *n* function evaluations (where *n* is the integer you entered).
In cases 2) and 3), the report is written into a file named PROGRESS_REPORT.GOP. This file's name can't be changed.
Note that when progress report is enabled, program execution speed is slightly smaller.

> While calculation takes place, you will see a lot of text flashing (or crawling, depending on your computers speed) over the screen. This is the output made by INPUTC. GOP will stop if it has found a minimum or if it cannot find one. If it has found a minimum, the result will be displayed. You can find the same information in the output file, too.

Possible Messages:

- *normal program termination:*

```
NO MINIMUM FOUND!
MAXIMUM NUMBER OF FUNCTION EVALUATIONS EXCEEDED
```
Try the calculation again with a bigger number of allowed function evaluations. You can find the parameter values of the last calculation made in the temporary file 'temp$1.gen', or in the progress report file, if you have enabled progress report.

```
NO MINIMUM FOUND!
COULDN'T EVALUATE QUADRATIC SURFACE FITTED
```
The simplex algorithm got stuck in a supposed minimum, but couldn't evaluate the quadratic fit because the information matrix of the quadratic surface was not positive semi-definite.
Try to restart with other starting values or generate a progress report to see what went wrong.

```
NO MINIMUM FOUND!
```

```
NUMBER OF PARAMETERS < 1
```
Try the calculation again but specify at least one parameter.

- *abnormal program termination*
```
ERROR READING/WRITING xxx.gen
```
The .gen file you specified could not be found or opened by GOP.


```
Unable to execute inputc.exe. Please check path    or
Unable to execute iconc.exe. Please check path
```
Make sure that inputc and/or iconc are located in your working directory and that all necessary files are present.

If this message appears after some calculations have already taken place, see 'known bugs'.

Algorithm used:

The simplex algorithm used in GOP was found on the internet as freeware. Here are the credits:

A PROGRAM FOR FUNCTION MINIMIZATION USING THE SIMPLEX METHOD.

FOR DETAILS, SEE NELDER & MEAD, THE COMPUTER JOURNAL, JANUARY 1965

PROGRAMMED BY D.E.SHAW,
CSIRO, DIVISION OF MATHEMATICS & STATISTICS
P.O. BOX 218, LINDFIELD, N.S.W. 2070

WITH AMENDMENTS BY R.W.M.WEDDERBURN
ROTHAMSTED EXPERIMENTAL STATION
HARPENDEN, HERTFORDSHIRE, ENGLAND

Further amended by Alan Miller
CSIRO Division of Mathematics & Statistics
Private Bag 10, CLAYTON, VIC. 3169

Fortran 90 conversion by Alan Miller, June 1995
Latest revision - 14 September 1995

There were some changes made to the file to allow redirection of the output into a file, but none of these affect the algorithm in any way. Take a look at the GOP source code if you are interested in details, or try `http://www.nag.co.uk/nagware/Examples/mead_plus.f90` for the original source, or `http://WWW.mel.dms.CSIRO.AU/~alan/` for Alan Millers home page.

See Nelder & Mead, The Computer Journal, January 1965, or a book dealing with numerical recipes or algorithms for an explanation of the simplex method. It is interesting that the applied algorithm makes a quadratic surface fit, to make sure a minimum has really been found.

known bugs:

Because of a fault in the portlib library of the Microsoft Fortran PowerStation 4.0 compiler, only a limited amount of calls to INPUTC and ICONC are possible. On the machine used for testing (Pentium Pro 200, 64MB RAM, Windows NT 4.0), after about 1180 function evaluations the message

`'Unable to execute inputc.exe. Please check path'` appeared. The cause of this message: No more resources!

It is therefore not possible to make unlimited calculations. It may even be that on machines with less resources the program will stop earlier. The number of function evaluations used for the examples was below 500, so these should present no problem.

'Workaround':
If you need to make a calculation that needs more than the possible function evaluations, try to make a report file and set the number of function evaluations to a value below which the bug will occur (note that the algorithm will not stop exactly at the value specified, but somewhere above it.). Start the calculation. You will get the message 'MAXIMUM NUMBER OF FUNCTION EVALUATIONS EXCEEDED'. Open the progress report file 'PROGRESS_REPORT.GOP' and look for the smallest value the algorithm has found so far. Take the parameter values of this calculation as new starting values and restart the calculation. Repeat until you have found the minimum.

We will eliminate this bug as soon as we purchase a new compiler.

You may try to compile the program on a different compiler, but then you will have to change the compiler-specific source file 'INPUTC_ICONC.f90'.

Examples:

I.

The file H2O_GOP.gen describes a water molecule (after iterations of charges and 1+κ and δ) and contains three variations. Let's try the simplest first: Start GOP, enter H2O_GOP as .gen file name, choose 'use variations in .gen file to choose parameters' (option #1), then 'use default settings' (option #1). GOP will start calculations. When it is finished, the following message will appear:

```
A total of          70   Function evaluations were used.

 MINIMUM =    -10.229218760
 FOUND AT:


    vector  [1-3]   param. value
    ------  -----   ------------
        2      2     104.61056
        2      1         .95665
        1      1         .95668
```

(The numbers may differ a little from machine to machine.)

Note that the same information is also available in a file named E_MIN.OUT.

We may like to get an even better result, so we can try again choosing 'choose individual settings' from the second menu. Then choose option #3, 'stopping criterion' and enter the value 1.e-7 (the point is needed by FORTRAN!). Then choose option #0, 'exit'. Calculation starts. We get:

```
A total of          124   Function evaluations were used.

 MINIMUM =    -10.229218860
 FOUND AT:


    vector  [1-3]   param. value
    ------  -----   ------------
        2      2     104.60423
        2      1         .95663
        1      1         .95663
```

II.

Take a look at the file CH4.gen. Let's try if GOP can find the regular tetrahedron structure if we place the five atoms into one plane:

Run GOP, specify CH4 as filename. Select `choose parameters individually`. You will be asked to make some input. The screen will look as follows (fat characters = your inputs):

```
How many parameters do you want to optimize (max. 12)? 4

The specified .gen file contains the following vectors:

vector- vector    distance bond-      dihedral-
number                     angle      angle
------- -------   -------- ---------  ---------
   1       1   2    .80000 125.26440 45.00000
   2       1   3    .80000 125.26440 225.00000
```

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```
3       1   4      .80000 54.73561  135.00000
4       1   5      .80000 54.73561  315.00000
```

```
Parameters for variation; Please choose:
```
• vector number
• Var. of 1=distance, 2=bond angle, 3=dihedral angle

```
Param. vector   Var.of
number number   [1-3]
---------------------
1     : 1         3
2     : 2         3
3     : 3         3
4     : 4         3
```

You have now chosen to optimize the four dihedral angles in the molecule.

From the following menu, select 'choose individual settings'. Then try 'starting values for parameters'.

We would like to have the five atoms in one plane at the beginning of the calculation; the four hydrogens placed in a square around the carbon atom. So we choose

```
Type in new starting values:

param.  vector  [1-3]   new
 no.                    value
------  ------  ------ --------
   1      1       3 :     0.
   2      2       3 :   180.
   3      3       3 :     0.
   4      4       3 :   180.
```

We want to leave the rest of the settings, so we choose exit. We get the following results:

```
 A total of        291   Function evaluations were used.

 MINIMUM =   -14.343944270
 FOUND AT:

    vector  [1-3]   param. value
    ------  ------   ------------
        1      3        40.89309
        2      3       220.89813
        3      3       -49.09139
        4      3       130.91446
```

This describes again a regular tetrahedron, although slightly rotated in comparison to the other. You may wish to get a higher precision, as described in Example I. But then it may be necessary to increase the maximum number of function evaluations allowed (select choose individual settings, and then option# 4), or after calculation you might get a message like:
NO MINIMUM FOUND!
MAXIMUM NUMBER OF FUNCTION EVALUATIONS EXCEEDED

because more function evaluations than specified as maximum value are needed to solve the problem. If this occurs, you may want to open the temporary file 'temp$1.gen', check the parameter values of the last calculation and restart the calculation with these as new starting values.

III.

In 2-H2O_GOP.gen you will find defined two interacting water molecules. It would be nice to locate a minimum concerning the length of the hydrogen bridge (vector #3, pointing from atom 1 to atom 4) and the angle (bond angle of vector #3) between the plane defined by the first molecule (atoms 1-3) and the bond above.

We have tried this with various starting values for the parameters:

(initial step size distance=0.05, stopping criterion=1.e-4)

starting value distance	starting value angle	initial step size angle	distance found	angle found	minimal energy
1,75000	70,00000	1,00000	3,06878	71,10612	-20,458461500
1,75000	140,00000	1,00000	1,78385	146,10894	-20,464232320
1,75000	200,00000	1,00000	1,79167	211,58330	-20,464361780
2,00000	110,00000	0,50000	NO	MINIMUM	FOUND
2,00000	110,00000	1,00000	1,78427	146,22675	-20,464232700
2,00000	190,00000	1,00000	1,77889	213,44728	-20,464412090
3,00000	70,00000	1,00000	2,83077	0,57838	-20,460594150

The algorithm finds four different minimums for various starting values.
In one case no minimum was found. The following message appeared (see 'Algorithm used'):
COULDN'T EVALUATE QUADRATIC SURFACE FITTED
We included this example to show you that sometimes a small change in the settings can determine if you will get a result or not.

The first and the last of the minimums found are not really interesting, because the distance of the hydrogen bridge is so big that other interactions than the one we're interested in will play a bigger role. The interesting results lie at 146° and 213°. Take a look at the following graph:

Energy Hypersurface for Interaction between two water molecules
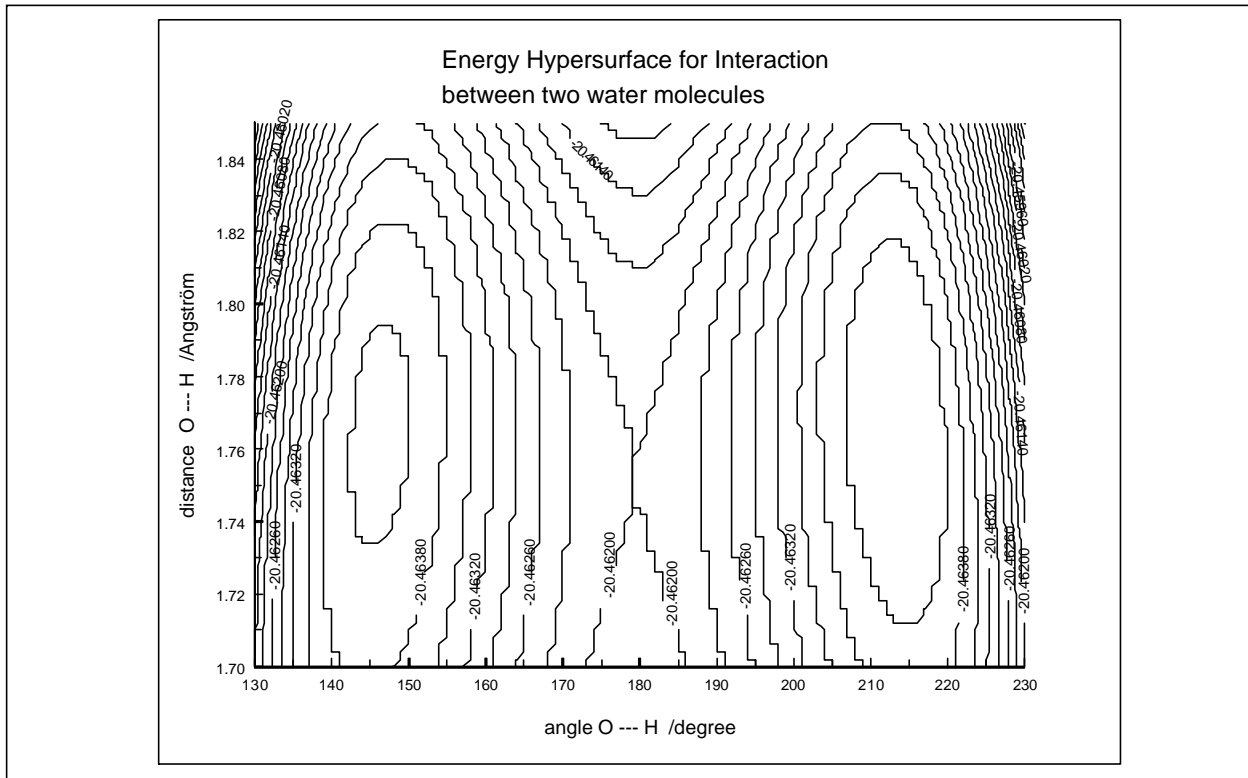
We can see clearly the same minimums as found with GOP. Note that 360° - 146.5° = 213.5°.

The minimums in this problem are relatively flat. Be aware that in such cases, the point where the simplex algorithm will stop depends more than elsewhere on the starting values:

starting value distance	step size	starting value angle	step size	stopping criterion	distance found	angle found	minimal energy
1,75000	0,010	140,00000	1,000	1,0E-07	1,78388	146,18871	-20,464232480
1,78000	0,005	146,00000	0,100	1,0E-07	1,78529	146,06743	-20,464232620
1,78000	0,005	213,00000	0,100	1,0E-07	1,78110	213,64971	-20,464413100
1,75000	0,010	210,00000	0,700	1,0E-10	1,78068	213,64915	-20,464412980

IV.

We would like to check if all C-C bonds in a D_{6h}-benzene are of the same length. We start GOP with the file BENZENE.GEN and choose 5 parameters (the distances between the carbon atoms (vectors 2-6)). As starting values we enter:

```
Type in new starting values:

param.   vector   [1-3]      new
 no.                        value
------   ------   ------   --------
     1        2        1 :    1.34
     2        3        1 :    1.4
     3        4        1 :    1.34
     4        5        1 :    1.4
     5        6        3 :    1.34
```

These settings correspond to the (wrong) idea that a benzene ring contains three double bonds.

Then we set the stopping criterion to 1.e-6 because we are varying quite a lot of parameters. We get:

```
A total of          221    Function evaluations were used.

 MINIMUM =    -80.688233870
 FOUND AT:

     vector   [1-3]   param. value
     ------   ------   ------------
        2       1        1.41068
        3       1        1.41065
        4       1        1.41070
        5       1        1.41064
        6       1        1.41067
```

To demonstrate that GOP can solve higher-dimensional problems too, we start the calculation of BENZENE.GEN once more. This time, we choose 11 parameters, all bond lengths in the molecule (excluding the one from dummy atom 13 to atom 1). We leave the starting values as they are in the .gen file, only set the precision to 1.e-8. We get:

```
A total of          744    Function evaluations were used.

 MINIMUM =    -80.688680270
 FOUND AT:

     vector   [1-3]   param. value
     ------   ------   ------------
        2       1        1.41036
        3       1        1.41040
        4       1        1.41036
        5       1        1.41039
        6       1        1.41037
        7       1        1.06194
        8       1        1.06196
        9       1        1.06194
       10       1        1.06198
       11       1        1.06193
       12       1        1.06197
```

There is a progress report file (benzene1.pgr.gop) and the output file (benzene1.E_min.out) available for this calculation.

Additional Examples you may want to try:

- 2h2oag_distance.gen
- 2h2oag_angle.gen
- C2h2.gen
- C2h4.gen
- C60.gen (contains no variations)

2.6 Datafiles

INPUT FILES	INPUTC	ATOMDEF.DAT, VOI.DAT, FOI.DAT
	ICONC	Files created by INPUTC with extension *.KAR
	EDiT	Files created by INPUTC&ICONC with extension *.GEN and *.MO Files which must be edited by the user with extension *.EDI
	GOP	Files created by INPUTC with extension *.GEN
	Q-TOOLS	Files created by INPUTC with extension *.GEN

OUTPUT FILES	INPUTC	*.GEN, *TEMP*.KAR, *TEMP*.VAR
	ICONC	*filename*.OUT, *ENERTOT*.DAT, *ENERNI*.DAT, *filename*.MO
	EDiT	*filename*.EDO
	GOP	E_MIN.OUT (or user-specific) PROGRESS_REPORT.GOP if progress report is enabled
	Q-TOOLS	Various files, depending on the options used. Filenames are user-specific, extensions can be *.MAT, *.ENE, *.ENM, *.VAR, *:VA1, *.VA2, *.COR, *.ALL, *.MIN

2.7 Examples

A number of example input files have been added to make it easy to familiarize with the different aspects of ICON-EDiT. Some of them are listed below. You can run them by the following procedure:

> ICONC < *filename*.KAR > *filename*.OUT
> e.g. ICONC < *H2O*.KAR > *H2O*.OUT
> OR
> EDiT < *filename*.EDI > *filename*.EDO
> e.g. EDiT < *MNO4-*.EDI > *MNO4-*.EDO

2-H2O_GOP.GEN	GOP example III.
2H2OAG_ANGLE.GEN	GOP additional example.
2H2OAG_DISTANCE.GEN	GOP additional example.
AG2.GEN	Input example, Ag_2 molecule, d(Ag-Ag) = 0.5 - 4 Å.
ALOALOH3.KAR	Input example, $(OH)_3Al-O-Al(OH)_3$. Charge iteration on all atoms.
BENZENE.GEN	GOP example IV.
BENZENE1.PGR.GOP	GOP report file for above example.
BENZENE1.E_MIN.OUT	GOP output file for above example.
BIPY.GEN	Input example, bipyridyl molecule. Internal coordinates with variation of the angle between the two aromatic rings along the C-C and the C-H bonds.
BIPY.KAR	Input example, bipyridyl molecule at equilibrium geometry.
CH4.GEN	Input example, methane molecule. Internal coordinates with variation along the C-H bonds. GOP example II.
C2H2.GEN	GOP additional example.
C2H4.GEN	GOP additional example.
C60.GEN	GOP additional example.
CHNCLPT.GEN	Input example, $[H_2C=CH_2][N-(CH_3)_2]Pt$ = *trans*-Dichloromethyl-aminoethyleneplatinum(II). Internal coordinates with variation of the $[H_2C = CH_2]$ -Pt$[Cl_2]$ bond angle.
CRF63-.KAR	Input example, chromium hexafluoride at equilibrium geometry. Charge iteration on Cr only.
CUH.GEN	Input example, CuH molecule, d(Cu-H) = 1.0 - 5 Å.
ETHANE.KAR	Input example, H_3C-CH_3 molecule at equilibrium geometry. Internal coordinates with variation along the C-C and the C-H bonds.
ETHENE.GEN	Input example, H_2C-CH_2 molecule. Internal coordinates with variation along the C-C and the C-H bonds.
ETHENFMO.GEN	Input example, ethene molecule at equilibrium geometry, split into two neutral methylene fragments. Geometry is given in internal coordinates.

ETHINE.GEN	Input example, HCCH molecule. Internal coordinates with variation along the C-C and the C-H bonds.
GLYCIN.KAR	Input example, glycine molecule at equilibrium geometry.
H2.GEN	Input example, H_2 molecule, d(H-H) = 0.5 - 5 Å.
H2O_GOP.GEN	GOP example I.
H2O.KAR	Input example, H_2O molecule at equilibrium geometry.
H2OIT.KAR	Input example, H_2O molecule at equilibrium geometry. Charge iteration on all atoms.
H2OFA1.GEN	Input example, H_2O molecule. Internal coordinates with variation along the totally symmetric A1 stretching and bending modes: 0.9 Å ≤ r_1, r_2 ≤ 1.1 Å and 100^0 ≤ ϕ ≤ 160^0.
H2OFB1.GEN	Input example, H_2O molecule. Internal coordinates with variation along the asymmetric stretching mode B1: 0.9 Å ≤ r_1, r_2 ≤ 1.1 Å and α = 105^0.
MNO4-.KAR	Input example, permanganate at equilibrium geometry. Charge iteration on Mn only.
PROPEN_F.GEN	Two FMO examples are added: Input example, propene molecule at equilibrium geometry, split into a neutral methyl fragment. Geometry in internal coordinates.
ZEISE.GEN	Input example, ($H_2C = CH_2$) - $Pt[Cl_3]$ bond angle.

FORMAL.EDI	$\pi^* \leftarrow \pi$ in formaldehyde.
MNO4-.EDI	Input file to calculate the first electronic transition in permanganate. It is the LMCT transition responsible for the violet color of MnO_4^-.
RUBIPY3.EDI	Input file to calculate the first few MLCT transitions in $[Ru(bipy)_3]^{2+}$.

3   Quick Start

Copy the unpacked files of the distribution into a directory of your choice.

3.1 ICONC

Enter the following line at the command prompt to run a calculation with an input file containing Cartesian coordinates (e.g. H2O.KAR):

```
ICONC < H2O.KAR > H2O.OUT
```

3.2 EDiT

Enter the following line at the command prompt for an oscillator strength calculation with the example file FORMAL.EDI:

```
EDiT.bat FORMAL
```

4 Explanation of the *.GEN* Files

The *.GEN* files consist of two parts, namely geometry information necessary to create cartesian coordinates and the EHMO input. INPUTC creates these files automatically. The following information can be useful if you want to change these files for special purposes.

```
       Input file : ZEISE.GEN
a      10   2   4   0
       10   1   4   0

b      ZEISE-SALT

c       0  10 -1   0   0   1FFFFFFFFF 2.00   .000   .000FFFFFFFFFFFFFFFFFFFFFFFF

d             .350000

e      11    1    2.09000 180.00000    .00000
        1    2    2.30000 180.50000    .00000
        1    3    2.30000  90.50000 -90.00000
        1    4    2.30000  90.50000  90.00000
       11    5     .73500  90.00000    .00000
       11    6     .73500 -90.00000    .00000
        5    7   1.08000 109.50000  90.00000
        5    8   1.08000 109.50000 -90.00000
        6    9   1.08000-109.50000  90.00000
        6   10   1.08000-109.50000 -90.00000

f       * *CLCL *C * H H H

g      PT 10   61.9720 -9.08   61.3330 -5.48   54.0840-12.59 .7980 1.840 .3520
       CL  7   32.2270-30.00   31.9160-15.00
        C  4   21.6250-21.40   21.6250-11.40
        H  1   11.3000-13.60

m      10    5  3 10.000000
       10 *  6  3 10.000000
```

REGION a Control parameters for variation (1) and conversion (2).

	A	B	C	D
1	10	2	4	0
2	10	1	4	0

1A =   number of connection vectors: **e**
1B =   number of coordinate variation cards: **m** (number of parameter rows)
1C =   number of atom definition rows plus rows needed for charge iteration parameters: **g**, **h**
1D =   number of rows needed for specified and non integer orbital occupation (**l**), FMO specifications (**i**), individual $1 + \kappa$, δ specification (**i**) and omit atoms from repulsion energy option (**k**). 1D corresponds to number of lines to be copied at each variation.
2A =   the same as 1A
2B =   number of dummy atoms
2C =   the same as 1C
2D =   not used

REGION b   title card, in this example: ZEISE-SALT

REGION c   parameters for ICONC

0	10	-1	0	0	1	FFFFFFFFF	2	. 000	. 000	FFFFFFFFFFFFFFFFFFFFFFF
NH	NA	KA	ME	IP	IU	F1-F9		CON	PEEP	COULH PRT(I) I = 1 - 23

FORMAT(I3,I4,4I3,9L1,F5.2,2F6.3,23L1)

NH	=	not used
NA	=	number of atoms
KA	=	charge of the molecule
ME	=	charge iteration method. 0 = without, 2 = with charge iteration on each atom, 4 = with charge iteration on atom groups
IP	=	IPRINT, see below
IU	=	IPU if 1, distance dependent weighted W.-H. formula, otherwise 0
F1	=	if .T., specified and non integer orbital occupation
F2	=	used for other purposes
F3	=	used for other purposes
F4	=	used for other purposes
F5	=	if .T., the weighted H_{ij} formula is used
F6	=	if .T., FMO calculation is selected
F7	=	if .T., individual k, d specification is used
F8	=	if .T., omit atoms from repulsion energy option is selected
F9	=	if .T., user specified atomic electron configuration is selected
CON	=	κ used in H_{ij} formula; $1 + \kappa$ in distance dependent κ
PEEP	=	not used
COULH	=	not used
PRT(I)	=	setting PRT(I) = .TRUE. will **suppress the printing of the matrix**

CODE NUMBER I		IPRINT						
	PRINT-OPTION TABLE							
		1	1	0	-1	-2	-3	-4
1	Coordinates, Parameters	x	x	x	x	x	x	x
2	Overlap integrals	x	x	x	x	x	x	
3	Distance matrix	x	x	x	x	x	x	
4	Overlap matrix	x	x	x	x	x	x	
5	Madelung parameters	x	x	x	x	x		
6	Input hamiltonian matrix	x						
7	Hamiltonian matrix for next cycle	x						
8	Energy levels	x	x	x	x	x		
9	Total energy	x	x	x	x	x		
10	Wavefunctions	x	x	x	x			
11	Density matrix	x						
12	Overlap population matrix	x	x					
13	Reduced overlap population matrix	x	x	x				
14	Complete charge matrix	x	x					
15	Reduced charge matrix	x	x	x				
16	Net charges and populations	x	x	x				
17	Energy matrix	x						
18	Reduced energy matrix	x	x	x				
19	Energy partitioning	x						
20	Reduced energy partitioning	x	x					
21	Core core repulsion energy matrix	x						
22	Moby output							
23	Write EDI-File							

REGION d   .350000 = Parameter d in the distance dependent weighted W.-H.formula.

REGION e   Connection vectors; see examples in section 2.2 INPUTC.

REGION f   Atom card
* *CLCL * C * H H H
The „*" correspond to Pt, Cl, C and H in region g.

REGION g   Atom definition card as read from ATOMDEF.DAT.
```
PT  10 61.9720 -9.08  61.3330 -5.48  54.0840-12.59 .7980 1. 840 .352
CL   7 32.2270-30.00  31.9160-15.00
C    4 21.6250-21.40  21.6250-11.40
H    1 11.3000-13.60
```

PT	10	6	1,97	-9,08	6	1,33	-5,48	5	4,08	-12,59	0,79	1,84	0,35
SYMB	VELEC	NS	EXPS	COULS	NP	EXPP	COULP	ND	EXPD1	COULD	C1	EXPD2	C2

FORMAT(A2,I3,3(I3,2F6.3),F6.4,F6.3,F6.4)
SYMB   symbol of atom
VELEC   number of valence electrons for neutral atom
NS   s electron principal quantum number
EXPS   s electron exponent

ICON-EDiT, Summer 2000   Gion Calzaferri

COULS	s electron H_{ii}*
EXPP	p electron exponent
COULP	p electron H_{ii}*
ND	d electron principal quantum number
$EXPD_1$	d electron first exponent
COULD	d electron H_{ii}*
C_1	coefficient of $EXPD_1$
$EXPD_2$	d electron exponent 2
C_2	coefficient of $EXPD_2$

C_1, $EXPD_2$ and C_2 are required if double ζ orbitals are used:

$$R_{ND}(r) = r^{(ND-1)}(C_1 \cdot e^{-EXPD_1 \cdot r} + C_2 \cdot e^{-EXPD_2 \cdot r})$$

* When using charge iteration, COULS, COULP and COULD serve as initial guesses for the Coulomb integrals H_{ii}.

REGION h   Charge iteration parameters;
see Chapter 4.1 and examples MNO4-.KAR, ALOALOH3.KAR.

REGION i   FMO specifications, if FMO calculation selected; see ETHENFMO.GEN.

First (evtl. second) line:	Assignment of atoms to fragment numbers. FORMAT(78I1)
Second (evtl. third) line:	Integer charges of each fragment. FORMAT(9I3)
	FMO print options. FORMAT(7L1)

REGION j   Individual 1 + k, δ specifications, if selected.
First line: Number of atom pairs. FORMAT(I3).
Succeeding lines: Atom pairs for specific l + k, δ. If δ = 0.0, global value will be used. FORMAT(2I4,2F10.5)

REGION k   Omit atoms from core-core repulsion energy specifications, if chosen.
Number of atoms to be omitted, atom numbers of atoms to be omitted.
FORMAT(11I4)

REGION l   Individual and noninteger orbital occupation.
See example *CRF63*-.INP.

REGION m   Variation parameters.
Number of variations: In order to have a bond length varied from 1.0 to 2.0 Å you will have to choose 11 variations at an increment of 0.1 Å.
Lines containing an asterisk will be coupled to the preceding line.
(Both variations will be done at the same step.)
Vector to be varied: Line number of section **e**.
Type of variation: 1 $\equiv$ r, 2 $\equiv$ a, and 3 $\equiv$ ξ (cf. section 2.2 for an explanation).

Number of variations	Coupling	Vector to be varied	Type of variation	Increment per step
10		5	3	10.000000
10	*	6	3	10.000000

FORMAT(I3,A2,2I3,F10.6)

4.1 Charge Iteration

If selected, the program performs a self-consistent charge calculation. The procedure can be used to iterate on the charges of all atoms in the molecule, on the charges of atom groups or only on the charges of selected atoms or atom groups. The diagonal Hamiltonian matrix elements are given by $H_{ii} = -VSIE(Q)$ where $VSIE(Q)$ is the valence state ionization energy of orbital i when the atom has a total charge Q. The off-diagonal Hamiltonian matrix elements are calculated in the normal manner. The $VSIE(Q)$ functions are assumed to be of the following form (d_0, d_1 and d_2 are parameters, stored in VOI.DAT and FOI.DAT):

$$VSIE(Q) = d_0 + d_1 Q + d_2 Q^2$$

We give a detailed description of the VSIE concept in chapter 5.3. A damping scheme is employed during the charge iteration procedure. The orbital occupations are summed separately over the s, p and d orbitals on each atom. The resulting s, p and d occupations are damped according to:

$$\rho_r^{input_{k+1}} = \rho_r^{input_k} + \lambda \left(\rho_r^{output_k} - \rho_r^{input_k} \right)$$

where ρ is the summed orbital occupation of a given type, s, p, or d, indexed by r on the kth cycle and λ is a damping parameter. During the iterative process, the correction factor multiplying λ can become very small. For a constant value of λ this leads to slow convergence because of the necessity of having λ small at the beginning of the iteration. In the iterative technique used by ICONC λ is defined by the equation

$$\lambda = ADJUST/DENOM^k, \text{ where } DENOM^k = \max \left| \rho_r^{output_k} - \rho_r^{input_k} \right|$$

$DENOM^k$ is the maximum difference of the absolute value of the summed orbital occupation types s, p or d which are indexed by r. ADJUST is a constant which is decremented under certain conditions to be described below. DENOM will decrease as convergence is achieved and provides the variation in λ. In order to insure stability in the iterative process, values for λ are compared to a fixed constant λ' (LAMPRI). The value of λ' represents an upper limit above which the procedure will usually diverge. λ' depends significantly on the charge dependence. If the charge dependence is high, λ' should be small ($\lambda' \leq 0.10$). For reduced charge dependences a larger value of λ' may be used.

The following equations are used to determine values for ADJUST at various stages in the iterative calculations:
1. For the first cycle, ADJUST = $DENOM^k$ (i.e. $\lambda = 1.0$). The first cycle is a normal extended-Hückel calculation. Thus, the initial guess for the orbital occupations is determined by the input values of COULS, COULP and COULD.
2. For the second cycle, ADJUST = DAMP1*$DENOM^k$. $0 < DAMP1 \leq \lambda$. DAMP1 is usually set to 0.10, but can be increased if the initial guess is known to be particularly good.
3. ADJUST = DAMP2*$DENOM^k$ is used whenenver λ becomes equal to or greater than λ'. $0 < DAMP2 \leq \lambda'$. DAMP2 should be nearly equal to λ' as possible.
4. Whenever $\max \left[\left(\rho_r^{output_k} - \rho_r^{input_k} \right) \right]$ is of different sign than $\max \left[\left(\rho_r^{output_{k-1}} - \rho_r^{input_{k-1}} \right) \right]$, two options are possible:

      a) DAMP3 $\neq$ 0. ADJUST = DAMP3*ADJUST where $0 < DAMP3 \leq 1.0$

      b) DAMP3 = 0. The program calculates a value for λ using a linear interpolation
      between cycles k and k - 1. The value of ADJUST is left unchanged.

Convergence is assumed when $DENOM^k < DELTAC$ and the iteration procedure is terminated.

5 Theory

Applications of the extended-Hückel procedure has influenced the contemporary way of reasoning in different fields. In addition to its transparency, one of the most fascinating aspects of this method is that it can be applied to study molecules, clusters, solids and the interaction of molecules on surfaces. It is well known that the EHMO method in its original form does not correctly include electrostatic interaction and therefore often fails to yield good potential energy curves for stretching modes. This problem has been solved to some extent by adding a two-body electrostatic correction term which leads to the EHMO-ASED (atom superposition and electron repulsion) procedure. Another feature we have recently implemented is an option to calculate electronic transition oscillator strengths (EDiTs) by including all off-diagonal elements.

5.1 The EHMO Theory

In this chapter we introduce the semiempirical EHMO-procedure as used to calculate properties of molecules, complexes and clusters. Later we will learn how EHMO reasoning can be applied to learn more about reactivities, about electronically excited states and we will discuss an extension which makes it possible to describe solids, surface states and surface molecules.

The LCAO-MO procedure – LCAO-MO signifies **L**inear **C**ombination of **A**tomic **O**rbitals to **M**olecular **O**rbitals – as it is described here, represents the simplest possible access to the quantum mechanical description of molecule properties not limited to a particular class of compounds.

The qualitative comprehension and the interpretation of the results are usually considered more difficult than the calculation itself. We will therefore start with a qualitative description of the procedure and introduce its quantitative formulation at a later stage.

5.1.1 The most simple MO-approach

In simple cases, molecular orbitals can be constructed with the following four rules:

A) *Molecular orbitals can be approximated by a linear combination of the atomic orbitals.*
The molecular orbitals must be normalized.

Completion: usually the valence orbitals of the atoms are used. This limitation can be dropped when required.

This rule can be illustrated with the H_2 molecule.

$$\Psi_{\sigma_u} = (1s(H_1) - 1s(H_2)) \cdot \frac{1}{\sqrt{2(1-S)}}$$

$$\Psi_{\sigma_g} = (1s(H_1) + 1s(H_2)) \cdot \frac{1}{\sqrt{2(1+S)}} \qquad (5.1)$$

$$S = \langle 1s(H_1)|1s(H_2)\rangle$$
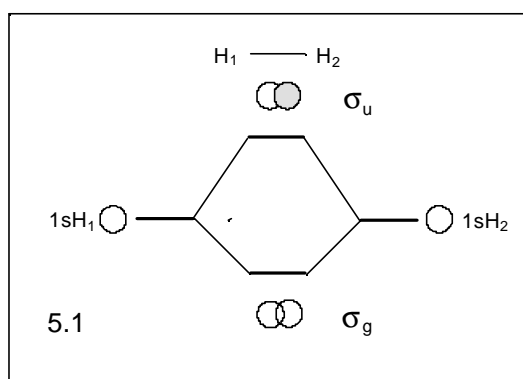
Scheme 5.1

S signifies the overlap integral. In this example it describes the spatial overlap of the two 1s-functions. The course of the 1s-function and the molecular orbitals are calculated and illustrated in the Mathcad program *1s-ovl.mcd*.
The molecular orbitals (5.1) are normalized.

$$\langle\Psi_{\sigma_u}|\Psi_{\sigma_u}\rangle = 1 \quad \text{and} \quad \langle\Psi_{\sigma_g}|\Psi_{\sigma_g}\rangle = 1 \tag{5.2}$$

We want to prove this statement for the Ψ_{σ_u} orbital:

$$\langle\Psi_{\sigma_u}|\Psi_{\sigma_u}\rangle = \langle(1s(H_1) - 1s(H_2))|(1s(H_1) - 1s(H_2))\rangle \cdot \frac{1}{2(1-S)} \tag{5.3}$$

$$\langle\Psi_{\sigma_u}|\Psi_{\sigma_u}\rangle = \{\langle1s(H_1)|1s(H_1)\rangle + \langle1s(H_2)|1s(H_2)\rangle - 2\langle1s(H_1)|1s(H_2)\rangle\} \cdot \frac{1}{2(1-S)} \tag{5.4}$$

$$\langle\Psi_{\sigma_u}|\Psi_{\sigma_u}\rangle = (1 + 1 - 2S) \cdot \frac{1}{2(1-S)} = 1 \tag{5.5}$$

B) *Only orbitals with the same symmetry can interact with each other.*

For the qualitative construction of molecular orbitals of simple molecules with sufficient symmetry, this rule can be applied particularly well if linear combinations of the atomic orbitals (AO's) of the outer atoms are first built and then combined with the AO's of the atoms located in the deeper interior. This procedure is called TASO which states for *Terminal Atom Symmetry Orbitals*. The significance of this is illustrated below with the linear *H—Be—H*.
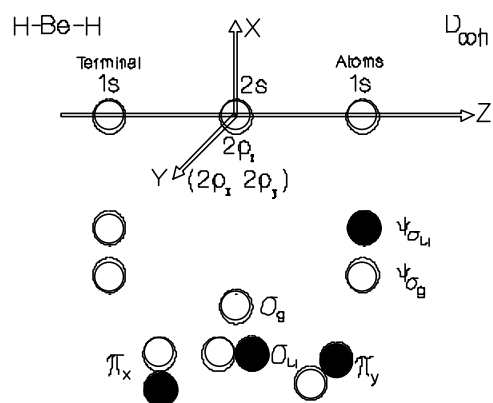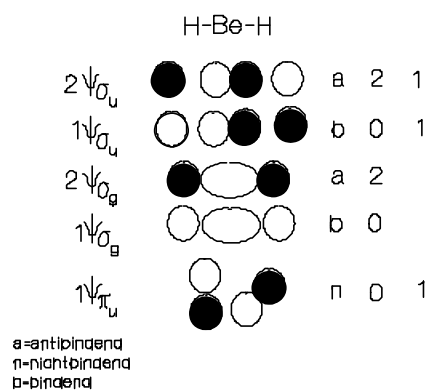
Scheme 5.2   **Scheme 5.3**

Scheme **5.2** shows the TASO's for *H—Be—H*. Linear combination of these symmetrically arranged atomic orbitals results in the molecular orbitals sketched in **5.3**. The first column to the right of **5.3** indicates the number of nodes of the molecular orbitals perpendicular to the bond axis. The second column indicates the number of angular nodes of the AO's involved.

C) *The energy of the MO's constructed in this way increases with the number of nodes perpendicular to the bond axes.*

The energy of the nonbonding orbitals lies between the energy of the accompanying bonding and anti-bonding orbitals. Orbitals without a node in a plane containing the bond axis are called σ−orbitals, those containing one node are called π−orbitals and those with two nodes are called δ-orbitals; corresponding to the s-, p- and d-functions of the atoms.

D) **The electrons are filled in corresponding to the Aufbau Principle, starting with the lowest energy levels, continuing with higher and higher energy levels, filling them with as many electrons as the Pauli principle allows.**

This is how the **electron configuration** of the electronic ground state is obtained.

The application of rules C) and D) on the *H—Be—H* molecule results in the qualitative MO diagram shown in Figure 5.1.

HOMO = Highest Occupied Molecular Orbital
LUMO = Lowest Unoccupied Molecular Orbital
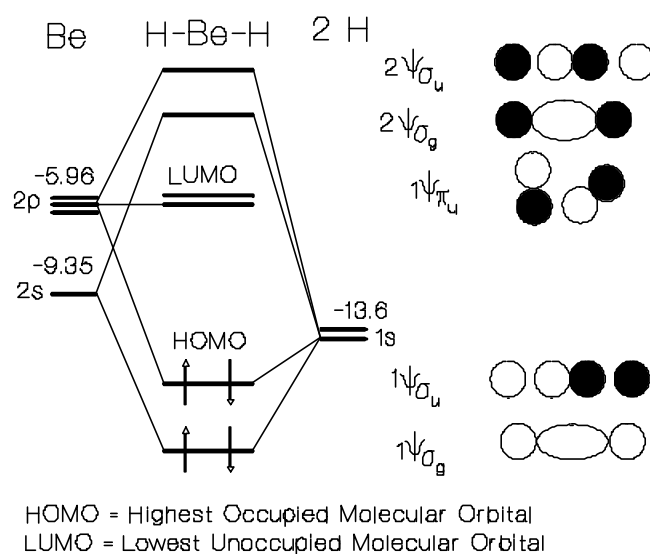
Figure 5.1: Qualitative MO-diagram of the linear *H—Be—H* molecule. For orbitals with the same symmetry, the MO's are numbered advancing from low energy towards higher energy. The determination of the 1s orbitals of H and of the 2s and the 2p orbitals of Be on the basis of the experimental ionization energy will be discussed later.

Corresponding to the MO-diagram, the electron configuration of the *H—Be—H* molecule is defined by:

$$\left(1\Psi_{\sigma_g}\right)^2 (1\Psi_{\sigma_u})^2 \tag{5.6}$$

The highest occupied orbital HOMO is of σ-type and is built from the p_z orbital of beryllium. In view of the 1s shell of the Be, the following three ionization processes IP_1, IP_2 and IP_3 can be expected to occur in BeH_2:

$$IP_1: (1s)^2\left(\Psi_{\sigma_g}\right)^2(\Psi_{\sigma_u})^1 \leftarrow (1s)^2\left(\Psi_{\sigma_g}\right)^2(\Psi_{\sigma_u})^2$$

$$IP_2: (1s)^2\left(\Psi_{\sigma_g}\right)^1(\Psi_{\sigma_u})^2 \leftarrow (1s)^2\left(\Psi_{\sigma_g}\right)^2(\Psi_{\sigma_u})^2 \tag{5.7}$$

$$IP_3: (1s)^1\left(\Psi_{\sigma_g}\right)^2(\Psi_{\sigma_u})^2 \leftarrow (1s)^2\left(\Psi_{\sigma_g}\right)^2(\Psi_{\sigma_u})^2$$

The lowest unoccupied orbital LUMO is of π-type and is doubly degenerated. It cannot be reached by electronic stimulation because $\pi \leftarrow \sigma$ electronic transitions are forbidden in molecules of this high symmetry.

Illustration of the LCAO-MO idea   1s-OVL.MCD

1s orbital s_H of the hydrogen atom:

Constants: $\qquad a_0 := 0.529 \qquad\qquad Z := 1 \qquad \zeta := \dfrac{Z}{a_0}$

Distance $\rho = r \cdot (Z/a_0)$: $\qquad \rho := -7 \cdot \zeta, -6.75 \cdot \zeta .. 7 \cdot \zeta$

1s orbital: $\qquad\qquad N_H := \sqrt{\dfrac{1}{4 \cdot \pi}} \cdot 2 \cdot \zeta^{\frac{3}{2}} \qquad s_H(\rho) := N_H \cdot e^{-|\rho|}$

1s-orbital of the hydrogen atom

$s_H(\rho)$

Value of the function

ρ

Distance from the nucleus
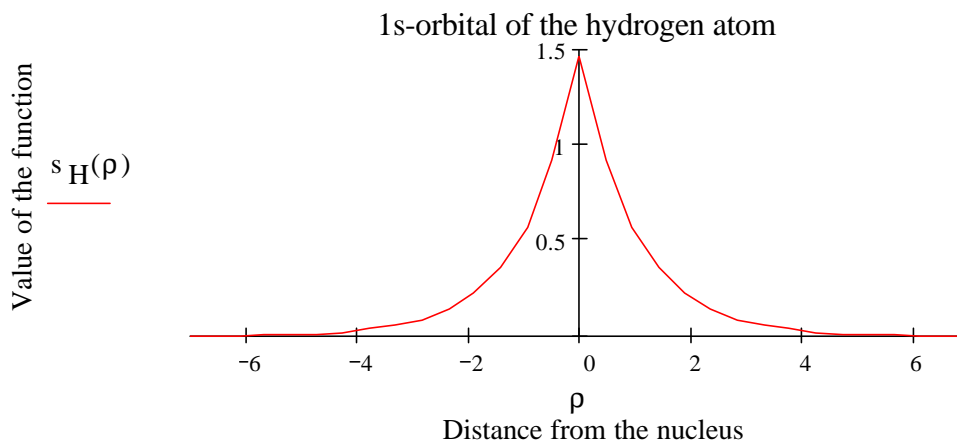
The two 1s orbitals interfere in a *constructive* and in a *destructive* manner. This corresponds to a positive ($1s_H + 1s_H$) and to a negative ($1s_H - 1s_H$) linear combination. The positive linear combination results in a bonding interaction, abbreviated as σ_g:

$\qquad \sigma_g \sim (1s_H + 1s_H)$

The negative linear combination results in the antibonding interactions:

$\qquad \sigma_u \sim (1s_H - 1s_H)$

For the following we need some definitions:

$N_{points} := 53 \quad i := 0..\, N_{points} \quad j := 0..\, N_{points} \qquad R_e := 0.7414 \qquad \zeta := \dfrac{1.3}{a_0} \qquad \rho_e := R_e \cdot \zeta$

$\delta R := \dfrac{8 \cdot R_e}{N_{points}} \qquad r_i := \left(i - \dfrac{N_{points}}{2} \right) \cdot \delta R \qquad\qquad \rho_i := r_i \cdot \zeta \qquad x_i := \rho_i \qquad y_i := \rho_i$

Orbitals of the two H atoms: $\qquad s_{H1}(\rho) := N_H \cdot e^{-|\rho_i + \rho_e|} \qquad s_{H2}(\rho) := N_H \cdot e^{-|\rho_i - \rho_e|}$

Overlap S of the 1s functions
of the two H atoms:

$$S_e := \left(1 + \rho_e + \frac{\rho_e^2}{3}\right) \cdot e^{-\rho_e}$$

Bonding linear combination:

$$\sigma_g(\rho) := \frac{1}{\sqrt{2 + 2 \cdot S_e}} \cdot \left(s_{H1}(\rho) + s_{H2}(\rho)\right)$$

Antibonding linear combination:

$$\sigma_u(\rho) := \frac{1}{\sqrt{2 - 2 \cdot S_e}} \cdot \left(s_{H1}(\rho) - s_{H2}(\rho)\right)$$

$\sigma_g(\rho)$ —

$s_{H1}(\rho)$ ⋯

$s_{H2}(\rho)$ - - -

$\sigma_u(\rho)$ —

$s_{H1}(\rho)$ ⋯

$-s_{H2}(\rho)$ - - -
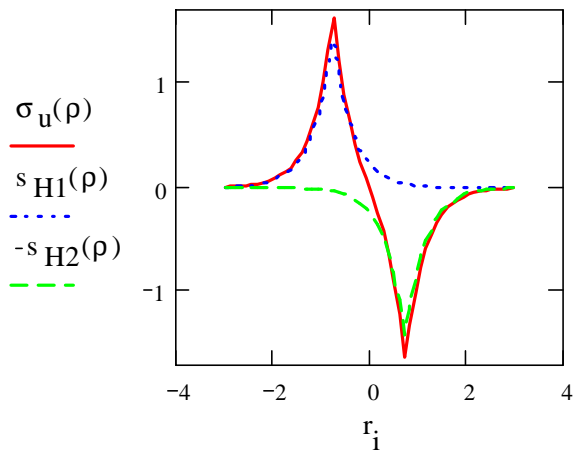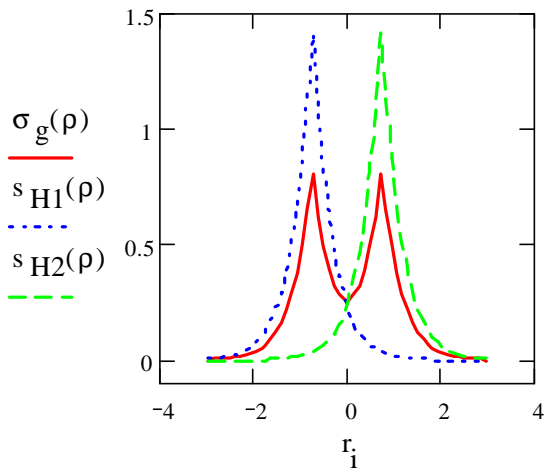
3-dimensional
illustration:

$$s_1(x,y) := N_H \cdot e^{-\left[(x + \rho_e)^2 + y^2\right]^{.5}} \qquad s_2(x,y) := N_H \cdot e^{-\left[(x - \rho_e)^2 + y^2\right]^{.5}}$$

$$\sigma_{g_{i,j}} := \left(s_1(x_i, y_j) + s_2(x_i, y_j)\right) \cdot \frac{1}{\sqrt{2 \cdot (1 + S_e)}} \qquad \sigma_{u_{i,j}} := \left(s_1(x_i, y_j) - s_2(x_i, y_j)\right) \cdot \frac{1}{\sqrt{2 \cdot (1 - S_e)}}$$

Bonding MO

Antibonding MO

σ_g

σ_u

2
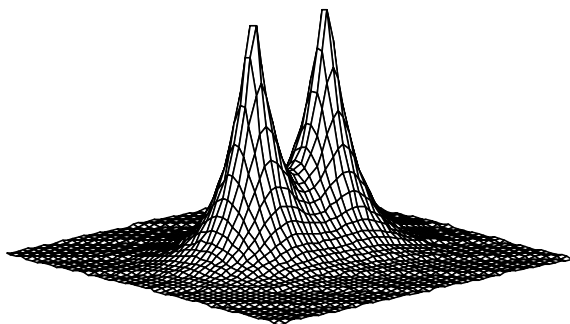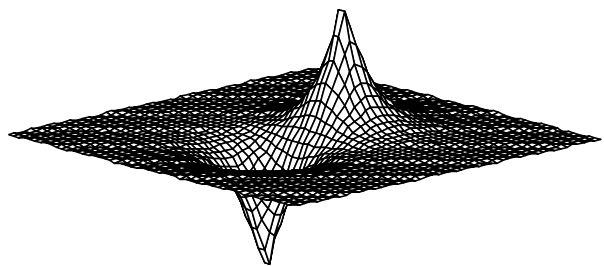
The electronic absorption spectrum of BeH_2 is described by the following two transitions:

$$\left(2\Psi_{\sigma_g}\right)^2 (1\Psi_{\sigma_u})^1 \left(1\Psi_{\sigma_g}\right)^1 \leftarrow \left(1\Psi_{\sigma_g}\right)^2 (1\Psi_{\sigma_u})^2 \tag{5.8}$$

$$\left(2\Psi_{\sigma_g}\right)^1 (1\Psi_{\sigma_u})^2 \left(1\Psi_{\sigma_g}\right)^1 \leftarrow \left(1\Psi_{\sigma_g}\right)^2 (1\Psi_{\sigma_u})^2$$

If one tries to bend BeH_2, the $1\Psi_{\sigma_u}$ orbital is destabilized as a result of the antibonding interaction between the two 1s orbitals of the H-atoms, whereas the energy of the Ψ_{σ_g} orbital remains nearly unchanged. Within the framework of the LCAO-MO description, this explains why BeH_2 is a linear molecule.

Because of the relative location of the energy of the Be(2s) orbitals compared to the energy of the $1s_H$ orbital, it can be assumed that the electron density is moved from Be to H, as a result of which the hydrogen in BeH_2 is of hydridic nature. During the reaction from n × BeH_2 to $(BeH_2)_n$, this hydridic hydrogen can, as nucleophil, interact with the LUMO located at the Be, leading to the polymer connected by hydrogen bridges observed in condensed phase. Thus, the LUMO is a „Lewis-Acid Acceptor-Orbital".

5.1.2 Quantitative formulation of the theory

We will first apply the quantitative formulation of the EHMO-theory to a diatomic molecule

A------------B

starting out from the following formula.

$$E(R) = \Delta E_{EHMO}(R) + E_{rep}(R) \tag{5.9}$$

The affiliated Hamilton operator can be expressed in the following way:

$$\hat{H} = \hat{H}_{EHMO} + \hat{H}_{rep} \tag{5.10}$$

Only the valence orbitals of the atoms A and B, which contribute with N_A and N_B electrons, respectively, are taken into account.

The wave function of the $N_A + N_B$ valence electrons of this molecule is described as a product of the molecular orbitals Ψ_i:

$$\Phi(1, 2, 3, ..., N_A + N_B) = \tag{5.11}$$

$$\Psi_1(1)\alpha(1)\Psi_1(2)\beta(2)\Psi_2(3)\alpha(3)...\Psi_{\frac{N_A+N_B}{2}}(N_A + N_B)\beta(N_A + N_B)$$

This function would now have to be expressed as Slater determinant. We are not going to do this, however. For molecules with a closed shell, this does not lead to any formal difference. If necessary, the antisymmetrization can be carried out at a later stage. The electrons are filled in the molecular orbitals corresponding to the *Aufbau Principle*. By doing so, the non-distinguishability — i.e. the non-numerability — of the electrons is not explicitly taken into account. For the interpretation of the calculation results, however, the non-distinguishability must be strictly observed.

The result of such a calculation is the **electron configuration of the molecule**. From this electron configuration, symmetry states can be deduced if desired.

The simplifications carried out so far lead to the EHMO-calculation procedure if

A) molecular orbitals Ψ_i are represented as linear combinations of atomic orbitals χ_A, χ_B.

B) if the $\hat{H}_{EHMO}$ operator is interpreted as a sum of one-electron operators $\hat{h}(o)$ acting on the corresponding electron o.

The first problem thus consists of finding solutions for

$$\hat{H}_{EHMO}\Phi(1, 2, 3..., N_A + N_B) = E_{EHMO}\Phi(1, 2, 3, ..., N_A + N_B) \tag{5.12}$$

with

$$\hat{H}_{EHMO} = \sum_{o}^{N_A + N_B} \hat{h}(o) \tag{5.13}$$

In this description, the interactions between the molecules are not taken into account explicitly, but only globally. Each electron moves within the averaged field of the remaining electrons.

In order to achieve a consistent numbering of the wave functions, the following agreements are valid:

o   numbers the electrons
i   numbers the molecular orbitals
l, k   numbers the atomic centers
r_k, s_l numbers the atomic orbitals at the atomic centers

Application on a diatomic molecule with the centers *l* and *k* leads to:

$$\Psi_i = \sum_{r_k} c_{ir_k}\chi_{r_k} + \sum_{s_l} c_{is_l}\chi_{s_l} \tag{5.14}$$

For simplification purposes, the calculation will first be carried out for a diatomic molecule with only one atomic orbital each, χ_A and χ_B.

A--------------B

χ_A-------------χ_B

For the molecular orbitals, the following simple formula with the coefficients c_A, c_B results:

$$\Psi(c_A, c_B) = c_A\chi_A + c_B\chi_B \tag{5.15}$$

The „monoelectronic-atomic orbitals" χ_A, χ_B are results of the following two equations:

$$\hat{h}_A\chi_A = E_A\chi_A \quad \text{with} \quad \hat{h}_A = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + U_A$$
$$\tag{5.16}$$
$$\hat{h}_B\chi_B = E_B\chi_B \quad \text{with} \quad \hat{h}_B = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + U_B$$

The potential terms U_A and U_B represent the averaged field of the remaining electrons with their nuclei at the centers A and B, respectively. This means that the functions χ_A, χ_B describe the movement of the electron in the field of the corresponding nucleus and the averaged field of the remaining electrons of the atoms A or B, respectively.

In a two center bonding, with the distance R between the two centers, the electron moves within the simultaneous field U_A+U_B in such a way that the following EHMO operator results:

$$\hat{H}_{EHMO} = \sum_{o}^{N_A+N_B} \hat{h}(o) \quad \text{with} \quad \hat{h}(o) = -\frac{\hbar^2}{2m}\Delta(o) + U_A(o) + U_B(o) \tag{5.17}$$

$$\Delta(o) = \left(\frac{\partial^2}{\partial x_o^2} + \frac{\partial^2}{\partial y_o^2} + \frac{\partial^2}{\partial z_o^2} \right) \tag{5.18}$$

Assuming that the molecule has two electrons, the following formula is valid:

$$\Phi(1,2) = \Psi_1(1) \cdot \Psi_2(2) \tag{5.19}$$

Since each one-electron operator $\hat{h}(0)$ only acts on the respective o-electron, the equation becomes separable.

$$\hat{H}_{EHMO}\Phi(1,2) = \hat{h}(1)\Psi_1(1)\Psi_2(2) + \hat{h}(2)\Psi_1(1)\Psi_2(2) \tag{5.20}$$

$$\hat{H}_{EHMO}\Phi(1,2) = \Psi_2(2)\hat{h}(1)\Psi_1(1) + \Psi_1(1)\hat{h}(2)\Psi_2(2)$$

Multiplication from the left with the wave function and integration results in:

$$\left\langle \Phi(1,2) \middle| \hat{H}_{EHMO} \middle| \Phi(1,2) \right\rangle =$$

$$\langle \Psi_2(2)|\Psi_2(2)\rangle \left\langle \Psi_1(1) \middle| \hat{h}(1) \middle| \Psi_1(1) \right\rangle + \langle \Psi_1(1)|\Psi_1(1)\rangle \left\langle \Psi_2(2) \middle| \hat{h}(2) \middle| \Psi_2(2) \right\rangle \tag{5.21}$$

Because the wave functions are to be orthonormalized, we can write:

$$\left\langle \Phi(1,2) \middle| \hat{H}_{EHMO} \middle| \Phi(1,2) \right\rangle = E_{EHMO}\langle \Phi(1,2)|\Phi(1,2)\rangle = E_{EHMO} \tag{5.22}$$

This leads to:

$$E_{EHMO} = \left\langle \Psi_1(1) \middle| \hat{h}(1) \middle| \Psi_1(1) \right\rangle + \left\langle \Psi_2(2) \middle| \hat{h}(2) \middle| \Psi_2(2) \right\rangle \tag{5.23}$$

The two-electron problem has thus been reduced to two one-electron equations. What remains is to find the eigenfunctions and the eigenvalues of

$$\boxed{\hat{h}\Psi = \varepsilon\Psi \quad \text{with} \quad \Psi = c_A\chi_A + c_B\chi_B} \tag{5.24}$$

For this purpose, Ψ is inserted:

$$\hat{h}(c_A\chi_A + c_B\chi_B) = \varepsilon(c_A, c_B)(c_A\chi_A + c_B\chi_B) \tag{5.25}$$

We write $\varepsilon = \varepsilon(c_A, c_B)$ to indicate that the energy ε depends upon the choice of the coefficients c_A and c_B.

Multiplication of the eigenvalue equation $\hat{h}\Psi = \varepsilon\Psi$ from the left with Ψ^* and integration results in:

$$\left\langle \Psi \middle| \hat{h} \middle| \Psi \right\rangle = \varepsilon(c_A, c_B)\langle \Psi|\Psi\rangle \tag{5.26}$$

The eigenvalue $\varepsilon(c_A, c_B)$ could be put in front of the integral sign here, because it is a dimensionless number. Solving for ε results in:

$$\varepsilon(c_A, c_B) = \frac{\langle \Psi|\hat{h}|\Psi\rangle}{\langle \Psi|\Psi\rangle} \tag{5.27}$$

In order to obtain more detailed information, the integrals $\left\langle \Psi \middle| \hat{h} \middle| \Psi \right\rangle$ and $\langle \Psi|\Psi\rangle$ need to be evaluated. For this purpose, Ψ is explicitly inserted:

$$\left\langle \Psi \middle| \hat{h} \middle| \Psi \right\rangle = \left\langle (c_A\chi_A + c_B\chi_B) \middle| \hat{h} \middle| (c_A\chi_A + c_B\chi_B) \right\rangle \tag{5.28}$$

$$\langle\Psi|\hat{h}|\Psi\rangle = c_A^2\langle\chi_A|\hat{h}|\chi_A\rangle + c_B^2\langle\chi_B|\hat{h}|\chi_B\rangle + c_Ac_B\langle\chi_A|\hat{h}|\chi_B\rangle + c_Bc_A\langle\chi_B|\hat{h}|\chi_A\rangle$$

$$\langle\Psi|\hat{h}|\Psi\rangle = c_A^2 h_{AA} + c_B^2 h_{BB} + 2c_Ac_B h_{AB}$$

Since $\hat{h}$ is hermitian by precondition, the following is valid:

$$\langle\chi_A|\hat{h}|\chi_B\rangle = \langle\chi_B|\hat{h}|\chi_A\rangle \tag{5.29}$$

If the following abbreviations are applied,

$$h_{AA} = \langle\chi_A|\hat{h}|\chi_A\rangle \qquad\qquad h_{AB} = \langle\chi_A|\hat{h}|\chi_B\rangle \tag{5.30}$$

$$h_{BB} = \langle\chi_B|\hat{h}|\chi_B\rangle \qquad\qquad S = \langle\chi_A|\chi_B\rangle \tag{5.31}$$

we obtain, taking into account that χ_A, χ_B are orthonormalized functions:

$$\langle\Psi|\hat{h}|\Psi\rangle = c_A^2 h_{AA} + c_B^2 h_{BB} + 2c_Ac_B h_{AB} \tag{5.32}$$

$$\langle\Psi|\Psi\rangle = c_A^2 + c_B^2 + 2c_Ac_B \cdot S \tag{5.33}$$

Insertion of these results in the expression for c_A and c_B leads to

$$\varepsilon(c_A, c_B) = \frac{c_A^2 h_{AA} + c_B^2 h_{BB} + 2c_Ac_B h_{AB}}{c_A^2 + c_B^2 + 2c_Ac_B S} \tag{5.34}$$

The coefficients c_A, c_B must be chosen in such a way that the energy values correspond to a physically acceptable situation. Because $\Psi^2 = c_A^2\chi_A^2 + c_B^2\chi_B^2 + 2c_Ac_B\chi_A\chi_B$ is a measure for the electron density distribution, we have to choose c_A, c_B in such a way that the energetically most favorable electron density distribution is obtained. This means that the minimum of $\varepsilon(c_A, c_B)$ needs to be found. At the energy minimum, the variation $\delta\varepsilon$ equals zero. This is illustrated in Scheme 5.4.
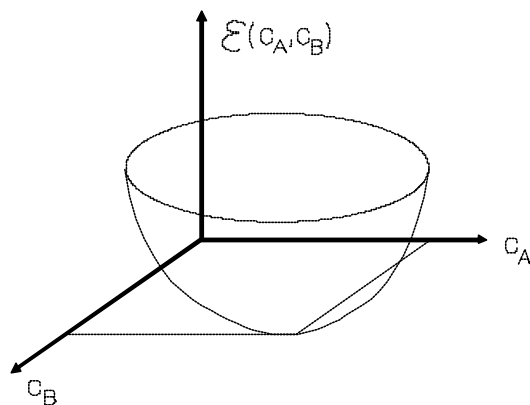
$$\delta\varepsilon = \frac{\partial\varepsilon}{\partial c_A}\delta c_A + \frac{\partial\varepsilon}{\partial c_A}\delta c_B = 0$$

Energy minimum of the EHMO approach.

Scheme 5.4

For this condition to be met, the individual derivatives must disappear. For the calculation it is useful to take advantage of the following relations:

$$\varepsilon = \frac{Z}{N} \qquad \frac{\partial\varepsilon}{\partial c_i} = \frac{1}{N}\frac{\partial Z}{\partial c_i} + Z\frac{\partial}{\partial c_i}\left(\frac{1}{N}\right) \qquad Z = \text{numerator, } N = \text{denominator} \tag{5.35}$$

Now we can write:

$$\frac{\partial\varepsilon}{\partial c_A} = \frac{1}{N}(2c_A h_{AA} + 2c_B h_{AB} + \frac{-Z}{N^2}(2c_A + 2c_B S) = 0$$

$$\frac{\partial \varepsilon}{\partial c_A} = 2c_A h_{AA} + 2c_B h_{AB} - \varepsilon(2c_A + 2c_B S) = 0$$

$$\frac{\partial \varepsilon}{\partial c_A} = c_A h_{AA} + c_B h_{AB} - \varepsilon(c_A + c_B S) = 0$$

$$\frac{\partial \varepsilon}{\partial c_B} = c_B h_{BB} + c_A h_{AB} - \varepsilon(c_B + c_A S) = 0$$

The last two equations must be arranged properly in c_A and c_B:

$$c_A(h_{AA} - \varepsilon) + c_B(h_{AB} - \varepsilon S) = 0 \tag{5.36}$$

$$c_A(h_{AB} - \varepsilon S) + c_B(h_{BB} - \varepsilon) = 0$$

or:

$$\begin{pmatrix} h_{AA} - \varepsilon & h_{AB} - \varepsilon S \\ h_{AB} - \varepsilon S & h_{BB} - \varepsilon \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = 0 \tag{5.37}$$

From this equation, ε, c_A and c_B need to be calculated. To do so, we apply the linear algebra theorem according to which *eigenvalue equations* of this nature only have an unambiguous solution if the determinant of the matrix equals zero:

$$\begin{vmatrix} h_{AA} - \varepsilon & h_{AB} - \varepsilon S \\ h_{AB} - \varepsilon S & h_{BB} - \varepsilon \end{vmatrix} = 0 \tag{5.38}$$

This leads to the following problem:

$$(h_{AA} - \varepsilon)(h_{BB} - \varepsilon) - (h_{AB} - \varepsilon S)^2 = 0$$

$$\varepsilon^2(1 - S^2) + \varepsilon(2h_{AB}S - h_{AA} - h_{BB}) + h_{AA}h_{BB} - h_{AB}^2 = 0 \tag{5.39}$$

with the solutions:

$$\varepsilon_-^+ = \frac{(h_{AA}+h_{BB}) - 2h_{AB}S \pm \sqrt{(h_{AA}+h_{BB}-2h_{AB}S)^2 - 4(1-S^2)(h_{AA}h_{BB}-h_{AB}^2)}}{2(1-S^2)} \tag{5.40}$$

The meanings of these solutions will be discussed at a later stage. First we will see how the coefficients c_A and c_B can be determined. Since two eigenvalues ε_+ und ε_- result from the two energy levels h_{AA} and h_{BB}, there obviously must be two possible electron density distributions, which are determined by the coefficients (c_A^+, c_B^+) and (c_A^-, c_B^-).

The eigenvalue-equation alone always lacks one equation for the calculation of the eigenvectors, which is how these coefficients are called. The missing equation can be obtained by making use of the orthonormalization condition for eigenfunctions:

$$\langle \Psi^+|\Psi^+ \rangle = 1 \quad \langle \Psi^-|\Psi^- \rangle = 1 \quad \langle \Psi^+|\Psi^- \rangle = 0 \tag{5.41}$$

Calculation results in:

$$\langle \Psi^+|\Psi^+\rangle = \langle (c_A^+\chi_A + c_B^+\chi_B)|(c_A^+\chi_A + c_B^+\chi_B)\rangle$$

$$\langle \Psi^+|\Psi^+\rangle = (c_A^+)^2 + (c_B^+)^2 + 2c_A^+c_B^+S = 1$$

$$\langle \Psi^-|\Psi^-\rangle = \langle (c_A^-\chi_A + c_B^-\chi_B)|(c_A^-\chi_A + c_B^-\chi_B)\rangle$$

$$\langle \Psi^-|\Psi^-\rangle = (c_A^-)^2 + (c_B^-)^2 + 2c_A^-c_B^-S = 1$$

Now the equations

$$\boxed{1 = c_A^2 + c_B^2 + 2c_Ac_BS \qquad c_A = -c_B\frac{h_{AB}-\varepsilon S}{h_{AA}-\varepsilon}} \tag{5.42}$$

are available for the numerical calculation of the eigenvectors c_A^+, c_B^+ and c_A^-, c_B^-.

These results will first be discussed with the more accessible **homonuclear diatomic molecules with 1 to 4 valence electrons**.

5.1.3 Homonuclear diatomic molecules with 1 to 4 valence electrons.

For these molecules the following simplifications are valid:

$$h_{AA} = h_{BB} \qquad c^+ = c_A^+ = c_B^+ \qquad c^- = c_A^- = -c_B^+$$

and correspondingly

$$c^+ = 1/\sqrt{2+2S} \quad and \quad c^- = 1/\sqrt{2-2S}$$

This leads to the following results:

$$\boxed{\begin{vmatrix} h_{AA}-\varepsilon & h_{AB}-\varepsilon S \\ h_{BA}-\varepsilon S & h_{AA}-\varepsilon \end{vmatrix} = 0 \qquad\qquad\qquad \\[2mm] \varepsilon_-^+ = \frac{h_{AA}\pm h_{AB}}{1\pm S} \qquad\qquad \Psi_-^+ = \frac{1}{\sqrt{2\pm 2S}}(\chi_A \pm \chi_B)}$$

To understand the meanings of these equations it is important to take into account that the so called Coulomb integrals h_{AA} and h_{AB} are negative quantities.

Linear combination of two atomic orbitals to form two molecular orbitals results in an orbital $\{\varepsilon^+, \Psi^+\}$ which, compared with the initial state, is stabilized and in a destabilized orbital $\{\varepsilon^-, \Psi^-\}$. The orbital stabilization energy $\Delta\varepsilon^+$ and the orbital destabilization $\Delta\varepsilon^-$ energy are expressed as:

$$\Delta\varepsilon^+ = \frac{h_{AA}+h_{AB}}{1+S} - h_{AA} \quad\Rightarrow\quad \Delta\varepsilon^+ = \frac{h_{AB}-Sh_{AA}}{1+S} \tag{5.43}$$

$$\Delta\varepsilon^- = \frac{h_{AA}-h_{AB}}{1-S} - h_{AA} \quad\Rightarrow\quad \Delta\varepsilon^- = \frac{h_{AB}-Sh_{AA}}{1-S} \tag{5.44}$$

The meaning of these solutions can be understood by inspection of Scheme 5.5. If n^+ stands for the number of electrons in the bonding orbital Ψ^+ and n^- stands for the number of electrons in the antibonding orbital Ψ^-, the following is true for the orbital stabilization energy ΔE_{EHMO}:

$$\Delta E_{EHMO} = n^+\Delta\varepsilon^+ + n^-\Delta\varepsilon^- \tag{5.45}$$

For a system to be stable within the EHMO theory, ΔE_{EHMO} must compensate the core-core repulsion, so that the following is true:

$$\Delta E_{EHMO} + E_{rep} < 0 \tag{5.46}$$
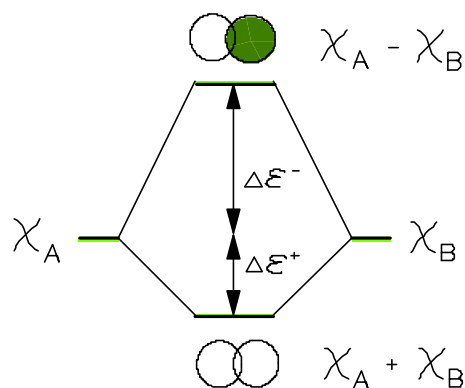
Scheme 5.5

In a qualitative discussion, it is often sufficient to only take the orbital term into account because with growing distance, the repulsion decreases faster than ΔE_{EHMO} increases. The explained theory already allows to discuss the stability of the homonuclear molecules

H_2, Li_2, Na_2, K_2, Cs_2, Rb_2
He_2, Be_2, Mg_2, Ca_2, Sr_2, Ba_2
Cu_2, Ag_2, Au_2, Zn_2, Cd_2, Hg_2

and also to make conclusions concerning their cations and anions. Because of the dominating Coulomb repulsion, the doubly charged ions are always unstable.

The following diagram shows the orbital stabilization energies for the indicated occupations. After what has been said above, it is clear that a system is not stable if ΔE_{EHMO} equals zero or becomes positive. The estimation is simplified by the fact that S represents the overlapping between the ns valence orbitals (n = main quantum number) of the above mentioned compounds and thus only adopts values between 0 and 1.
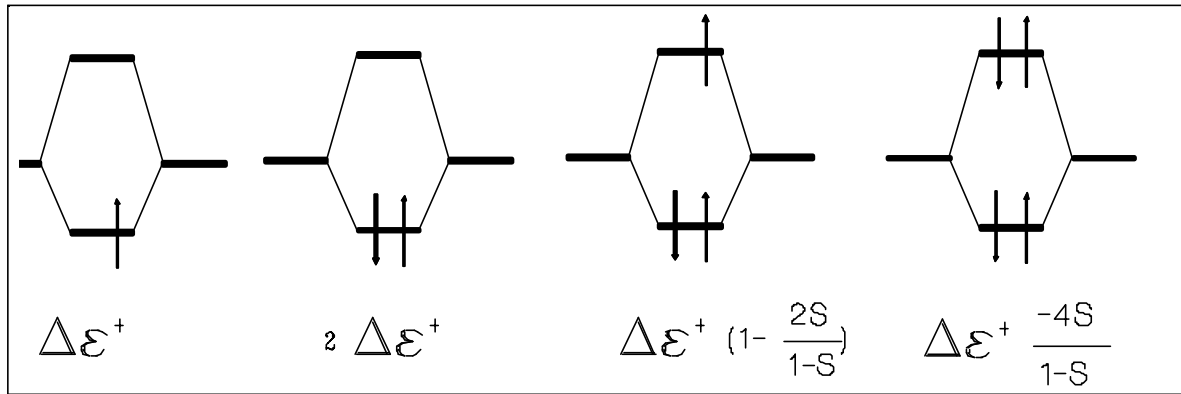
Figure 5.3: Orbital stabilization energies ΔE_{EHMO} in units of $\Delta\epsilon^+$ for the electron configurations $(\Psi_{\sigma_g})^1$, $(\Psi_{\sigma_g})^2$, $(\Psi_{\sigma_g})^2(\Psi_{\sigma_u})^1$, $(\Psi_{\sigma_g})^2(\Psi_{\sigma_u})^2$ with $(n^+, n^-) = (1,0), (2,0), (2,1), (2,2)$.

In Figure 5.3, the $\langle ns|ns \rangle$ overlap integrals of H_2, Li_2, Na_2 and K_2 are, for illustration purposes, shown as function of the distance. A striking feature is the gap between H_2 and Li_2, which coincides with the jump in the dissociation energy reported in Table 5.2.
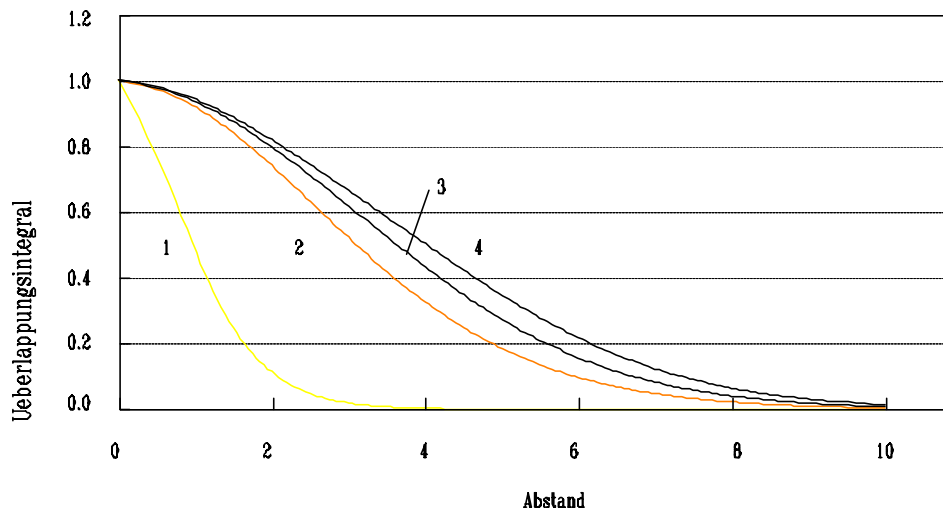
Figure 5.4: $\langle ns|ns \rangle$ overlap integrals of H_2, Li_2, Na_2 and K_2 as function of the distance (in Å). 1: n=1, ζ=1.3; 2: n=2, ζ=0.64; 3: n=3, ζ=0.733; 4: n=4, ζ=0.816.

It is interesting to observe that the orbital stabilization $\Delta\epsilon^+$ and the orbital destabilization $\Delta\epsilon^-$ as function of the bond distance never change their signs. This statement can be easily proved by dividing $\Delta\epsilon^+$ by $\Delta\epsilon^-$ because integrals of the type $\langle ns|ms \rangle$ are always larger or equal zero:

$$\frac{\Delta\epsilon^+}{\Delta\epsilon^-} = \frac{1-S}{1+S} \geq 0 \quad \text{for} \quad 0 \leqslant S < 1 \tag{5.47}$$

From this we can derive that the negative quantity h_{AB} is always smaller than Sh_{AA}. Thus we obtain the certainty that $h_{AB}-Sh_{AA}$ always stays negative or, if there is no interaction, becomes zero. From the diagrams in Figure 5.2, we can now draw the conclusions compiled in Table 5.1.

Table 5.1

number of electrons	ΔE_{EHMO}	sign of ΔE_{EHMO}	consequences
1	$\Delta\varepsilon^+$	negative	H_2^+, Li_2^+, Na_2^+, K_2^+, Cs_2^+, Rb_2^+ Cu_2^+, Ag_2^+, Au_2^+ **stable**
2	$2\,\Delta\varepsilon^+$	negative	H_2, Li_2, Na_2, K_2, Rb_2, Cs_2 Cu_2, Ag_2, Au_2 **stable**
3	$\Delta\varepsilon^+(1-\frac{2S}{1-S})$	$S<1/3$ negative $S>1/3$ positive	3-electron dimers always show a larger bond distance than 2-electronen dimers. He_2^+, Be_2^+, Mg_2^+, Ca_2^+, Sr_2^+, Ba_2^+ Zn_2^+, Cd_2^+, Hg_2^+ (H_2^-), Li_2^-, Na_2^-, K_2^-, Rb_2^-, Cs_2^- Cu_2^-, Ag_2^-, Au_2^- **stable**
4	$1-\Delta\varepsilon^+(-\frac{4S}{1-S})$	positive	He_2, Be_2, Mg_2, Ca_2, Sr_2, Ba_2 Zn_2, Cd_2, Hg_2 **unstable**

To the results in Table 5.1, it is necessary to add that H_2^- disintegrates into H_2 + e. Moreover, we know that for a stability description of Cu_2^-, Ag_2^- and Au_2^- at least the corresponding p atom orbitals need to be taken into account as well.

We can gain further insight without expressing the integrals h_{AA}, h_{AB} explicitly. If ΔE_{EHMO} represents a measure for the bond energy, the dissociation energy D_e is expected to be proportional to ΔE_{EHMO}:

$$D_e \sim -\Delta E_{EHMO}$$

This means for the molecules *H_2, Li_2, Na_2, K_2, Rb_2, Cs_2* and in less good approximation also for *Cu_2, Ag_2, Au_2*, the following relation holds:

$$D_e \approx -2\frac{h_{AB}-h_{AA}S}{1+S} = -2\Delta\varepsilon^+ \tag{5.48}$$

At equilibrium distance, we find for the overlap integrals: $S(H_2) = 0.618$, $S(Li_2) = 0.58$ and $S(Na_2) = 0.6$. It is therefore interesting to use the same value $S = 0.6$ for these molecules, which allows an easy comparison.
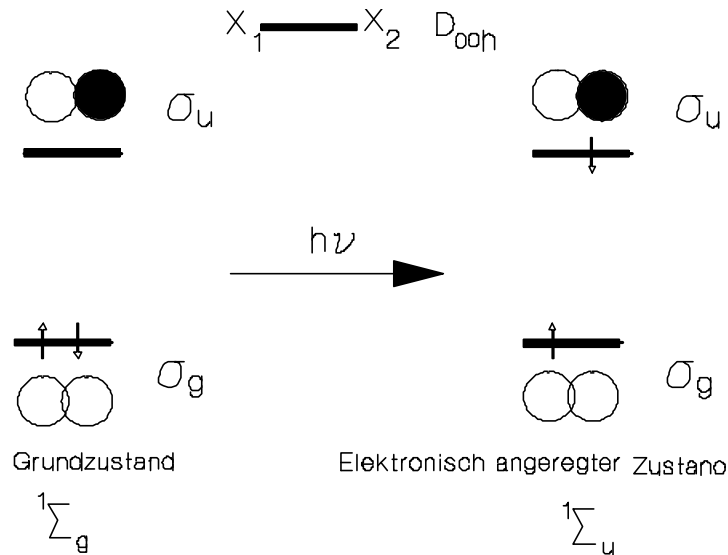
Figure 5.5: We illustrate the electronic ground state configuration σ_g^2 and the first excited state configuration $\sigma_g^1\sigma_u^1$. Indicated are also the symbols of the corresponding symmetry states.

In order to excite an electron from the σ_g to the σ_u orbital according to Figure 5.5, the excitation energy

$$\Delta E(\sigma_u \leftarrow \sigma_g) = h\nu \tag{5.49}$$

$$\Delta E(\sigma_u \leftarrow \sigma_g) = \varepsilon^-(\sigma_u) - \varepsilon^+(\sigma_g) = -2\frac{h_{AB}-h_{AA}S}{1+S}\frac{1}{1-S}$$

$$\Delta E(\sigma_u \leftarrow \sigma_g) = \frac{-2\Delta\varepsilon^+}{1-S}$$

needs to be absorbed. Insertion of (5.48) leads to the interesting relation:

$$\Delta E(\sigma_u \leftarrow \sigma_g) \sim \frac{D_e}{1-S} \tag{5.50}$$

From this we can infer that the energy necessary for the allowed electronic $\sigma_u \leftarrow \sigma_g$ excitation is considerably higher than the dissociation energy of the molecules. For the verification of this statement, the experimental quantities ω_e, D_0 and $\Delta E(B^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+)$ are compiled in Table 5.2. The conversion from D_0 to D_e is carried out by: $D_e = D_o + \omega_e/2$. We remark that $\Delta E(B^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+)$ corresponds to $\Delta E(\sigma_u \leftarrow \sigma_g)$.

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Table 5.2

Molecule	D_o (eV)	ω_e(cm^{-1})	$\Delta E(B^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+)$ [eV]
H_2	4.4781	4395.2	11.37
Li_2	1.046	351.43	1.744
Na_2	0.72	159.12	1.820
K_2	0.51	92.02	1.488
Rb_2	0.49	…	(1.1-1.4)
Cs_2	0.394	42.02	(1.0-1.4)
Fr_2	~0.4	…	…
Cu_2	2.03	264	(2.7)*
Ag_2	1.66	192.4	(2.85)*
Au_2	2.30	190.9	(2.44)*
			*classification uncertain

We note that the first excited state configuration $\sigma_g^1\sigma_u^1$ resulting from the ns atomic orbitals leads in all cases to a dissociative state as can easily be seen by calculating the orbital stabilization energy. While this result is correct for H_2 it is necessary to stabilize the $\sigma_g^1\sigma_u^1$ configuration for all the other diatomics, by taking into account the mixing of e.g. np or/and (n+1)s atomic orbital contributions. This means that in a more precise discussion of the electronic excitation energy, at least the influence of the np-functions would have to be taken into account. For the description of the electronically excited states this influence is imperative.

On condition that no major relaxation processes occur during the ionization process

$$X_2 \rightarrow X_2^+ \tag{5.51}$$

which takes place within about 10^{-15} s, it is expected that the first ionization energy of these molecules is approximately equal to the orbital energy $\varepsilon^+(\sigma_g)$:

$$Ip(X_2) \sim \varepsilon^+(\sigma_g) = -\frac{h_{AA}+h_{AB}}{1+S} \tag{5.52}$$

The use of
$$\frac{D_e}{2} = -\frac{h_{AA}+h_{AB}}{1+S} + h_{AA} \tag{5.53}$$

leads to:
$$Ip(X_2) \sim -h_{AA} + \frac{D_e}{2} \tag{5.54}$$

$$IP(X_2) = IP(X) - \triangle + De/2$$
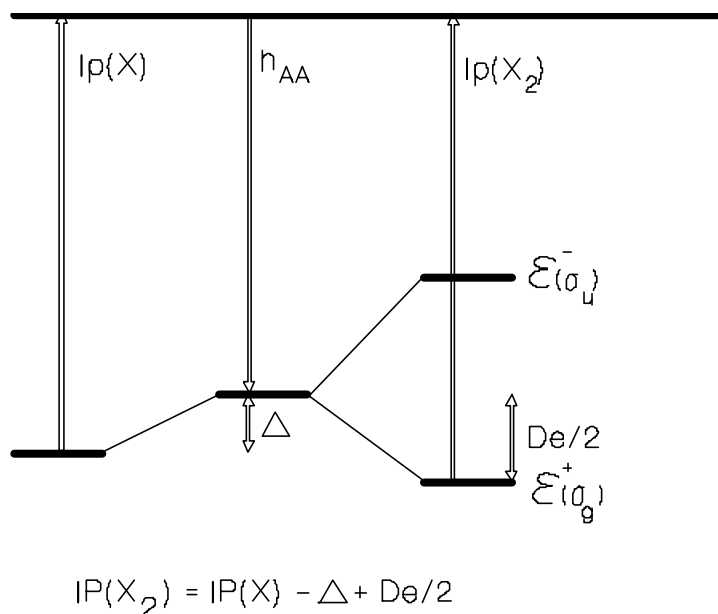
<u>Figure 5.6:</u> Correlation between the ionization energy of the atoms X, the molecules X_2 and the dissociation energy.

Because $-h_{AA}$ approximately equals the ionization energy IP(X) of $X(ns)^1 \rightarrow X^+(ns)^0$, we write:

$$h_{AA} = -IP(X) + \Delta \tag{5.55}$$

Δ is a term which takes the different electron-electron interactions in X_2 and X into account. From (5.54) follows

$$IP(X_2) = IP(X) - \Delta + \frac{D_e(X_2)}{2} \tag{5.56}$$

Empirical observation: The results compiled in Figure 5.6 from H through Ag show that $Ip(X_2)$ and $Ip(X)$ are proportional to each other. The same is true for $Ip(X_2)$ and $D_e(X_2)$. This is expressed in the corresponding correlation coefficients. We can thus establish the following simple relation:

$$Ip(X_2) \approx b + m \cdot IP(X) \tag{5.57}$$

A comparison with (5.52) leads to:

$$IP(X_2) = -\frac{h_{AA}+h_{AB}}{1+S} = m \cdot IP(X) + b \tag{5.58}$$

If we adopt the suggestion of R.S. Mulliken to express the resonance term h_{AB} for homonuclear molecules as

$$h_{AB} = S \cdot k \cdot h_{AA} \tag{5.59}$$

where k is a parameter which must be determined empirically, this leads to:

$$-\frac{h_{AA}+h_{AB}}{1+S} = -\frac{1+kS}{1+S} \cdot h_{AA} \tag{5.60}$$

This means that the relation between $Ip(X_2)$ and $Ip(X)$ can be expressed as follows:

$$Ip(X_2) = \frac{1+kS}{1+S} \cdot Ip(X) - \frac{1+kS}{1+S} \cdot \Delta = \frac{1+kS}{1+S} \cdot Ip(X) + b \tag{5.61}$$

Substitution of $Ip(X_2)$ by $IP(X_2) = m \cdot IP(X) + b$ leads to a relation from which the parameter k can be determined for the molecules investigated here:

$$k = \frac{m(1+S)-1}{S} \tag{5.62}$$

With S = 0.6 we obtain k = 1.59.

$$\mathbf{IPX}_2 := \begin{bmatrix} 15.5 \\ 5.145 \\ 4.895 \\ 4.064 \\ 3.9 \\ 3.7 \\ 7.89 \\ 7.56 \end{bmatrix} \qquad \mathbf{IPX} := \begin{bmatrix} 13.6 \\ 5.39 \\ 5.138 \\ 4.339 \\ 4.176 \\ 3.893 \\ 7.68 \\ 7.54 \end{bmatrix} \qquad \mathbf{D}_e := \begin{bmatrix} 4.75 \\ 1.07 \\ 0.73 \\ 0.52 \\ 0.49 \\ 0.4 \\ 2.04 \\ 1.68 \end{bmatrix}$$

Energies are in eV.

$$\mathbf{S} := 0.6 \qquad \mathbf{i} := 0..7$$

$$\mathbf{m} := \mathbf{slope}\left(\mathbf{IPX}, \mathbf{IPX}_2\right)$$

$$\mathbf{d} := \mathbf{intercept}\left(\mathbf{IPX}, \mathbf{IPX}_2\right) \qquad \mathbf{d} = {}^-1.32 \qquad \mathbf{corr}\left(\mathbf{IPX}, \mathbf{IPX}_2\right) = 1$$

$$\mathbf{D} := {}^-\mathbf{intercept}\left[\left(\mathbf{IPX} + 0.5 \cdot \mathbf{D}_e\right), \mathbf{IPX}_2\right] \qquad \mathbf{D} = 0.6 \qquad \mathbf{corr}\left(\mathbf{D}_e, \mathbf{IPX}_2\right) = 1$$

$$\mathbf{Y}_{\mathbf{IPX}} := \mathbf{m} \cdot \mathbf{IPX} + \mathbf{d} \qquad\qquad \mathbf{RES1} := \mathbf{Y}_{\mathbf{IPX}} - \mathbf{IPX}_2$$

$$\mathbf{Y}_{\mathbf{D}} := \mathbf{IPX} + 0.5 \cdot \mathbf{D}_e - \mathbf{D} \qquad\qquad \mathbf{RES2} := \mathbf{Y}_{\mathbf{D}} - \mathbf{IPX}_2$$

Wolfsberg-Helmholz constant k:

$$k := \frac{\mathbf{m} \cdot (1 + \mathbf{S}) - 1}{\mathbf{S}} \qquad \mathbf{k} = 1.59$$

<u>Figure 5.7:</u> Correlation between the ionization potential of the atoms with the ionization potential and with the dissociation energy of the diatomic molecules.

We will return to the estimation of the resonance integrals h_{AB} later and introduce it in a way which will allow it to be applied to whatever molecule or complex. But first we look at an example of the input and result of an EHMO calculation (H_2):

H2.GEN   (Contains the input information in internal coordinates.)

```
     1   1   1   0
     1   0   1   0
HYDROGEN MOLECULE
 0  2 0 0 0 1FFFFFFFFFF 1.58 .000 .000FFFFFFFFFFFFFFFFFFFFFFFF
      .410000
 1   2   .74140    .00000    .00000
```

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```
 * H
 H 1 11.3000-12.60
 35  1  1  .100000
```

H2.OUT   (result of the EHMO-calculation.)

```
    HYDROGEN MOLECULE                              .741
      delta =   .4100,  1+kappa =  1.5800


   ATOM         X            Y            Z             S
                                            N EXP    COUL
    H 1      .00000       .00000       .00000 1 1.3000 -12.6000
    H 2      .00000       .00000      -.74140 1 1.3000 -12.6000


DISTANCE MATRIX
          1      2
    1    .0000  .7414
    2    .7414  .0000


OVERLAP MATRIX
                    1      2
   H 1(S)        1.0000  .6355
   H 2(S)         .6355 1.0000


RESULTS OF CALCULATION   HYDROGEN MOLECULE                              .741


ENERGY LEVELS (eV)
   E( 1) =      .52452            .0000
   E( 2) =   -15.52546            2.0000


SUM OF ONE-ELECTRON ENERGIES =     -31.05091405 eV
ORBITAL STABILIZATION ENERGY =      -5.85091405 eV
CORE-CORE REPULSION ENERGY =         1.43419059 eV
STABILIZATION + REPULSION =         -4.41672346 eV


WAVE FUNCTIONS MO'S IN COLUMNS, AO'S IN ROWS
                      1      2
   H 1(S)         -1.1711  .5529
   H 2(S)          1.1711  .5529


REDUCED OVERLAP POPULATION MATRIX, ATOM BY ATOM
           1      2
    1    .6115  .7771
    2    .7771  .6115


REDUCED CHARGE MATRIX, MO'S IN COLUMNS, ATOMS IN ROWS, NORMALIZED TO 2 ELECTRONS REGARDLESS OF OCCUP.
           1      2
    1    1.0000 1.0000
    2    1.0000 1.0000


ATOM      NET CHG.       ATOMIC ORBITAL OCCUPATION FOR GIVEN MO OCCUPATION
                                 S          X          Y          Z
   H 1      .00000              1.00000
   H 2      .00000              1.00000


REDUCED ENERGY MATRIX, ATOM BY ATOM
           1        2
    1    -7.7043 -15.6424
    2   -15.6424  -7.7043
```

5.1.4 Heteronuclear diatomic molecules with 1 to 4 valence electrons

For the discussion of heteronuclear dimers it is useful as well to first start from a two level system.
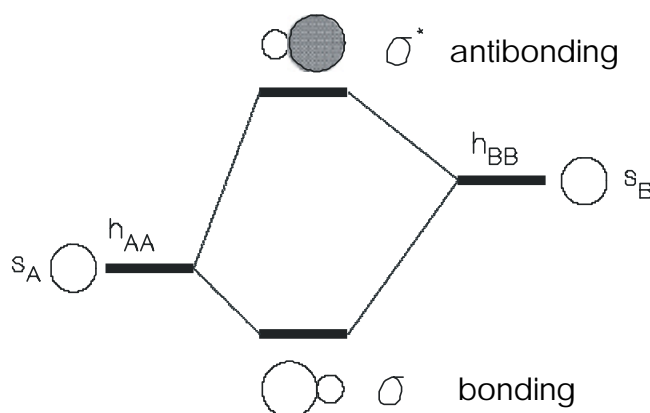
Figure 5.8: Molecular orbitals σ and σ^*, which result from the s_A and s_B atomic orbitals.

It will prove useful to introduce the following definitions:

$$\alpha = \frac{h_{AA}}{|h_{BB}|} \quad \text{and} \quad \beta = \frac{h_{AB}}{|h_{BB}|} \tag{5.63}$$

Insertion of these definitions in equation (5.40) results in:

$$\varepsilon_-^+ = \frac{\alpha - 1 - 2\beta S}{2(1 - S^2)} \cdot \left[1 \pm \sqrt{1 + 4(1 - S^2)\frac{\alpha + \beta^2}{(\alpha - 1 - 2\beta S)^2}} \right] \tag{5.64}$$

As is similarly the case for homonuclear diatomic molecules, the evaluation of this equation leads to information about dimers that can be described in first approximation on the basis of (ns_A, ms_B) atomic orbitals, where n and m are the respective main quantum numbers. Dimers of this type are: XLi, XNa, XK, XRb, XCs, XCu, XAg, XAu, XHe, XBe, XMg, XCa, XBa, XZn, XCd, XHg, with X = H, Li, Na, K etc., the cations of which XY$^+$ and the anions of which XY$^-$, as long as they do not have more than 4 valence electrons. The approximation that these dimers can be described with linear combination of (ns_A) and (ms_B) is not as good as in the case of the corresponding homonuclear dimers because p-orbitals play a more important role. But it is nevertheless useful to study this simple case.

Because the electron density distribution can be calculated from the wave function, we will first calculate the coefficients c_A, c_B in

$$\Psi = c_A \chi_A + c_B \chi_B \tag{5.65}$$

with the use of

$$\begin{pmatrix} \alpha - \varepsilon & \beta - \varepsilon S \\ \beta - \varepsilon S & -1 - \varepsilon \end{pmatrix} \cdot \begin{pmatrix} c_A \\ c_B \end{pmatrix} = 0 \tag{5.66}$$

The necessary equations are:

$$c_A^2 + c_B^2 + 2c_A c_B S = 1 \tag{5.67}$$

$$(\alpha - \varepsilon)c_A + (\beta - \varepsilon S)c_B = 0$$

which, with

$$c_B = -\frac{\alpha - \varepsilon}{\beta - \varepsilon S} c_A \quad q := -\frac{\alpha - \varepsilon}{\beta - \varepsilon S} \quad c_A^2 + q^2 c_A^2 + 2c_A^2 q S = 1 \tag{5.68}$$

can be brought to the following form:

$$c_A = \frac{1}{\sqrt{1+2qS+q^2}}, \quad c_B = \frac{q}{\sqrt{1+2qS+q^2}} \tag{5.69}$$

These equations are valid with ε_+ for $c_A{}^+$, $c_B{}^+$ and with ε_- for $c_A{}^-$, $c_B{}^-$.

We imagine that N_+ electrons are in the orbital Ψ_+, $N_+ = 0$, 1or 2. The electron density distribution in this orbital is described by

$$N_+(\Psi_+)^2 = N_+(c_A^+)^2\chi_A^2 + 2N_+c_A^+c_B^+\chi_A\chi_B + N_+(c_B^+)^2\chi_B^2 \tag{5.70}$$

Electron density distributions can be depicted graphically, like the contour lines of a map. For many applications, however, it is desirable to express this information with only few figures. For this purpose, the equation is integrated:

$$N_+ < \Psi_+|\Psi_+ > = N_+(c_A^+)^2 < \chi_A|\chi_A > + 2N_+c_A^+c_B^+ < \chi_A|\chi_B > + N_+(c_B^+)^2 < \chi_B|\chi_B >$$

$$\Rightarrow \quad N_+ = N_+(c_A^+)^2 + 2N_+c_A^+c_B^+S + N_+(c_B^+)^2 \tag{5.71}$$

$N_+(c_A^+)^2$	is called *net population* at the centre A.
$N_+(c_B^+)^2$	is called *net population* at the centre B.
$2N_+(c_A^+c_B^+)S$	is called *overlap-population* n(A,B) between A and B.

The net charge Q(A) on an atom A is described as the difference between the *core charge* $N_0(A)$ and the *gross population* N(A).

$$N(A) = N_+((c_A^+)^2 + c_Ac_BS_{AB}) \quad \text{with} \quad Q(A) = N_0(A) - N(A) \tag{5.72}$$

$$N(B) = N_+((c_B^+)^2 + c_Ac_BS_{AB}) \quad \text{with} \quad Q(B) = N_0(B) - N(B)$$

The core charge $N_0(X)$ of an atom X is defined as charge after the abstraction of the valence electrons. Examples:

H(1s)^1	$\rightarrow$	H$^+$	N_0(H)	=	+1
Li(1s)^2(2s)^1	$\rightarrow$	Li$^+$(1s)^2	N_0(Li)	=	+1
Be(1s)^2(2s)^2	$\rightarrow$	Be$^+$(1s)^2	N_0(Be)	=	+2
B(1s)^2(2s)^2(2p)^1	$\rightarrow$	B$^+$(1s)^2	N_0(B)	=	+3

etc.

Now we have the necessary information for the evaluation of the equations (5.64) and (5.68). The resonance integrals h_{AB} are calculated with

$$h_{AB} = k \cdot S \cdot \frac{h_{AA} + h_{BB}}{2} \tag{5.73}$$

With the definitions (5.63) for α and β, this equation can be expressed in the following way:

$$\beta = \frac{k \cdot S}{2}(a - 1) \tag{5.74}$$

It is necessary to take into account that $\alpha = -1$ describes the special case $h_{AA} = h_{BB}$ and that h_{AA} and h_{BB} interchange their relative positions at the point where α becomes larger or smaller than -1.

<u>Orbital energies $\varepsilon(\sigma)$ and $\varepsilon(\sigma^*)$ and coefficients as a function of</u> α

$$i := 0 .. \, 2 \cdot N \qquad\qquad \alpha_i := -\frac{i}{N} \qquad\qquad \beta_i := 0.5 \cdot k \cdot S \cdot (\alpha_i - 1)$$

abbreviations: $\qquad f1_i := \dfrac{\alpha_i - 1 - 2 \cdot \beta_i \cdot S}{2 \cdot (1 - S^2)} \qquad\qquad f2_i := 4 \cdot (1 - S^2) \cdot \dfrac{\alpha_i + (\beta_i)^2}{(\alpha_i - 1 - 2 \cdot \beta_i \cdot S)^2}$

ORBITAL ENERGIES $\quad \varepsilon(\sigma) = \varepsilon b$ and $\varepsilon(\sigma^*) = \varepsilon a \qquad$ b = binding $\qquad$ a = antibinding

$$\varepsilon b_i := f1_i \cdot \left(1 + \sqrt{1 + f2_i}\right) \qquad\qquad \varepsilon a_i := f1_i \cdot \left(1 - \sqrt{1 + f2_i}\right)$$

abbreviations: --

$$qb_i := \frac{\beta_i - \varepsilon b_i \cdot S}{\alpha_i - \varepsilon b_i} \qquad\qquad\qquad qa_i := \frac{\beta_i - \varepsilon a_i \cdot S}{\alpha_i - \varepsilon a_i}$$

$$qcb_i := -\frac{1}{\text{if}\left(\left|qb_i\right| > 0, qb_i, qb_{i-1}\right)} \qquad\qquad qca_i := -\frac{1}{\text{if}\left(\left|qa_i\right| > 0, qa_i, qa_{i-1}\right)}$$

coefficients c_a and c_b for the bonding b and the antibonding a orbitals:

$$cb_{A_i} := \left[1. + 2. \cdot S \cdot qcb_i + (qcb_i)^2\right]^{-0.5} \qquad\qquad ca_{A_i} := \left[1 + 2. \cdot S \cdot qca_i + (qca_i)^2\right]^{-0.5}$$

$$cb_{B_i} := qcb_i \cdot cb_{A_i} \qquad\qquad\qquad\qquad ca_{B_i} := -qca_i \cdot ca_{A_i}$$

POPULATION ANALYSES: n_A, n_B = charge on A, B; op = overlap population

$$opb_i := 2 \cdot cb_{A_i} \cdot cb_{B_i} \cdot S \qquad nb_{A_i} := \frac{1}{2} \cdot opb_i + \left(cb_{A_i}\right)^2 \qquad nb_{B_i} := \frac{1}{2} \cdot opb_i + \left(cb_{B_i}\right)^2$$

$$opa_i := -2 \cdot ca_{A_i} \cdot ca_{B_i} \cdot S \qquad na_{A_i} := \frac{1}{2} \cdot opa_i + \left(ca_{A_i}\right)^2 \qquad na_{B_i} := \frac{1}{2} \cdot opa_i + \left(ca_{B_i}\right)^2$$

<u>Figure 5.9:</u> Heteronuclear diatomics
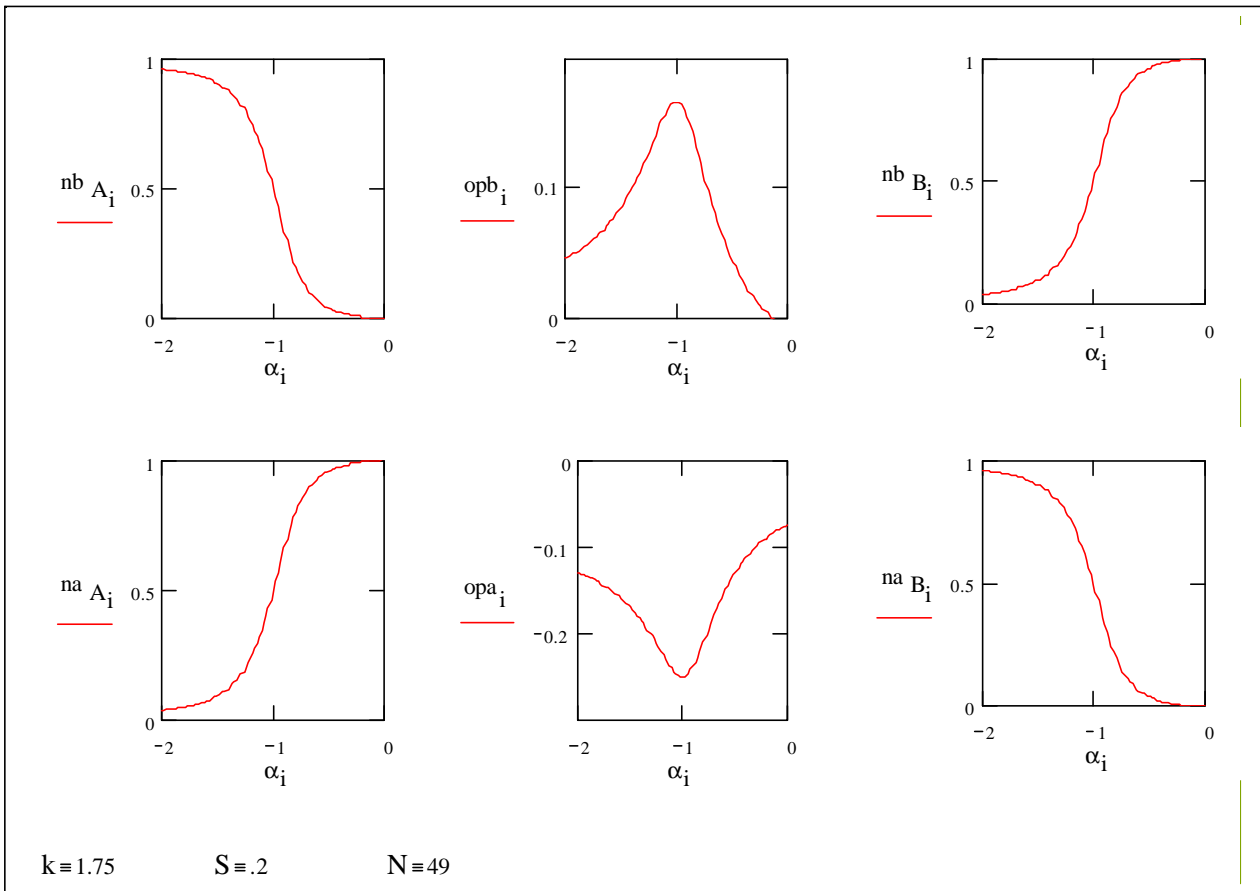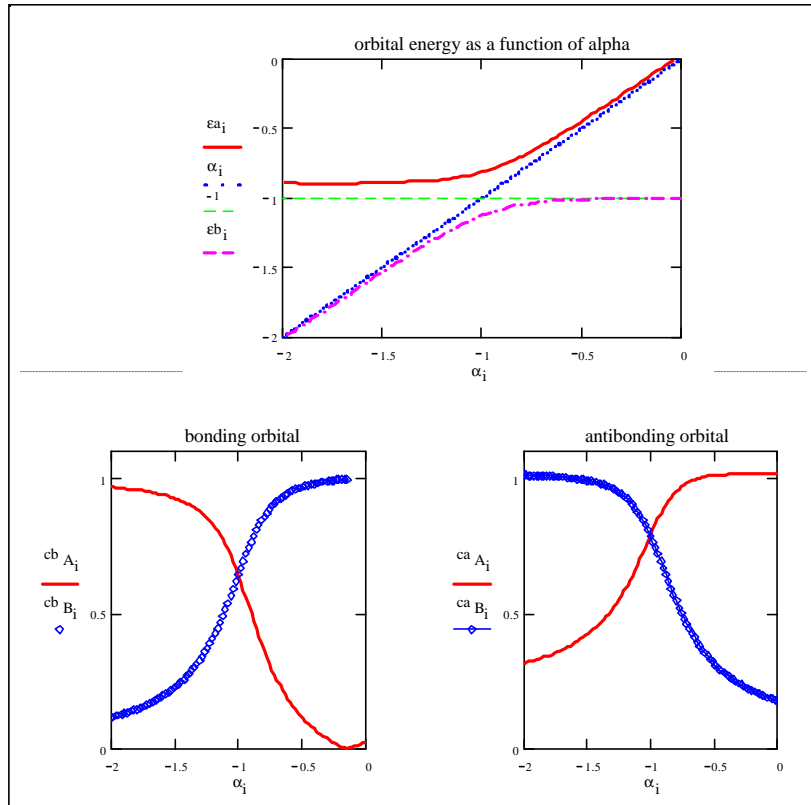
Figure 5.10: Heteronuclear diatomics

These results can be expressed in the following way:

> The **larger** the energy difference between two levels, the **smaller** their interaction.

> The **lower** level **is** *stabilized***,** the **higher** level is *destabilized*.

> The **larger** the energy difference between two levels, the **smaller** the perturbation in the wave functions of the atoms. (This means that the bonding orbital obtains its electron density mostly from the level situated below it, thus closest to it. In the diagrams, atomic levels having the same energy corresponding to the quantity $\alpha = -1$. They lead to an ideally covalent bond.)

Even though these results have been derived from the interaction between two s_A and s_B orbitals, they are generally valid. They can be illustrated as follows:
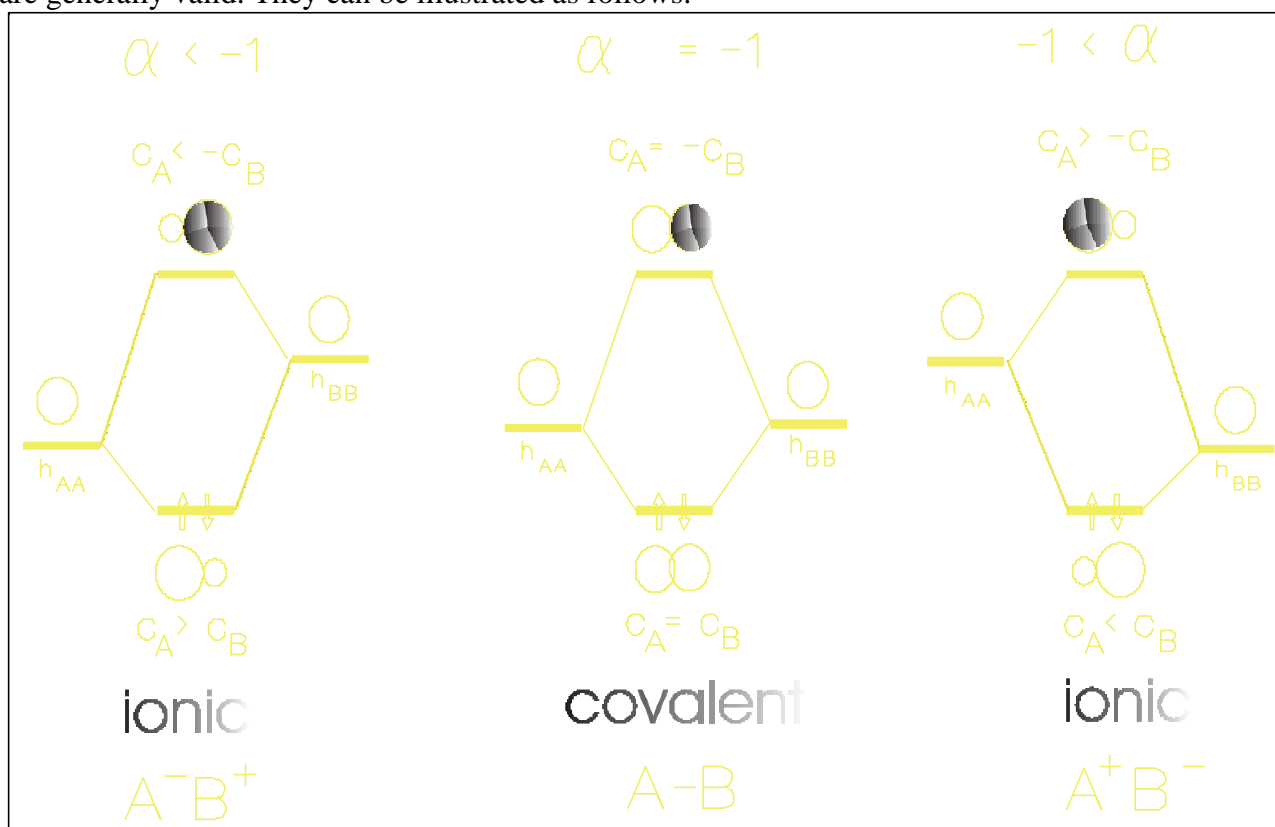
Figure 5.11: Qualitative comparison between covalent and ionic diatomics in the MO-picture.

The figures compiled in the following table express this correlation with numbers. It is striking that H is always negatively charged (except H_2, of course), which means that the electron density is shifted from the metal atoms in the direction of hydrogen. All these HX compounds are therefore of hydridic nature.

Table 5.3: Properties of HX molecules, X = Li, ..., Au.

X	H	Li	Na	K	Rb	Cs	Cu	Ag	Au
n	1	2	3	4	5	6	4	5	6
Ip(X)	13.6	5.4	5.1	4.3	4.2	3.9	7.7	7.5	9.2
α(HX)	-1	-0.4	-0.375	-0.316	-0.309	-0.287	-0.566	-0.551	-0.676
Q(H)	0	-0.759	-0.787	0.846	-0.856	-0.876	-0.553	-0.572	-0.405
Q(X)	0	0.759	0.787	0.846	0.856	0.876	0.553	0.572	0.405
OP(HX)	0.75	0.365	0.332	0.255	0.24	0.212	0.556	0.542	0.649
D_e[eV]	4.75	2.59	2.25	1.84	1.94	1.86	2.85	2.46	3.4
$\overline{\lambda_e}$ [cm^{-1}]	4'395	1'406	826	705.9	936.8	890.7	1'941	2'996	2'305

α, Q(H), Q(X) and the overlap population OP in this table have been calculated with the following quantities: S = 0.6, k = 1.75, h_{AA} = -Ip(H), h_{XX} = -Ip(X), α = -Ip(X)/Ip(H). In the following diagram, the population analysis of the $(s_A, s_B)\sigma$ orbital occupied by 2 electrons and the orbital stabilization energies $\Delta\varepsilon_+$ and $\Delta\varepsilon_-$ are represented as function of α in the region -1 to 0. This corresponds to the whole row HH to HAu in Table 5.3. The net charges Q(H), Q(X) and the overlap population OP(HX) are listed. Note that for energy levels of very different energy (α close to 0), OP(HX) becomes negative, which corresponds to a repelling interaction.

Charge distribution and orbital stabilization in HX diatomic molecules.
X = H, Li, Na,...,Au. The bonding orbital $\varepsilon(\sigma)$ orbital is occupied with 2 electrons.

$op_i := 2 \cdot cb_{H_i} \cdot cb_{X_i} \cdot S$ $\qquad S = 0.6$

$Q_{H_i} := 1 - 2 \cdot \left[\frac{1}{2} \cdot op_i + \left(cb_{H_i} \right)^2 \right]$

$Q_{X_i} := 1 - 2 \cdot \left[\frac{1}{2} \cdot op_i + \left(cb_{X_i} \right)^2 \right]$
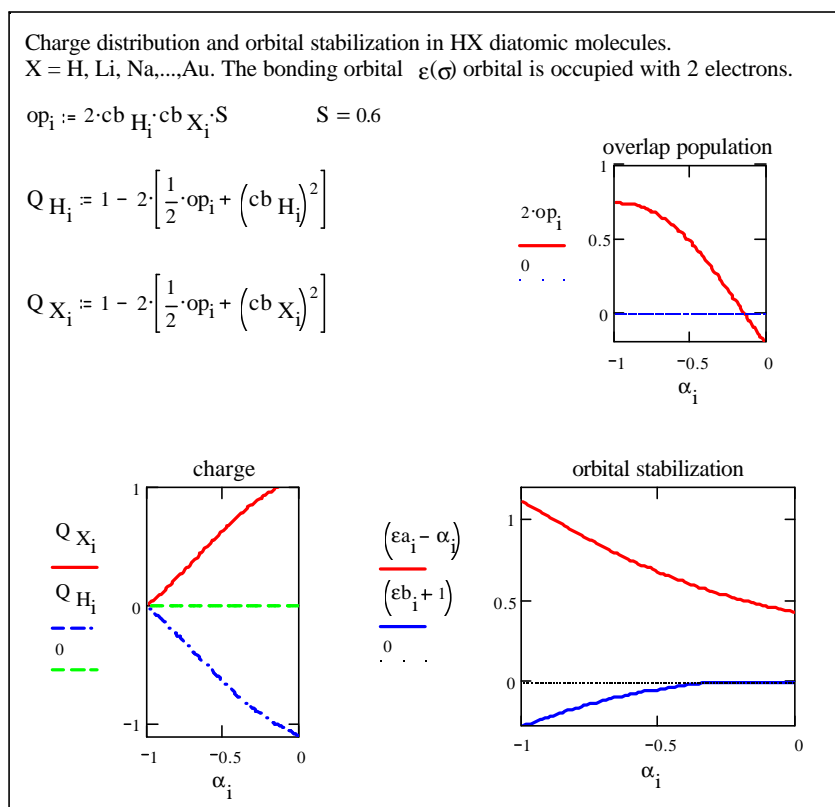
Figure 5.12: Illustration of the hydridic character of hydrogen bonded to a metal.

5.1.5 Consideration of the 2s and 2p orbitals and general case

The EHMO theory can only become a useful tool if it is put into a general form. This is not a particularly difficult task. We only have to expand the specialization used so far from two interacting levels to an unlimited number of levels. For the time being, we can limit ourselves to diatomic molecules because this leads to a result valid for any system.

In order to achieve a consistent numbering of the wave function, the agreements introduced on page 52 are valid, which are here repeated in expanded form:

o	numbers the electrons
i, j	number the molecular orbitals
l, k	number the atomic centers
r_k, s_l	number the atomic orbitals at the atomic centers k and l
μ, ν, ρ	are general indices with which atomic orbitals are numbered

Application on a diatomic molecule with the centers l and k leads to the wave function

$$\Psi_i = \sum_{r_k} c_{ir_k}\chi_{r_k} + \sum_{s_l} c_{is_l}\chi_{s_l} \tag{5.75}$$

and to the EHMO-Operator

$$\hat{H}_{EHMO} = \sum_{o}^{N_A+N_B} \hat{h}(o) \quad \text{with} \quad \hat{h}(o) = -\frac{h^2}{2m}\Delta(o) + U_A(o) + U_B(o) \tag{5.76}$$

In the same way as in (5.12) to (5.24),

$$\varepsilon(c_{1_k}c_{2_k}...c_{1_l}c_{2_l}...) = \frac{\langle \Psi|\hat{h}|\Psi\rangle}{\langle \Psi|\Psi\rangle} \tag{5.77}$$

can be deduced, where n is equal to total number of involved atomic orbitals,

$$\Psi = \sum_{r_k} c_{r_k}\chi_{r_k} + \sum_{s_l} c_{s_l}\chi_{s_l} = \sum_{\mu}^{n} c_\mu \chi_\mu \tag{5.78}$$

Insertion in the expression for $\varepsilon(c_1, c_2, \dots, c_n)$ results in:

$$\varepsilon = \varepsilon(c_1, c_2, ..., c_n) = \frac{\left\langle \sum_{\mu=1}^{n} c_\mu \chi_\mu \middle| \hat{h} \middle| \sum_{\nu=1}^{n} c_\nu \chi_\nu \right\rangle}{\left\langle \sum_{\mu=1}^{n} c_\mu \chi_\mu \middle| \sum_{\mu=1}^{n} c_\nu \chi_\nu \right\rangle} = \frac{Z}{N} \tag{5.79}$$

As explained in scheme 5.4, we look for the electron density distribution which corresponds to the energy minimum. At the minimum $\delta\varepsilon = 0$ is valid. $d\varepsilon = 0$ signifies:

$$d\varepsilon = \frac{\partial \varepsilon}{\partial c_1}dc_1 + \frac{\partial \varepsilon}{\partial c_2}dc_2 + ... + \frac{\partial \varepsilon}{\partial c_n}dc_n = 0 \tag{5.80}$$

Because the coefficients c_m and thus the dc_m are linearly independent, this condition can only be met if the individual derivatives disappear:

$$\frac{\partial \varepsilon}{\partial c_i} = 0 \;\forall i \tag{5.81}$$

The calculation is carried out for c_n:

$$\frac{\partial \varepsilon}{\partial c_\nu} = \frac{\partial}{\partial c_\nu}\frac{Z}{N} = \frac{N\frac{\partial Z}{\partial c_\nu} - Z\frac{\partial N\varepsilon}{\partial c_\nu}}{N^2} = \frac{\left[\frac{\partial Z}{\partial c_\nu} - \frac{Z}{N}\cdot\frac{\partial N}{\partial c_\nu}\right]}{N} = 0 \tag{5.82}$$

N is, as integral of square-normalized functions, always positive. Therefore we can multiply by N:

$$\frac{\partial Z}{\partial c_\nu} - \frac{Z}{N}\cdot\frac{\partial N}{\partial c_\nu} = \frac{\partial Z}{\partial c_\nu} - \varepsilon\frac{\partial N}{\partial c_\nu} = 0; \quad \nu = 1, 2, ..., n. \tag{5.83}$$

We introduce the following abbreviations:

$$h_{\mu\nu} := \langle \chi_\mu | \hat{h} | \chi_\nu \rangle \qquad\qquad S_{\mu\nu} := \langle \chi_\mu | \chi_\nu \rangle \tag{5.84}$$

$$\frac{\partial Z}{\partial c_\nu} = \frac{\partial}{\partial c_\nu} \cdot \left\langle \sum_{\mu=1}^{n} c_\mu \chi_\mu \Big| \hat{h} \Big| \sum_{\rho=1}^{n} c_\rho \chi_\rho \right\rangle \tag{5.85}$$

$$\frac{\partial Z}{\partial c_\nu} = \frac{\partial}{\partial c_\nu} \cdot \sum_{\mu=1}^{n} \sum_{\rho=1}^{n} c_\mu c_\rho \langle \chi_\mu | \hat{h} | \chi_\rho \rangle \tag{5.86}$$

$$\frac{\partial Z}{\partial c_\nu} = \frac{\partial}{\partial c_\nu} \cdot \sum_{\mu=1}^{n} \sum_{\rho=1}^{n} c_\mu c_\rho h_{\mu\rho} \tag{5.87}$$

Calculation results in:

$$\frac{\partial Z}{\partial c_\nu} = 2 \sum_{\mu=1}^{n} c_\mu h_{\nu\mu} \tag{5.88}$$

In similar manner, the following can be found:

$$\frac{\partial N}{\partial c_\nu} = 2 \sum_{\mu=1}^{n} c_\mu S_{\nu\mu} \tag{5.89}$$

Insertion of these results in

$$\frac{\partial Z}{\partial c_\nu} - \varepsilon \frac{\partial N}{\partial c_\nu} = 0 \tag{5.90}$$

leads to the important result:

$$2 \sum_{\mu=1}^{n} c_\mu h_{\nu\mu} - 2\varepsilon \sum_{\mu=1}^{n} c_\mu S_{\nu\mu} = 0 \tag{5.91}$$

It is reasonable to write this equation in the following way:

$$\sum_{\mu=1}^{n} c_\mu (h_{\nu\mu} - \varepsilon S_{\nu\mu}) = 0 \tag{5.92}$$

or written out in full:

$$c_1(h_{11} - \varepsilon S_{11}) + c_2(h_{12} - \varepsilon S_{12}) + ... + c_n(h_{1n} - \varepsilon S_{1n}) = 0 \tag{5.93}$$

$$c_2(h_{21} - \varepsilon S_{21}) + c_2(h_{22} - \varepsilon S_{22}) + ... + c_n(h_{2n} - \varepsilon S_{2n}) = 0 \tag{5.94}$$

…

$$c_n(h_{n1} - \varepsilon S_{n1}) + c_2(h_{n2} - \varepsilon S_{n2}) + ... + c_n(h_{nn} - \varepsilon S_{nn}) = 0 \tag{5.95}$$

The linear variation in the n coefficients c_n thus results in n homogeneous linear equations which, taking into account that $S_{nn} = 1$, can be written in the following way:

$$\begin{bmatrix} h_{11} - \varepsilon S_{11} & h_{12} - \varepsilon S_{12} & ... & h_{1n} - \varepsilon S_{1n} \\ h_{21} - \varepsilon S_{21} & h_{22} - \varepsilon S_{22} & ... & h_{2n} - \varepsilon S_{2n} \\ ... & ... & ... & ... \\ h_{n1} - \varepsilon S_{n1} & h_{n2} - \varepsilon S_{n2} & ... & h_{nn} - \varepsilon S_{nn} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ . \\ c_n \end{bmatrix} = 0 \tag{5.96}$$

$$\boxed{(H - \varepsilon S)C = 0} \tag{5.97}$$

A linear, homogeneous equation system does not have trivial solutions only if the determinant of the matrix disappears. Thus, the following must be valid:

$$\begin{vmatrix} h_{11} - \varepsilon S_{11} & h_{12} - \varepsilon S_{12} & ... & h_{1n} - \varepsilon S_{1n} \\ h_{21} - \varepsilon S_{21} & h_{22} - \varepsilon S_{22} & ... & h_{2n} - \varepsilon S_{2n} \\ ... & ... & ... & ... \\ h_{n1} - \varepsilon S_{n1} & h_{n2} - \varepsilon S_{n2} & ... & h_{nn} - \varepsilon S_{nn} \end{vmatrix} = 0 \tag{5.98}$$

For the special case $n = 2$, the following relation, which we have encountered several times, is valid:

$$\begin{vmatrix} h_{11} - \varepsilon & h_{12} - \varepsilon S_{12} \\ h_{21} - \varepsilon S_{21} & h_{22} - \varepsilon \end{vmatrix} = 0 \tag{5.99}$$

For the solution of eigenvalue problems, computer programs are available today, so that we may consider this part as a solved problem and can now turn to the interpretation of the calculation results. The coefficients c_m being known, we can in the following equation,

$$\varepsilon_i = \frac{\left\langle \sum\limits_{\mu-1}^{n} c_{i\mu}\chi_\mu \left| \hat{h} \right| \sum\limits_{v=1}^{n} c_{iv}\chi_v \right\rangle}{\left\langle \sum\limits_{\mu=1}^{n} c_{i\mu}\chi_\mu \left| \sum\limits_{\mu=1}^{n} c_{iv}\chi_v \right\rangle} \tag{5.100}$$

make use of the fact that the molecular orbitals Ψ_i are normalized, so that the following is valid:

$$\varepsilon_i = \left\langle \sum\limits_{\mu-1}^{n} c_{i\mu}\chi_\mu \left| \hat{h} \right| \sum\limits_{v=1}^{n} c_{iv}\chi_v \right\rangle = \sum\limits_{\mu}^{n} \sum\limits_{v}^{n} c_{i\mu} c_{iv} h_{\mu v} \tag{5.101}$$

This equation describes the orbital energy e_i of the molecular orbital Y_i. Arranging for the diagonal elements h_{mm} and the nondiagonal elements h_{nm} results in:

$$\varepsilon_i = \sum\limits_{\mu}^{n} c_{i\mu}^2 h_{\mu\mu} + 2 \sum\limits_{\mu < v}^{n} c_{i\mu} c_{iv} h_{\mu v} \tag{5.102}$$

The EHMO energy is obtained as a sum of the orbital energy multiplied by the occupation numbers b_i:

$$E_{EHMO} = \sum\limits_{i} b_i \varepsilon_i \tag{5.103}$$

5.1.6 Atomic orbitals, Coulomb and resonance integrals and repulsion term

In the EHMO procedure, the $(H - S\varepsilon)C = 0$ problem is entirely solved. For the calculation of S it is useful to depict the atomic orbitals explicitly. For the calculation of H, numeric quantities must be known for the Coulomb integrals h_{mm} and for the resonance integrals h_{nm}. For the determination of

$$E(R) = E_{Rep}(R) + \Delta E_{EHMO}(R) \tag{5.104}$$

a formula must be available for $E_{Rep}(R)$. $\Delta E_{EHMO}(R)$ is determined from

$$\Delta E_{EHMO}(R) = E_{EHMO} - \sum\limits_{\mu} b_\mu E_\mu^0 \tag{5.105}$$

$-\sum b_\mu E_\mu^0$ equals the sum of the valence state ionization energies of the atoms multiplied by the orbital occupation b_m. These aspects will be discussed in the following chapters, starting with the EHMO-ASED approach.

5.2 The EHMO-ASED approach

The EHMO method in its original form does not correctly include electrostatic interaction and therefore often fails to yield good potential energy curves for stretching modes. Anderson and Hoffmann have discussed this problem and they have suggested that a solution might be found by adding a two-body electrostatic correction term. To derive the two-body electrostatic interaction energy, the exact electronic charge density $r(R_\alpha, r)$ for a diatomic molecule $\alpha - \beta$ is written as

$$\rho(R_a, r) = \rho_a(R_a - r) + \rho_{NPF}(R_a, r) + \rho_\beta(r) \tag{5.106}$$

where the origin of the coordinate system is on nucleus b. $\rho_\beta(r)$ and $\rho_a(R_a - r)$ are atomic charge densities, centred on nucleus b and nucleus a. R and r are nuclear and electron coordinates, respectively. The densities are computed by using the same Slater orbitals as those in the extended-Hückel calculation. $\rho_{NPF}(R_a, r)$ is the „non-perfectly-following" correction to the atomic charge densities which makes eq. (5.106) exact. The energy $E(R)$ is expressed as the sum of the electrostatic two-body correction $E_{\alpha\beta}(R)$ and the extended-Hückel binding energy $\Delta E_{EHMO}(R)$. $\rho_{NPF}(R_a, r)$ can be estimated from the resulting wave functions.

$$E(R) = E_{\alpha\beta}(R) + \Delta E_{EHMO}(R) \tag{5.107}$$

The extended-Hückel binding energy $\Delta E_{EHMO}(R)$ is expressed as

$$\Delta E_{EHMO}(R) = E_{EHMO}(R) - \sum_s b_s^0 E_s^0 \tag{5.108}$$

where $\sum_s b_s^0 E_s^0$ is the sum of the atomic one electron energy levels E_s^0, each of them times the orbital occupation number b_s^0.

Encouraged by the results of Anderson's ASED-MO (atom superposition and electron delocalization) theory on diatomic molecules, we have adopted it, have eliminated some of the deficiencies encountered and we have generalized it for polyatomic molecules.[5-6] It was shown that reliable bond distances can be calculated without losing the transparency of the original extended-Hückel method.[7-8]

The Hellmann-Feynman theorem

In the adiabatic description of molecular states, it is assumed that the calculation of the electron energy at constant distances between the nuclei is possible. For the electronic wave function Ψ_{el}, which we abbreviate as Ψ, the Schrödinger equation is valid:

$$\hat{H}\Psi = (\hat{T} + \hat{V})\Psi = E\Psi \tag{5.109}$$

in which $\hat{T}$ is the kinetic energy operator of the electrons:

$$\hat{T} = -\frac{h^2}{2m} \cdot \sum_{i=1}^{N}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right) \qquad \text{N = number of electrons} \tag{5.110}$$

$\hat{V}$ is the potential energy operator. Provided that we limitate ourselves to a diatomic molecule, we can write:

$$\hat{V} = \frac{e^2 Z_1 Z_2}{R} - \sum_{i=l}^{N}\left(\frac{Z_1 e^2}{r_{1i}} + \frac{Z_2 e^2}{r_{2i}}\right) + \sum_{i>j}^{N}\frac{e^2}{r_{ij}} \tag{5.111}$$

r_{ij} is the distance between the electrons i and j. x_i, y_i, z_i are the cartesian coordinates of the electron i. r_{1i} is the distance of the electron i from the nucleus number 1 of the charge Z_1; r_{2i} is defined analogously.

The Hellmann-Feynman theorem states that for the exact eigenfunction Ψ of a Hamilton operator $\hat{H}$ with the accompanying eigenvalue E for a parameter λ, which appears in $\hat{H}$, the following is true:

$$\frac{\partial E}{\partial \lambda} \langle \Psi | \Psi \rangle = \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \Psi \right\rangle \tag{5.112}$$

For the normalized eigenfunction, $\langle \Psi | \Psi \rangle = 1$ is valid.

Example

In the adiabatic description of molecular states, the core-core distance R only appears as a parameter. The consequence for the kinetic energy is that the differentiation by R disappears:

$$\frac{\partial \hat{T}}{\partial R} = 0 \tag{5.113}$$

For the force F_R, which is active along the bond axis of diatomic molecules, the following is derived from the Hellmann-Feynman Theorem:

$$F_R = -\frac{\partial E}{\partial R} = -\left\langle \Psi \left| \frac{\partial \hat{V}}{\partial R} \right| \Psi \right\rangle \tag{5.114}$$

The application of $\hat{V}$, eq. (5.111), to the formula given above leads to:

$$\frac{\partial \hat{V}}{\partial R} = -\frac{e^2 Z_1 Z_2}{R^2} + \sum_{i=1}^{N} \left(\frac{Z_1 e^2}{r_{1i}^2} \cdot \frac{\partial r_{1i}}{\partial R} + \frac{Z_2 e^2}{r_{2i}^2} \cdot \frac{\partial r_{2i}}{\partial R} \right) \tag{5.115}$$

Proof of the Hellmann-Feynman theorem

Since the core-core distance is defined as a parameter, we can calculate a potential curve E(R), with $R(R_e)$ as minimum. It will now be shown that the following is true:

$$\frac{\partial E}{\partial R} = \left\langle \frac{\partial \hat{V}}{\partial R} \right\rangle = \int_{r_1} \int_{r_2} ... \int_{r_N} \left\{ \Psi^* \left(\frac{\partial \hat{V}}{\partial R} \right) \Psi \right\} d\tau_1 d\tau_2 ... d\tau_N \tag{5.116}$$

with $d\tau_i = dx_i \cdot dy_i \cdot dz_i$. The integration is carried out over the whole space.

λ is defined as parameter of $\hat{H}$, analogous to R. The system is in a stationary state, which means that no fast time-dependent processes are allowed. With $\langle \Psi | \Psi \rangle = 1$, the following is valid:

$$E = \left\langle \Psi | \hat{H} | \Psi \right\rangle \tag{5.117}$$

and therefore:

$$\frac{\partial E}{\partial \lambda} = \left\langle \frac{\partial \Psi}{\partial \lambda} \middle| \hat{H} \middle| \Psi \right\rangle + \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \Psi \right\rangle + \left\langle \Psi \middle| \hat{H} \middle| \frac{\partial \Psi}{\partial \lambda} \right\rangle \tag{5.118}$$

$\hat{H}$ being a hermitian operator, with $\left\langle \Psi | \hat{H} | \Phi \right\rangle = \left\langle \hat{H}\Psi | \Phi \right\rangle$, we can write

$$\left\langle \Psi \middle| \hat{H} \middle| \frac{\partial \Psi}{\partial \lambda} \right\rangle = \left\langle \hat{H}\Psi \middle| \frac{\partial \Psi}{\partial \lambda} \right\rangle = \left\langle \frac{\partial \Psi}{\partial \lambda} \middle| \hat{H}\Psi \right\rangle = real \tag{5.119}$$

Because of $\hat{H}\Psi = E\Psi$ and $\hat{H}\Psi^* = E\Psi^*$ the following can be derived:

$$\frac{\partial E}{\partial \lambda} = \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \Psi \right\rangle + E \left\langle \frac{\partial \Psi}{\partial \lambda} \middle| \Psi \right\rangle + E \left\langle \Psi \middle| \frac{\partial \Psi}{\partial \lambda} \right\rangle \tag{5.120}$$

$$\frac{\partial E}{\partial \lambda} = \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \Psi \right\rangle + E \frac{\partial}{\partial \lambda} \langle \Psi | \Psi \rangle \tag{5.121}$$

$$\frac{\partial E}{\partial \lambda} = \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \Psi \right\rangle \tag{5.122}$$

Because $\hat{T}$ is not dependent on λ, the following is true:

$$\frac{\partial \hat{H}}{\partial \lambda} = \frac{\partial \hat{T}}{\partial \lambda} + \frac{\partial \hat{V}}{\partial \lambda} = \frac{\partial \hat{V}}{\partial \lambda} \tag{5.123}$$

with which the Hellmann-Feynman theorem is proven:

$$\frac{\partial E}{\partial \lambda} = \left\langle \Psi \left| \frac{\partial \hat{V}}{\partial \lambda} \right| \Psi \right\rangle \tag{5.124}$$

In classical physics, the force F_R, which acts along the bond axis, equals the negative derivative of the potential V by the coordinate R:

$$F_R = -\frac{\partial V}{\partial R} \tag{5.125}$$

The quantum mechanical analog to this is:

$$F_R = \left\langle \frac{\partial V}{\partial R} \right\rangle \tag{5.126}$$

5.2.1 Application of the Hellmann-Feynman theorem

First we will examine the relation

$$F_R = \left\langle \frac{\partial V}{\partial R} \right\rangle \tag{5.127}$$

of a two centre system A_1—A_2 with the nuclear charges Z_1, Z_2:

$$F_R = \frac{Z_1 Z_2 e^2}{R^2} - \sum_{i=1}^{N} \int_{\tau_1} \int_{\tau_2} ... \int_{\tau_N} \left\{ \Psi^* \left(\frac{Z_1 e^2 \partial r_{1i}}{r_{1i}^2 \partial R} + \frac{Z_2 e^2 \partial r_{2i}}{r_{2i}^2 \partial R} \right) \Psi \right\} d\tau_1 d\tau_2 ... d\tau_N \tag{5.128}$$

Because the bracketed operator in the preceding equation leaves Ψ unchanged, the integration is best carried out *over all electron coordinates*, except the coordinate i. In order to do so, we first write:

$$\rho(x_i, y_i, z_i) = \int_{\tau_1} ... \int_{\tau_{i-1}} \int_{\tau_{i+1}} ... \int_{N} \Psi^* \Psi \cdot d\tau_1 ... d\tau_{i-1} d\tau_{i+1} ... d\tau_N \tag{5.129}$$

$r(x_i, y_i, z_i)$ is the probability density of electron *i* at x_i, y_i, z_i. We can write $r(x_i, y_i, z_i)$ as $r_i(x, y, z)$ and abbreviate it as r_i. $er_i dt_i$ equals the charge contribution of electron *i* in the volume element dt_i.

Now we can write:

$$F_R = \frac{Z_1 Z_2 e^2}{R^2} - \sum_{i=1}^{N} \int_{\tau_i} \left(\frac{Z_1 e^2 \partial r_{1i}}{r_{1i}^2 \partial R} + \frac{Z_2 e^2 \partial r_{2i}}{r_{2i}^2 \partial R} \right) \rho_i d\tau_i \tag{5.130}$$

This equation can be evaluated for concrete cases. We will now discuss such an example. The value of the above defined integrand only depends on its location in space τ. If we examine the volume element $d\tau$ at the location (x, y, z), we can write:

$$\frac{Z_1 e^2}{r_{1i}^2} \frac{\partial r_{1i}}{\partial R} + \frac{Z_2 e^2}{r_{2i}^2} \frac{\partial r_{2i}}{\partial R} = \frac{Z_1 e^2}{r_{1j}^2} \frac{\partial r_{1j}}{\partial R} + \frac{Z_2 e^2}{r_{2j}^2} \frac{\partial r_{2j}}{\partial R} = \frac{Z_1 e^2}{r_1^2} \frac{\partial r_1}{\partial R} + \frac{Z_2 e^2}{r_2^2} \frac{\partial r_2}{\partial R} \tag{5.131}$$

Interchanging the sum with the integral and summarizing ρ_i to the entire probability density

$$\rho(x, y, z) = \sum_{i=1}^{N} \rho_i(x, y, z) \tag{5.132}$$

results in the following equation

$$F_R = \frac{Z_1 Z_2 e^2}{R^2} - \int_{\tau} \left(\frac{Z_1 e^2}{r_1^2} \frac{\partial r_1}{\partial R} + \frac{Z_2 e^2}{r_2^2} \frac{\partial r_2}{\partial R} \right) \rho d\tau \tag{5.133}$$
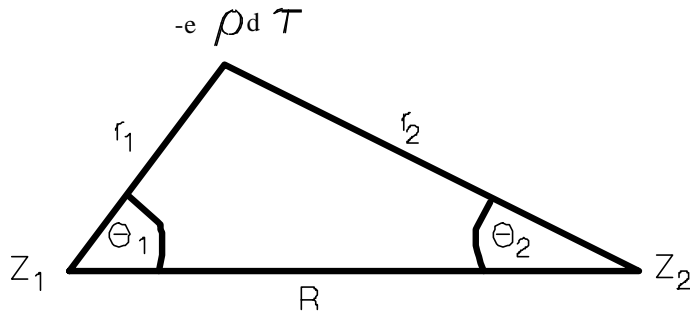
Figure 5.13

Looking at figure 5.13 it is easy to understand the following:

$$r_2 = fix : \frac{\partial r_1}{\partial R} = \cos \theta_1 \text{ and } \frac{\partial r_2}{\partial R} = 0 \qquad (5.134)$$

$$r_1 = fix : \frac{\partial r_2}{\partial R} = \cos \theta_2 \text{ and } \frac{\partial r_1}{\partial R} = 0 \qquad (5.135)$$

The derivative for r_2 = fix is furnished by f_1 , and the one for r_2 = fix is furnished by f_2:

$$f_1 = \frac{Z_1}{r_1^2} \cdot \cos \theta_1 \qquad\qquad f_2 = \frac{Z_2}{r_2^2} \cdot \cos \theta_2 \qquad (5.136)$$

Therefore, the following is true for f = f_1 + f_2 and F_R:

$$f = \frac{Z_1}{r_1^2} \cdot \cos \theta_1 + \frac{Z_2}{r_2^2} \cdot \cos \theta_2 \qquad (5.137)$$

$$F_R = \frac{Z_1 Z_2 e^2}{R^2} - \frac{e^2}{2} \int_\tau f\rho d\tau \qquad (5.138)$$

$e^2 f$ equals the *force component* which acts on the nucleus of a unit charge at the location (x, y, z). Depending on the location, f is positive or negative. Therefore, *bonding* and *antibonding* spaces can be defined:

$$F_R = \frac{Z_1 Z_2 e^2}{R^2} - \frac{e^2}{2} \int_{f>0}^{bonding} f\rho d\tau - \frac{e^2}{2} 2 \int_{f<0}^{antibonding} f\rho d\tau \qquad (5.139)$$

The bonding forces hold the nuclei together and the antibonding forces *pull them apart*. At equilibrium distance, the integral compensates *over this region* the core-core repulsion, leading to F_R= 0. Since ρ and dτ are always positive, the sign of fρdτ is defined by the one of f. We can conclude:

f > 0: bonding region   f = 0: nonbonding area   f < 0: antibonding region

In order to apply this result, we will define the nature of the area f = 0, which separates the bonding from the antibonding area. We will therefore define the nature of the following curve:

$$f = \frac{Z_1}{r_1^2} \cdot \cos \theta_1 + \frac{Z_2}{r_2^2} \cdot \cos \theta_2 = 0 \qquad (5.140)$$

The discussion is simplified by the fact that A_1—A_2 has a C_∞ axis along the connecting line. A suitable coordinate system which simplifies the solution of the problem is shown in 6.2. We define

$$x = \frac{1}{2}R\xi \qquad\qquad y = \frac{1}{2}R\eta \qquad\qquad a = \frac{Z_1}{Z_2} \leq 1 \qquad (5.141)$$

Gion Calzaferri
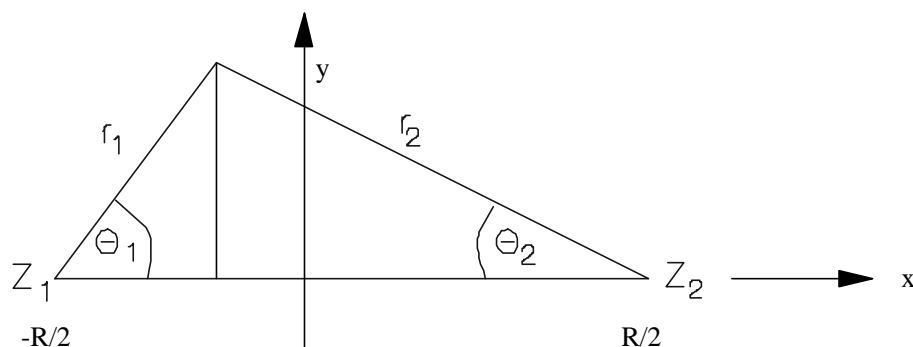
Figure 5.14

According to figure 5.14, we find:

$$r_1^2 = (\tfrac{1}{2}R + x)^2 + y^2 = \tfrac{1}{4}R^2\big[(1+\xi)^2 + \eta^2\big] \tag{5.142}$$

$$r_2^2 = (\tfrac{1}{2}R - x)^2 + y^2 = \tfrac{1}{4}R^2\big[(1-\xi)^2 + \eta^2\big] \tag{5.143}$$

$$r_1 \cdot \cos\theta_1 = \tfrac{1}{2}R + x = \tfrac{1}{2}R(1+\xi) \tag{5.144}$$

$$r_2 \cdot \cos\theta_2 = \tfrac{1}{2}R - x = \tfrac{1}{2}R(1-\xi) \tag{5.145}$$

Transformation of the *initial equation*s leads to:

$$a \cdot \frac{\tfrac{1}{2}R(1+\xi)}{\big\{\tfrac{1}{4}R^2[(1+\xi)^2+\eta^2]\big\}^{3/2}} + \frac{\tfrac{1}{2}R(1-\xi)}{\big\{\tfrac{1}{4}R^2[(1-\xi)^2+\eta^2]\big\}^{3/2}} = 0 \tag{5.146}$$

From here, it is easy to get to the result.

$$\boxed{\left[\frac{1-\xi}{(1+\xi)a}\right] = -\left[\frac{(1-\xi)^2+\eta^2}{(1+\xi)^2+\eta^2}\right]^{3/2}} \tag{5.147}$$

Solving this equation, we have to consider that it only provides solutions for certain values of ξ. It does not provide solutions for $-1 < \xi < 1$. $\xi = \pm 1$ corresponds to the position of the nuclei. In the case of homonuclear molecules, the equation provides a solution for all other values of ξ. For heteronuclear molecules, the solutions which can be found for $\xi > 1$ are rapidly approaching $\pm\infty$. The negative range of ξ can easily be outlined by first chosing a small interval for $\xi < -1$ and gradually extending it in the direction of more negative values. We illustrate this in figure 5.15 for homonuclear diatomic molecules.

<u>Bonding and antibonding regions in diatomic molecules.</u>

An application of the Hellmann-Feynmann theorem for homonuclear diatomic molecules. The coordinates are defined as shown in Figure 5.9.

$i := 0 .. 80$ $\qquad$ $\xi_i := 1.0 + i \cdot 0.05$ $\qquad$ $\xi\mu_i := -\xi_i$

Starting value: $\qquad$ $\eta := 0.01$

Given $\qquad$ $\eta \geq 0$ $\qquad$ $\left[\dfrac{(1-\xi)}{(1+\xi)}\right] = -\left[\dfrac{(1-\xi)^2 + \eta^2}{(1+\xi)^2 + \eta^2}\right]^{\frac{3}{2}}$

$f(\xi) := \text{Find}(\eta)$ $\qquad$ $\eta_i := f(\xi_i)$
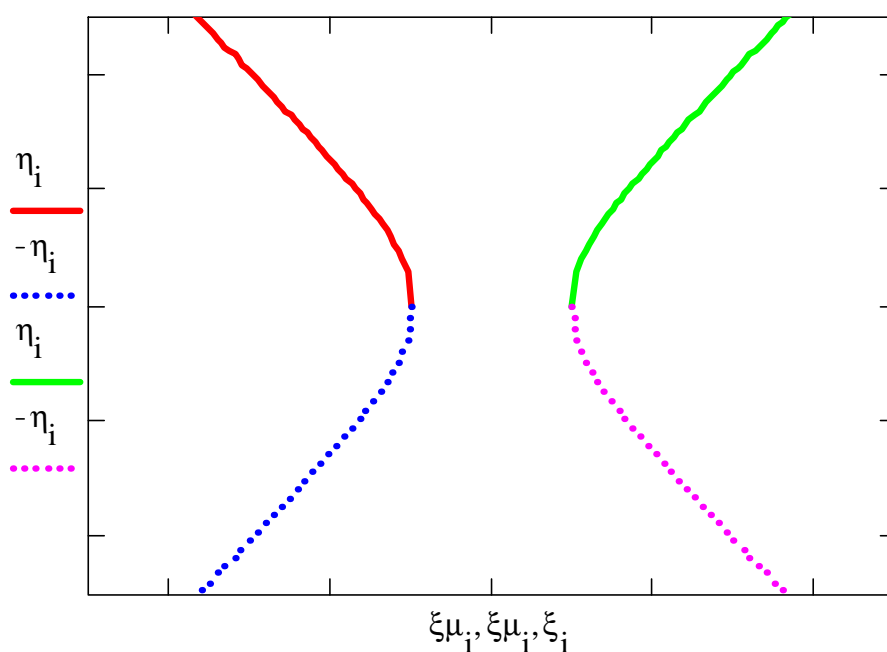
Figure 5.15: We observe that in the case of homonuclear molecules, the bonding region and the two antibonding regions are clearly separated. The bonding region mainly lies between the two nuclei, because with increasing $|\eta|$, the electron density decreases very rapidly.

Heteronuclear molecules:Solving this proplem is more delicate. Pay attention to the fact that solutions for ξ_i are restricted to limited regions.

First region:

$\alpha := 0.5$ $\qquad$ $\eta := 0.01$ $\qquad$ $j := 0 .. 100$ $\qquad$ $\xi1_j := 1.0 + j \cdot 0.01$

Given

$$\left[\frac{(1 - \xi1)}{(1 + \xi1) \cdot \alpha} \right] = - \left[\frac{(1 - \xi1)^2 + \eta^2}{(1 + \xi1)^2 + \eta^2} \right]^{\frac{3}{2}} \qquad \eta \geq 0 \qquad f(\xi1) := \text{Find}(\eta) \qquad \eta1_j := f\left(\xi1_j\right)$$

Second region:

$$\xi2_j := -1.0 - (j + 0.01) \cdot 0.0482 \qquad\qquad \eta := -0.001$$

Given

$$\left[\frac{(1 - \xi2)}{(1 + \xi2) \cdot \alpha} \right] = - \left[\frac{(1 - \xi2)^2 + \eta^2}{(1 + \xi2)^2 + \eta^2} \right]^{\frac{3}{2}} \qquad \eta \leq 0 \qquad f(\xi2) := \text{Find}(\eta) \qquad \eta2_j := f\left(\xi2_j\right)$$
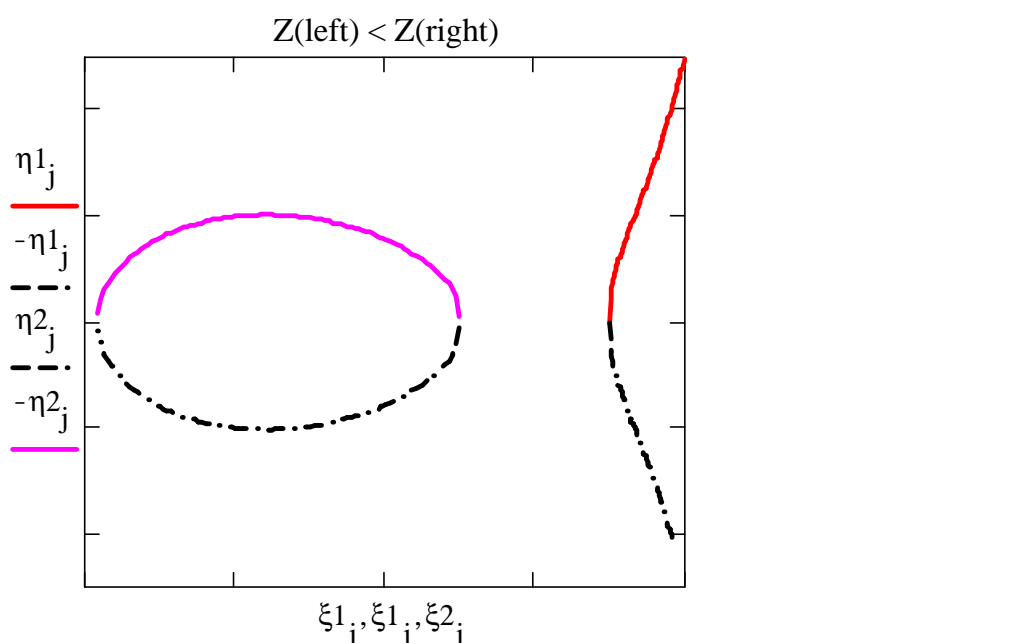
Figure 5.16: We observe that again the bonding region and the two antibonding regions are clearly separated. The antibonding region on the left side has an interesting shape.

The Pauli principle has not been taken into account so far. The consideration of this principle leads to the same result as T. Berlin has shown (J. Chem. Phys. **19** (1951) 208).

Application on large molecules

We will now use the theory of the previous chapters to introduce the *pairpotential*, which leads to an important extension of the EHMO (Extended Hückel Molecular Orbital) theory, which we define as EHMO-ASED (Atom Superposition and Electron Delocalization).

The idea of the EHMO-ASED procedure is to split the electron density distribution r in two parts: the part for the free atoms and the remaining part. The atomic components r_a of r in the free atoms are spherical symmetric and follow the atoms perfectly. The remaining part of the electron density distribution depends on the relative arrangement of the atoms and therefore does not perfectly follow the nuclei. We therefore define it as r_{npf} (not perfectly following). This leads to

$$\rho = \sum_{\alpha}^{atoms} \rho_a + \rho_{npf} \tag{5.148}$$

This splitting is useful because in almost all cases, r_{npf} is only a fraction of the whole electron density distribution. This means that the formation of a chemical bond only leads to a relatively small rearrangement of the electron density distribution in the free atoms. For a diatomic molecule a—b, the following equation corresponds:

$$\rho = \rho_a + \rho_\beta + \rho_{npf} \tag{5.149}$$

If we put the origin of the coordinates in the nucleus α, the following is true because of the spherical symmetry of r_a and r_b:

$$\rho(r, R\beta) = \rho_a(r) + \rho_\beta(|R_\beta - r|) + \rho_{pnf}(r, R_\beta) \tag{5.150}$$

r represents the electron coordinates and R the coordinates of the nucleus. The force F_{R_β}, which acts on the nucleus b, is given by:

$$F_{R_\beta} = F(R_\beta, \rho_a) + F(R_\beta, \rho_{npf}) \tag{5.151}$$

Or, expressed according to (5.114):

$$\frac{\partial E}{\partial R} = -Z_\beta \left\{ \frac{Z_a}{R_\beta^2} + \int \rho_a(r) \frac{\partial}{\partial R_\beta} \cdot \frac{1}{|R_\beta - r|} dr \right\} + F(R_\beta, \rho_{npf}) \tag{5.152}$$

The force F_{R_a}, which acts on the nucleus α, is defined by an analogous expression. The energy E(R), which needed to bring two atoms from infinity to the distance R', can therefore be expressed as:

$$E(R') = \int_\infty^{R'} \left\langle \frac{\partial \hat{V}}{\partial R} \right\rangle dR = \int_\infty^{R'} \left\{ \frac{1}{2} (F(R_\beta, \rho_a) + F(R_a, \rho_\beta)) + F(R, \rho_{npf}) \right\} dR \tag{5.153}$$

Because the integral of the first two *terms*, is purely repulsive and disappears at infinity, we can write

$$E(R) = E_{Rep}(R) + \Delta E_{npf}(R) \tag{5.154}$$

As it has been mentioned, $E_{Rep}(R)$ is a *pure* two-body repulsion term, which we can express in the following way:

$$E_{Rep}(R) = \frac{Z_a Z_\beta}{R} - \frac{1}{2} \left(Z_a \int_r \frac{\rho_\beta(r)}{|R - r|} dr + Z_\beta \int_r \frac{\rho_a(r)}{|R - r|} dr \right) \tag{5.155}$$

Since the electron density distributions r_a and r_b of atoms are generally known well enough, the calculation of $E_{Rep}(R)$ is not difficult. The calculation of $DE_{npf}(R)$ is much more difficult.

The EHMO-ASED procedure consists in the approximation of $DE_{npf}(R)$ with $DE_{EHMO}(R)$ and in the calculation of $E_{Rep}(R)$ by using the same *Slater function as in the EHMO calculations*. The example in figure 5.17 illustrates what can be obtained with optimized but physically very reasonable parameters for e.g. the hydrogen molecule.
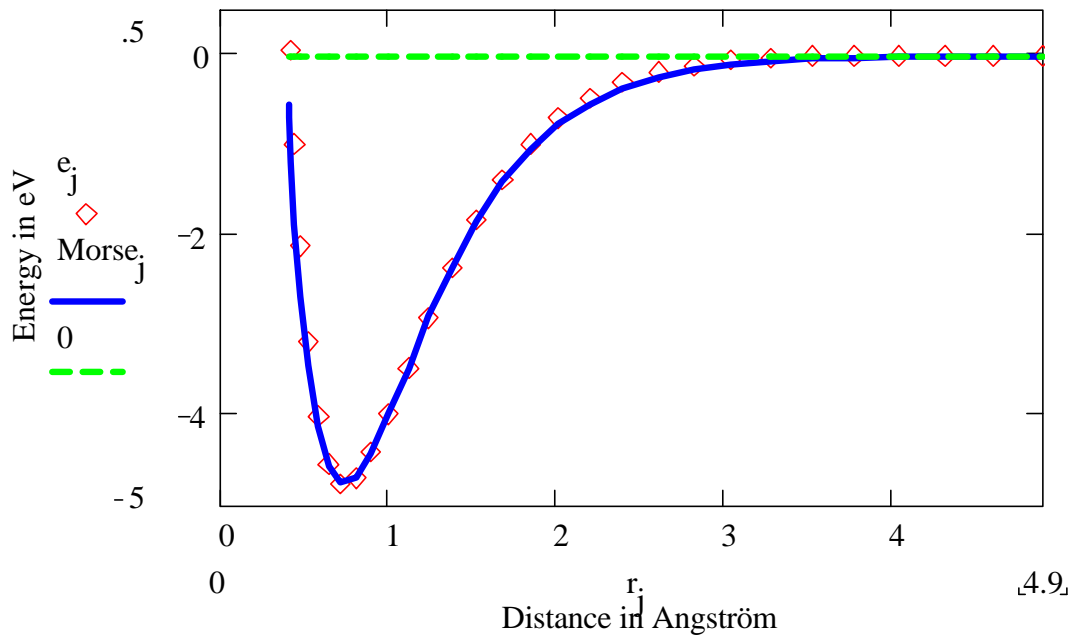
Figure 5.17:
Comparison of the result of an optimized EHMO-ASED calculation at the H₂ molecule (solid) with the Morse potential (diamonds).

The off-diagonal elements are calculated as

$$H_{ij} = \tfrac{1}{2}KS_{ij}(H_{ii} + H_{jj}) \tag{5.156}$$

More details are given in chapter 5.4.

The two-body correction $E_{ab}(R)$ for polyatomic molecules is calculated as a sum over all atom-atom interactions. Since it is always repulsive, we denote it as E_{Rep} and number the atoms with the indices α and β:

$$E_{Rep} = \sum_{\alpha<\beta} E_{Rep_{\alpha,\beta}} \tag{5.157}$$

E_{EHMO} is equal to the sum over the one electron states E_i times the occupation numbers b_i:

$$E_{EHMO} = \sum_i b_i E_i \tag{5.158}$$

$$E_i = \sum_{a_s} c_{i,a_s}^2 H_{a_s,a_s} + 2 \sum_{a_s<\beta_t} c_{i,a_s} c_{i,\beta_t} H_{a_s,\beta_t} \tag{5.159}$$

5.3 CHARGE ITERATION

The charge iteration procedure can be used to iterate on the charges of all atoms in the molecule or only on the charges of selected atoms. The diagonal Hamiltonian matrix elements are given by $H_{ii} = -VSIE(Q)$ where $VSIE(Q)$ is the valence state ionization energy of orbital i when the atom has a total charge Q. The off-diagonal Hamiltonian matrix elements are calculated in the normal manner.

The $VSIE(Q)$ functions are assumed to be of the form

$$VSIE(Q) = d_0 + d_1 Q + d_2 Q^2 \qquad (5.160)$$

where d_0, d_1 and d_2 are parameters, stored in VOI.DAT and FOI.DAT, which depend on the atom and the orbital.

We give a detailed description of the VSIE concept in the next paragraphs.

5.3.1 Valence state ionization energy VSIE

The term valence state ionization energy describes the energy necessary to remove an electron from a given orbital of either a specific configuration or a valence configuration. This definition is clarified using **ns** VSIEs of the particles shown below which contain only *ns* „valence electrons".

H	He$^+$							(1s)^1
Li	Be$^+$	B^{2+}	C^{3+}	N^{4+}	O^{5+}	F^{6+}	Ne^{7+}	(2s)^1
Na	Mg$^+$	Al^{2+}	Si^{3+}	P^{4+}	S^{5+}	Cl^{6+}	Ar^{7+}	(3s)^1
K	Ca$^+$	Ga^{2+}	Ge^{3+}	As^{4+}	Se^{5+}	Br^{6+}	Kr^{7+}	(4s)^1

All of them have only one *ns* „valence" electron. We know that the ionization energy $IP = E_{x^+} - E_x$ of H, He$^+$ and Li^{2+} depends only on the core charge Z and on the quantum number n:

$$IP/eV = 13.6 \cdot \frac{Z^2}{n^2} \qquad (5.161)1$$
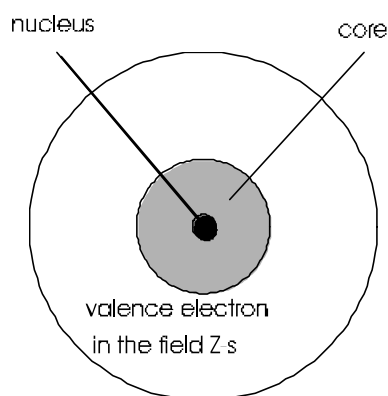
In case of Li, Be$^+$, … Kr^{7+} we assume that the $(ns)^1$ electrons move in an effective field $(Z{-}s)^2$ of the core shielded by the inner electrons. s is the shielding parameter. This concept is illustrated in Figure 5.18.

Figure 5.18: Valence electron in the effective field $Z{-}s$. s is the shielding parameter.

This concept suggests the following description of the ionization energy of atoms with one *ns* valence electron:

$$IP/eV = 13.6 \cdot \frac{(Z-s)^2}{n^2} = 13.6 \cdot \frac{1}{n^2} \cdot Z^2 - 13.6 \cdot 2 \cdot \left(\frac{s}{n^2}\right) \cdot Z + 13.6 \cdot \left(\frac{s}{n}\right)^2 \qquad (5.162)$$

This equation can be wirtten in a more general way as follows:

$$IP = A(n) \cdot Q^2 + B(n) \cdot Q + C(n) \qquad (5.163)$$

where A(n), B(n) and C(n) are empirical parameters. The parameters A(2), B(2) and C(2) for Li to F^{6+} are equal to 3.422 eV, 9.438 eV and 5.375 eV, respectively. In the next table we show that the $2s^1 \rightarrow 2s^0$ ionization potential of the mentioned species are described in a quantitative way by this approach. The same is found to be generally true.

Table 5.4

	Li	Be⁺	B²⁺	C³⁺	N⁴⁺	O⁵⁺	F⁶⁺	Ne⁷⁺
Q	0	1	2	3	4	5	6	7
IP$_{experiment}$	5.39	18.21	37.92	64.48	97.86	138.1	185.2	
IP$_{calculated}$	5.38	18.23	37.94	64.48	97.87	138.1	185.2	239.1

We now write the polynomial of second order as follows:

$$IP = d_0 + d_1 Q + d_2 Q^2 \qquad (5.164)$$

Q describes the charge of the atom T from which an electron is removed:

$$T^Q \quad \rightarrow \quad T^{Q+1} \quad + \quad IP \qquad (5.165)$$

d_0 is equal to the ionization energy of the neutral atom.

The charge dependence of the valence orbital ionization energies of hydrogen, helium, lithium is well described by the following expressions:

$$1sVSIE(1s^1) = 13.65 \cdot Q^2 + 27.15 \cdot Q + 13.6 \qquad (5.166)$$

$$1sVSIE(1s^2) = 13.57 \cdot Q^2 + 37.42 \cdot Q + 24.6$$

Polynomials of second order are sufficient to describe the VSIE also in case of many electron atoms.

Barycenter energy

The concept of the barycenter energy of an electron configuration is very useful. It allows the transfer of spectroscopic data of the atoms to chemically meaningful information[11]. The barycenter is the average energy of an electron configuration. It can be understood by looking at the example below which explains $E(1s^2 2s^2 2p^2)_{av}$ in case of the carbon atom.
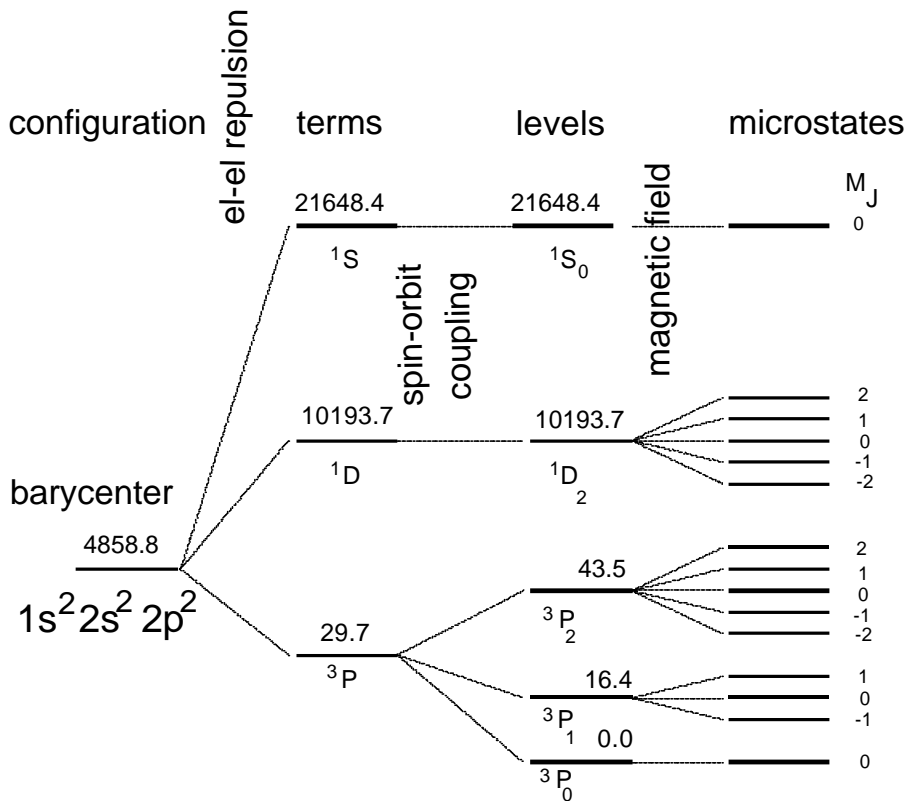
<u>Figure 5.19:</u> Definition of the barycenter of the electron configuration $1s^22s^22p^2$.

The barycenter is given by:

$$E(^3P) = \tfrac{1}{1+3+5}\{E(^3P_0) + 3E(^3P_1) + 5E(^3P_2)\} \tag{5.167}$$

$$E(^3P) = \tfrac{1}{9}\{0 + 3 \cdot 16.4 + 5 \cdot 43.5\} = 29.633\,cm^{-1} \tag{5.168}$$

From this we find:

$$E(1s^22s^22p^2)_{av} = \tfrac{1}{1+5+9}\{E(^1S) + 5E(^1D) + 9E(^3P)\} \tag{5.169}$$

$$E(1s^22s^22p^2)_{av} = \tfrac{1}{15}\{21648.4 + 5 \cdot 10193.7 + 9 \cdot 29.7\} = 4858.9\,cm^{-1}$$

We now explain by means of an example how it can be determined from experimental data. The $3p$ VSIE of the $...3s^23p^4$ configuration of S(I) is the energy of the ionization process

$$S([Ne]3s^23p^4) \quad \rightarrow \quad S([Ne]3s^23p^3) + e \tag{5.170}$$

The states $^{2S+1}L_J$, belonging to these electron configurations are:
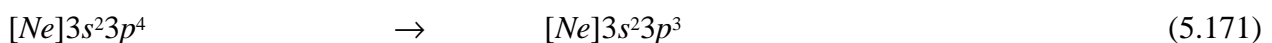
$[Ne]3s^23p^4$	$\rightarrow$	$[Ne]3s^23p^3$	(5.171)
$^1D_2$, $^3P_2$, $^3P_1$, $^3P_0$, $^1S_0$	$\rightarrow$	$^2D_{5/2}$, $^2D_{3/2}$, $^2P_{3/2}$, $^2P_{1/2}$, $^4S_{3/2}$	
degeneracy: $5 + 9 + 1$		degeneracy: $10 + 6 + 4$	

The energy of these states are shown in Figure 5.19. The symbols $S(\mathrm{I})$ for S^0 and $S(\mathrm{II})$ for S^{+1} are those used in atomic spectroscopy. $\mathrm{E}(S(\mathrm{I}), ...3p^4)_{av}$ and $\mathrm{E}(S(\mathrm{II}), ...3p^3)_{av}$ are determined as explained before. $P^{(0)}$ and $P^{(+)}$ are called *promotion energies*.

From this diagram follows:

$$\mathbf{3p}\,\mathrm{VSIE}([Ne]3s^23p^4) = IP - P^{(0)} + P^{(+)} = 83'559.3 + 14'802.4 - 4'676.0 = 93'666\,cm^{-1} \qquad (5.172)$$

The $3\mathbf{p}$ VSIE of S^+ or S^0 and $3\mathbf{s}$ VSIE of S^- can be determined in a similar way.

$$S([Ne]3s^23p^3) \qquad \rightarrow \qquad S([Ne]3s^23p^2) + e \qquad\qquad\qquad (5.173)$$

$$S([Ne]3s^23p^4) \qquad \rightarrow \qquad S([Ne]3s^13p^4) + e$$

$$S([Ne]3s^2\,3p^5) \qquad \rightarrow \qquad S([Ne]3s^23p^4) + e$$

ν denotes the number of valence electrons.

$$S^+: \mathbf{n} = 5, \ S^0: \mathbf{n} = 6, \ S^{-1}: \mathbf{n} = 7 \qquad\qquad\qquad\qquad\qquad (5.174)$$
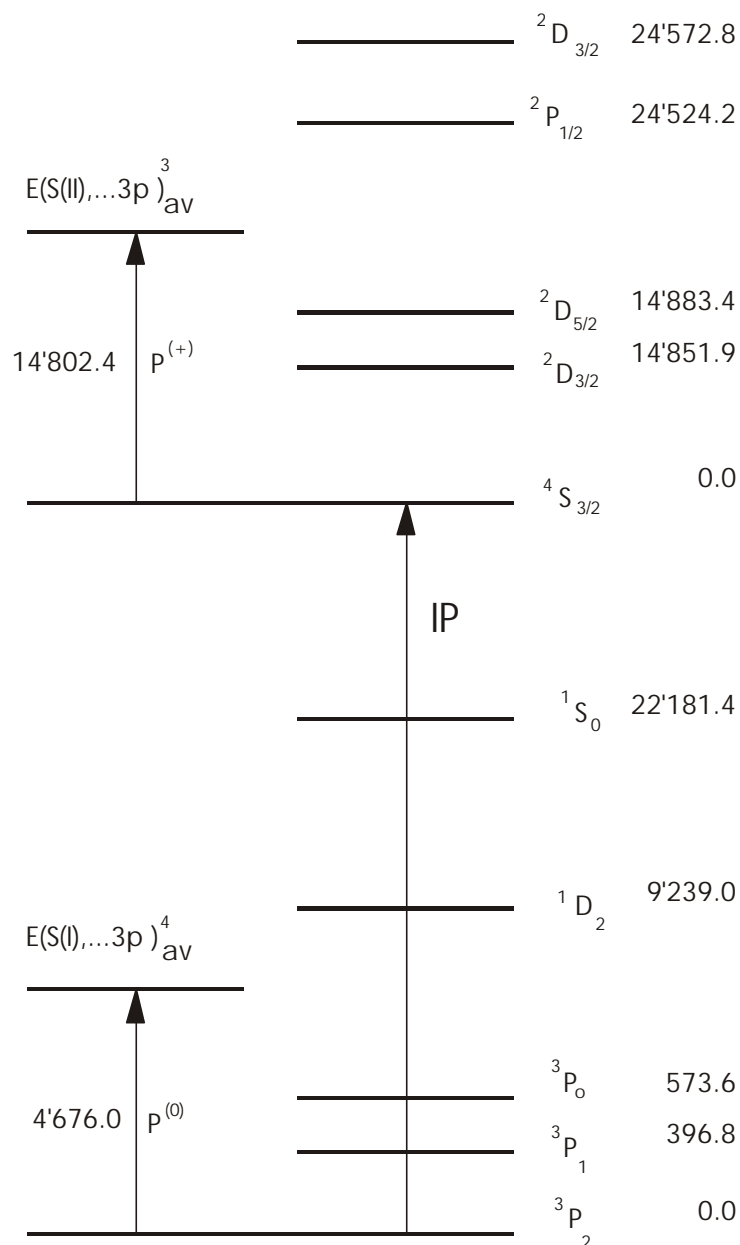
Figure 5.20: Levels, barycenters and promotion energies of sulfur S^0 and S^+ for the electron configurations $S[(I),..., 3p^4]$ and $S[(II),...,3p^3]$.

The charge Q is then expressed as: $Q = (6 – \textbf{n})$. This notation is used in the table below where the $3s$- and $3p$ VSIE of S^{-1}, S^0 and S^{+1} are reported.

Table 5.5

Orbital	Configuration	VSIE [eV]		
		S^{-1} $Q = -1$	S^0 $Q = 0$	S^{+1} $Q = +1$
$3s$	$...3s^23p^{v-2}$	11,04	20,7	33,4
$3p$	$...3s^23p^{v-2}$	2,65	11,61	22,2

The charge dependence of the VSIEs can be expressed in the same way as in case of Li^{2+}, He^+, H and Li^+, He, H^-:

3s $VSIE(2s^23p^{v-2}) = 1.52 \cdot Q^2 + 15.37 \cdot Q + 20.67$ (5.175)

3p $VSIE(2s^23p^{v-2}) = 1.63 \cdot Q^2 + 12.21 \cdot Q + 11.58$

5.3.2 Coulomb Integrals

The Coulomb integral H_{ii} is equal to the negative value of the *VSIE* of the c_i AO. The *VSIE* is understood to be evaluated in terms of both, an atomic charge Q and a configuration appropriate for that atom when incorporated in the molecule of interest. Thus

$$H_{ii} = E(Q+1) - E(Q) = -VSIE$$ (5.176)

where the electron which is removed and which increases the excess charge to $Q + 1$ is taken from the c_i AO. As explained in the previous section the charge dependence of the *VSIE* is expressed as

$$VSIE(Q) = d_0 + d_1 \cdot Q + d_2 \cdot Q^2$$ (5.177)

The coefficients d_0, d_1 and d_2 are stored in the files VOI.DAT for main group elements and in FOI.DAT for transition elements.

To understand the way the Coulomb integrals are calculated from the VSIE we consider a carbon atom of charge Q and of the electronic configuration $(2s)^s (2p)^p$

$$C^Q: \quad (2s)^s (2p)^p \quad \text{with } v = \sigma + \pi \text{ and } Q = 4 - v$$ (5.178)

and ask for the Coulomb integral:

$$H_{2s2s} = H_{2s2s}([He]2s^\sigma 2p^\pi)$$ (5.179)

The idea is to express $H_{2s2s}([He]2s^\sigma 2p^\pi)$ as a linear combination of the 2sVSIE(Q) belonging to the relevant electronic configurations $(2s)^2(2p)^{(n-2)}$ and $(2s)^1(2p)^{(n-1)}$:

$$-H_{2s2s}([He]2s^\sigma 2p^\pi) = 2sVSIE([He]2s^\sigma 2p^\pi)$$ (5.180)

$$= a \cdot 2sVSIE([He](2s)^2(2p)^{v-2}) + b \cdot 2sVSIE([He](2s)^1(2p)^{v-1})$$ with

$$2sVSIE([He](2s)^2(2p)^{v-2}) = 3.46 \cdot Q^2 + 17.56 \cdot Q + 19.42 = 29.06 eV$$

$$2sVSIE([He](2s)^1(2p)^{v-1}) = 3.47 \cdot Q^2 + 17.508 \cdot Q + 21.20 = 30.82 eV$$

The coefficients a and b can be calculated from

$$\sigma = a \cdot 2 + b \cdot 1, \quad \pi = a \cdot (v-2) + b \cdot (v-1)$$ (5.181)

from which follows

$$a = \frac{\sigma v - \pi - \sigma}{v}, \quad b = \frac{2\pi - \sigma(v-2)}{v}$$ (5.182)

We now consider a numerical example with s = 1.6, p = 1.9.
We find $v = 3.5$, $Q = 0.5$, $a = 0.6$, $b = 0.4$ and

2s $VSIE([He] (2s)^{1.6} (2p)^{1.9})$

$$= 0.6 \cdot 2sVSIE([He](2s)^2(2p)^{v-2}) + 0.4 \cdot 2sVSIE([He](2s)^1(2p)^{v-1})$$ (5.183)

$= 0.6 \cdot 29.06 + 0.4 \cdot 30.82 = 29.76$ eV

More electronic configurations must be considered for an appropriate description of the H_{ii} Coulomb integrals of transition elements. This is explained in the following example:

$$-H_{ss}(d^\delta s^\sigma p^\pi) = a \cdot sVSIE(d^{n-1}s^1) + b \cdot sVSIE(d^{n-2}s^2) + c \cdot sVSIE(d^{n-2}s^1p^1) \tag{5.184}$$

with $Q = Z - \sigma - \pi - \delta$

Z is the core charge, Q is the charge of the atom under consideration and s, p, d are the accumulated orbital occupations. The procedure for the calculation of the coefficients a, b, c is the same as before

$$a + b + c = 1 \qquad \rightarrow \qquad b = \sigma - 1 \tag{5.185}$$

$$a + 2b + c = \sigma \qquad \rightarrow \qquad a = 2 - \pi - \sigma$$

$$c = \pi$$

H_{pp} and H_{dd} can be expressed in a similar way.

$$-H_{ss}(d^\delta s^\sigma p^\pi) = (2 - \sigma - \pi) \cdot sVSIE(d^{n-1}s^1) + (\sigma - 1) \cdot sVSIE(d^{n-2}s^2) + \pi \cdot sVSIE(d^{n-2}s^1p^1)$$

$$-H_{pp}(d^\delta s^\sigma p^\pi) = (2 - \sigma - \pi) \cdot pVSIE(d^{n-1}s^1) + (\pi - 1) \cdot pVSIE(d^{n-2}p^2) + \sigma \cdot pVSIE(d^{n-2}s^1p^1)$$

$$-H_{dd}(d^\delta s^\sigma p^\pi) = (1 - \sigma - \pi) \cdot dVSIE(d^n) + \sigma \cdot dVSIE(d^{n-1}s^1) + \pi \cdot dVSIE(d^{n-1}p^1) \tag{5.186}$$

In the following table we show the d_0, d_1 and d_2 coefficients of chromium in [eV] in the way they are stored in FOI.DAT. For more details see [11]-[15].

Table 5.6

		d_2	d_1	d_0
sVSIE	$d^{n-1}s^1$	.99805	7.13513	6.59581
	$d^{n-2}s^2$	.99805	8.28815	7.84802
	$d^{n-2}s^1p^1$	.99805	7.49367	9.26140
pVSIE	$d^{n-1}p^1$	.89886	5.8953	3.521
	$d^{n-2}p^2$	.89886	6.5524	4.6865
	$d^{n-2}s^1p^1$	.89886	6.5524	4.7237
dVSIE	d^n	1.8287	9.2676	4.3517
	$d^{n-1}s^1$	1.2088	11.896	7.1785
	$d^{n-1}p^1$	1.2088	12.020	8.3935

5.4 Off Diagonal Elements

The off-diagonal elements H_{ij} are calculated as

$$H_{ij} = \tfrac{1}{2} K S_{ij}(H_{ii} + H_{jj})$$ (5.187)

The parameter K can be chosen as a constant[1] or it can be expressed by the weighted formula[16]. By default we use the weighted formula in its distance-dependent form[6-8].

5.4.1 Distance dependent K

We use by default the following equation for the distance dependent Wolfsberg-Helmholz parameter:

$$K = 1 + (\kappa + \Delta^2 - \Delta^4 \kappa)\frac{\exp[-\delta(R - d_0)]}{q}$$ (5.188)

$$with \quad \Delta = \frac{H_{ii} - H_{jj}}{H_{ii} + H_{jj}} \quad and \quad q = 1 + ([(R - d_0) - |R - d_0|] \cdot \delta)^2$$

δ determines how fast K decreases with increasing bond distance. d_0 is equal to the sum of the orbital radii and is calculated from the Slater exponents. The default values are $\kappa = 1.0$ and $\delta = 0.35$ Å^{-1}. The value $K = 1.75$ was originally chosen as a reasonable compromise between the desire to match the experimental barrier in ethane, and the necessity to work in a region where populations are stable. Addition of the two-body correction to the stabilization energy shifts the minimum of $E(R)$ to longer distances than that of the original $\Delta E_{EHMO}(R)$, thus a larger K-value at $R = d_0$ is generally needed.

d_0 is equal to the sum of the orbital radii $r_n(A) + r_n(B)$ which are defined by the following equation:

$$r_n = \frac{1}{\int\limits_0^\infty \frac{1}{r} R_{nl}^2(r) r^2 dr}$$ (5.189)

κ and δ are positive empirical parameters. The flexibility of this approach allows to simulate quite realistic potential energy curves as was shown in figure 5.17. Another example is given in figure 5.21.
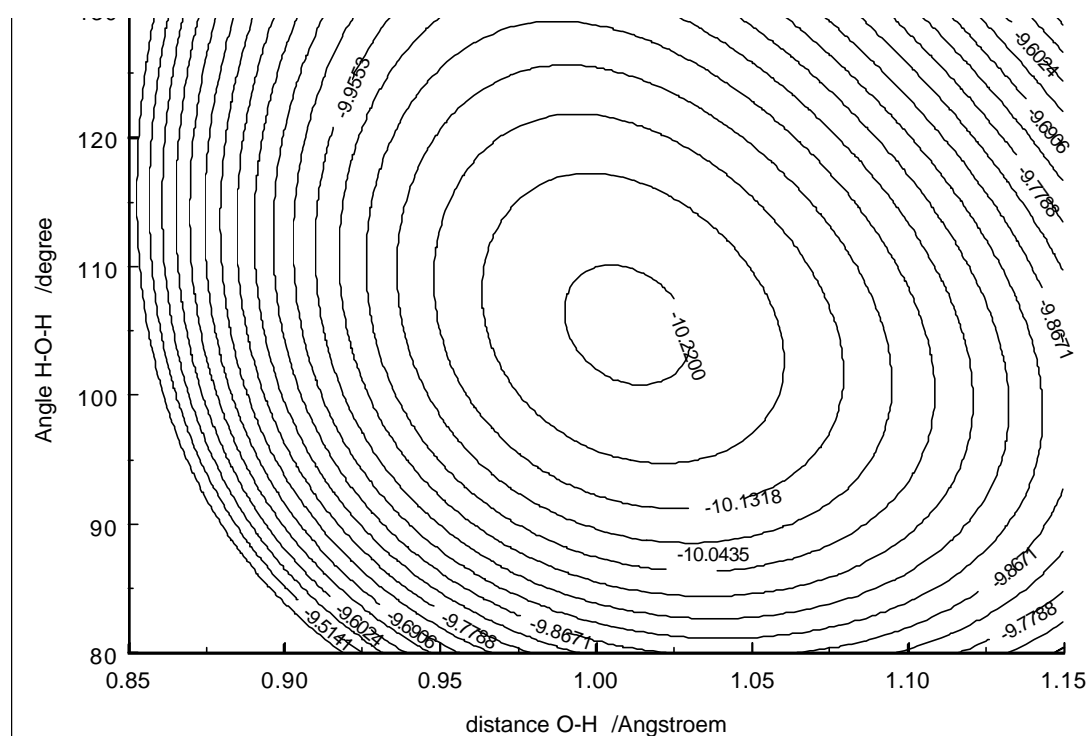
Figure 5.21 Energy hypersurface in [eV] for H_2O.

5.4.2 Comment on the weighted H_{ij} formula

The weighted formula has been introduced by Roald Hoffmann to overcome the problem of overestimating the „counterintuitive orbital mixing". It seems reasonable to approximate the overlap density $f_i f_j$ between orbitals i and j at different centres as a weighted average of the orbital densities $f_i f_i$ and $f_j f_j$, i.e.

$$\phi_i \phi_j = S_{ij}(a\phi_i \phi_i + b\phi_j \phi_j) \tag{5.190}$$

where $a + b = 1$ and S_{ij} has been included to meet the normalization condition

$$\langle \phi_i | \phi_j \rangle = S_{ij}(a\langle \phi_i | \phi_i \rangle + b\langle \phi_j | \phi_j \rangle) \tag{5.191}$$

If f_i and f_j have about the same degree of „diffuseness", a and b should be nearly equal and we can write

$$\phi_i \phi_j = \frac{S_{ij}}{2}(\phi_i \phi_i + \phi_j \phi_j) \tag{5.192}$$

That is the overlap population is essentially equally divided between atoms i and j. This is a simple way of rationalizing the Mulliken population analysis[17].

Reasoning along the same lines, we might expect that the integral $< \phi_i |H| \phi_j >$ would be given roughly by an expression of the form

$$H_{ij} = K\frac{S_{ij}}{2}(H_{ii} + H_{jj}) \tag{5.193}$$

the normal extended-Hückel formula for H_{ij} with K = CON.
The assumption of similar „diffuseness" should hold fairly well for molecules where all of the basis orbitals have reasonably large occupation numbers and similar energies, e.g. organic molecules.

However, in molecules where this condition is not met - e.g. transition metal complexes containing unoccupied, high energy s and p basis functions – the simplification $a = b$ is questionable. The obvious solution to this problem is to choose $a \neq b$ such that $f_i f_j$ is weighted in favour of the more contracted orbital.

One way in which this can be done is to assume that H_{ii} can be used as a measure of an orbitals „diffuseness" - a small H_{ii} indicating an unstable, diffuse orbital; a large H_{ii} indicating a stable, contracted orbital. Defining

$$\Delta = \frac{H_{ii} - H_{jj}}{H_{ii} + H_{jj}} \tag{5.194}$$

as a measure of the „relative diffuseness" of f_i and f_j, we can then write

$$H_{ij} = K \frac{S_{ij}}{2} \left[(1 + \Delta) H_{ii} + (1 - \Delta) H_{jj} \right] \tag{5.195}$$

where, in general, K is a function of Δ which we choose so as to meet the following conditions

$$\Delta = 0 \qquad\qquad H_{ij} = \frac{CON}{2} S_{ij} (H_{ii} + H_{jj}) \tag{5.196}$$

$$\Delta = 1 \qquad\qquad H_{ij} = S_{ij} H_{ii}$$
$$\Delta = -1 \qquad\qquad H_{ij} = S_{ij} H_{jj}$$

The $\Delta = 0$ condition is the normal Hückel formula.
This leads to the weighted H_{ij} formula

$$H_{ij} = [CON - (CON - 1)\Delta^2] \frac{S_{ij}}{2} \left[(1 + \Delta) H_{ii} + (1 - \Delta) H_{jj} \right] \tag{5.197}$$

which can be written in the more concise form

$$H_{ij} = k' \frac{S_{ij}}{2} (H_{ii} + H_{jj}) \quad \text{with} \quad k' = CON + \Delta^2 + \Delta^4 (1 - CON) \tag{5.198}$$

5.4.3 Electronic Transition Oscillator Strengths, EDiTs

For a detailed discussion and representative examples see „Electronic Transition Oscillator Strength by the Extended Hückel Molecular Orbital Method", G. Calzaferri and R. Rytz, J. Phys. Chem. (1995) 99, 12141-12150.

6 OUTPUT

In this section, main features of the output produced by ICONC are discussed in some detail. The description is not complete, but it is sufficient to help newcomers to get acquainted with the program. As a first example we choose the water molecule. We will then proceed to the problem of hyperconjugation which is used to illustrate some features of the FMO option.

6.1 The water molecule

The point symmetry of H_2O is C_{2v}. We therefore name the eigenfunctions and eigenvalues according to the C_{2v} character table.

Table1: Character table of the C_{2v} point group.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
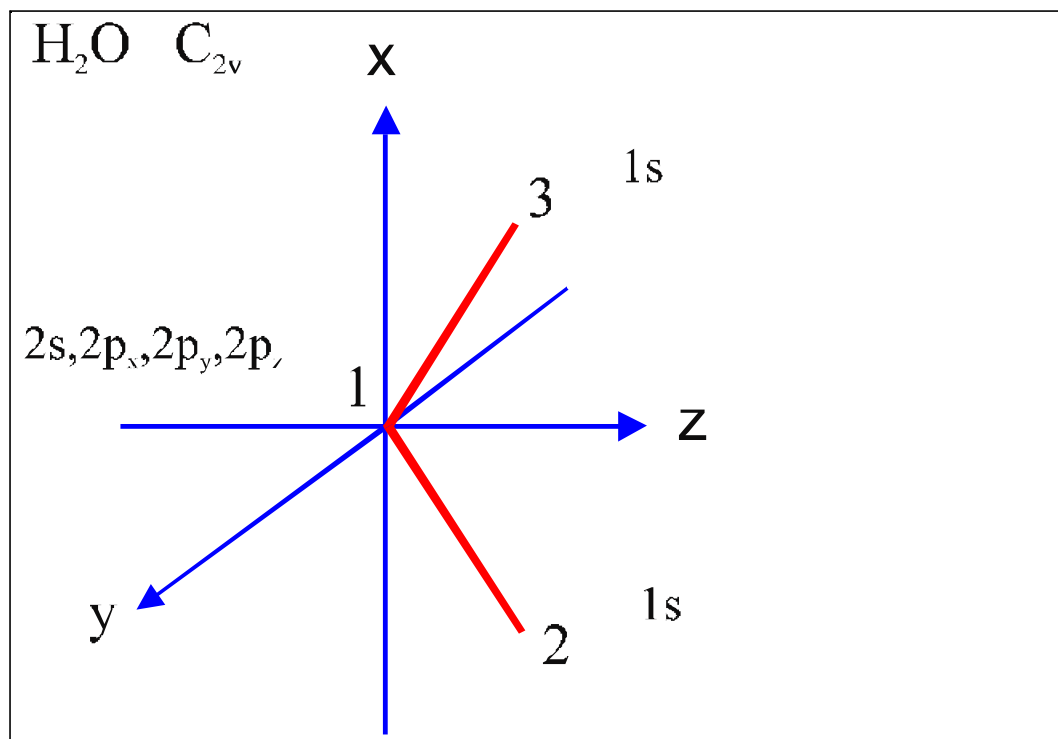
Figure 6.1: Coordinates and valence atomic orbitals.

The basis for constructing the LCAO-MO orbitals are the 1s valence orbitals of the two hydrogen atoms and the $2s$, $2p_x$, $2p_y$, $2p_z$ orbitals of the oxygen. From these 6 AO's we get 6 MO's Ψ_i:

$$\Psi_i = c_{i1}1s(H_1) + c_{i2}1s(H_2) + c_{i3}2s(O) + c_{i4}2p_x(O) + c_{i5}2p_y(O) + c_{i6}2p_z(O) \tag{6.1}$$

The atomic orbitals are expressed as Slater orbitals. The Slater exponents used by default are: $\zeta_{1s} = 1.3$ for hydrogen, $\zeta_{2s} = 2.575$ and $\zeta_{2p} = 2.275$ for oxygen. The default Coulomb integrals are: H_{1s1s} = -13.6 eV for the hydrogen atom, H_{2s2s} = -28.2 eV and H_{2p2p} = -12.4 eV for the oxygen atom. In the most simple cases the only input by the user are the atom symbols and the (internal) coordinates.

The program INPUTC which reads this information from *ATOMDEF.DAT* is a convenient tool for preparing the input files for The ICONC program. It generates the *name.GEN* files and it also transforms them into the *TEMP.KAR* files. The latter ones serve as input for ICONC.

ICONC INPUT FILE *H2O.GEN*

```
   2   0   2   0
   2   0   2   0
Water d(O-H)=0.96, angle=105.2
  0  3 0 0 2 1FFFFFFFFF 2.00 .000 .000FFFFFFFFFFFFFFFFFFFFFFFF
        .35
```

1	2	-.96	5.251	.0
1	3	-.96	-5.251	.0

```
 * * H
 O 6 22.5750-28.20 22.2750-12.40
 H 1 11.3000-13.60
```

Transforming this file into *TEMP.KAR* by running INPUTC and running ICONC < *TEMP.KAR* leads to the following result.

ICONC OUTPUT FILE *H2O.OUT*

Water d(O-H)=0.96, angle=105.2°

```
K IS CALCULATED WITH THE DISTANCE-DEPENDENT WEIGHTED FORMULA.
delta =     .35,   1+kappa =    2.0
```

INPUT

ATOM	X	Y	Z	s		p	
				N EXP	COUL	N EXP	COUL
O 1	.0	.0	.00000	2 2.5750 -28.2000		2 2.2750 -12.4000	
H 2	-.76172	.0	.58428	1 1.3000 -13.6000			
H 3	.76172	.0	.58428	1 1.3000 -13.6000			

DISTANCE MATRIX R_{ij}

```
        1          2          3
1    .0         .9600      .9600
2    .960       .0         1.5234
3    .9600      1.5234     .0
```

OVERLAP MATRIX $S_{ij} = \langle \chi_i \mid \chi_j \rangle$

	2s	2p$_x$	2p$_y$	2p$_z$	1s	1s
O 1(S)	**1.000**	.000	.000	.000	.4096	.4096
(X)	.000	**1.000**	.000	.000	-.3112	.3112
(Y)	.000	.000	**1.000**	.000	.000	.0
(Z)	.000	.000	.000	**1.000**	2.387	.2387
H 2(S)	.4096	-.3112	.000	.2387	**1.000**	.2230
H 3(S)	.4096	.3112	.000	.2387	0.2230	**1.000**

HUECKEL MATRIX $\quad h_{ij} = k(\kappa, \delta, R_{ij}) \cdot S_{ij} \cdot (h_{ii} + h_{jj})/2$

	2S	2p$_x$	2p$_y$	2p$_z$	1s	1s
O 1(S)	-28.2000	.0000	.0000	.0000	-17.5811	-17.5811
(X)	.0000	-12.4000	.0000	.0000	7.9773	-7.9773
(Y)	.0000	.0000	-12.4000	.0000	.0000	.0000
(Z)	.0000	.0000	.0000	-12.4000	-6.1190	-6.1190
H 2(S)	-17.5811	7.9773	.0000	-6.1190	-13.6000	-5.3992
H 3(S)	-17.5811	-7.9773	.0000	-6.1190	-5.3992	-13.6000

The information of the OVERLAP MATRIX and of the HUECKEL MATRIX is used by the program to solve the eigenvalue problem:

$$(h - e \cdot S) \cdot c = 0$$

$$\left(\begin{pmatrix} h_{11} & h_{12} & ... & h_{16} \\ h_{21} & h_{22} & & h_{26} \\ \vdots & \vdots & & \vdots \\ h_{61} & h_{62} & ... & h_{66} \end{pmatrix} - e \cdot \begin{pmatrix} S_{11} & S_{12} & ... & S_{16} \\ S_{21} & S_{22} & & S_{26} \\ \vdots & \vdots & & \vdots \\ S_{61} & S_{62} & ... & S_{66} \end{pmatrix} \right) \cdot c = 0$$

ENERGY LEVELS (eV)	**OCCUPATION NUMBERS** b_i		Experimental Ionization Energies
E(1) = 9.80746	.00		
E(2) = 2.69881	.00	LUMO	
E(3) = -12.40000	2.00	HOMO	IP1(exp)=12.6
E(4) = -13.39568	2.00		IP2(exp)=13.7
E(5) = -16.25167	2.00		IP3(exp)=17.2
E(6) = -30.83934	2.00		

SUM OF ONE-ELECTRON ENERGIES	=	-145.77337592 eV	$E_{EHMO} = \Sigma_i\, b_i E(i)$
ORBITAL STABILIZATION ENERGY	=	-12.57337592 eV	$\Delta E = \Sigma_i\, b_i E(i) - \Sigma_s\, b_s^0 E_s^0$
CORE-CORE REPULSION ENERGY	=	3.63881174 eV	$E_{Rep} = \frac{1}{2} \Sigma_{a,\beta}\, E_{Rep_{a,\beta}}$
STABILIZATION + REPULSION	=	-8.93456418 eV	$E = \Delta E + E_{Rep}$

WAVE FUNCTIONS: MO'S IN COLUMNS, AO'S IN ROWS $\qquad\qquad \Psi_i = \sum_{r_k=1}^{6} c_{ir_k} \chi_{r_k}$

		Ψ_1	LUMO Ψ_2	HOMO Ψ_3	Ψ_4	Ψ_5	Ψ_6
O 1	(S)	-.8645	.0000	.0000	-.2507	.0000	.7898
	(X)	.0000	-.9652	.0000	.0000	-.6328	.0000
	(Y)	.0000	.0000	1.0000	.0000	.0000	.0000
	(Z)	-.5795	.0000	.0000	.9004	.0000	-.0284
H 2	(S)	.7606	-.8264	.0000	.1534	.4174	.2107
H 3	(S)	.7606	.8264	.0000	.1534	-.4174	.2107

The calculated energy levels and the corresponding molecular orbitals are illustrated in figure 6.2 on the next page.
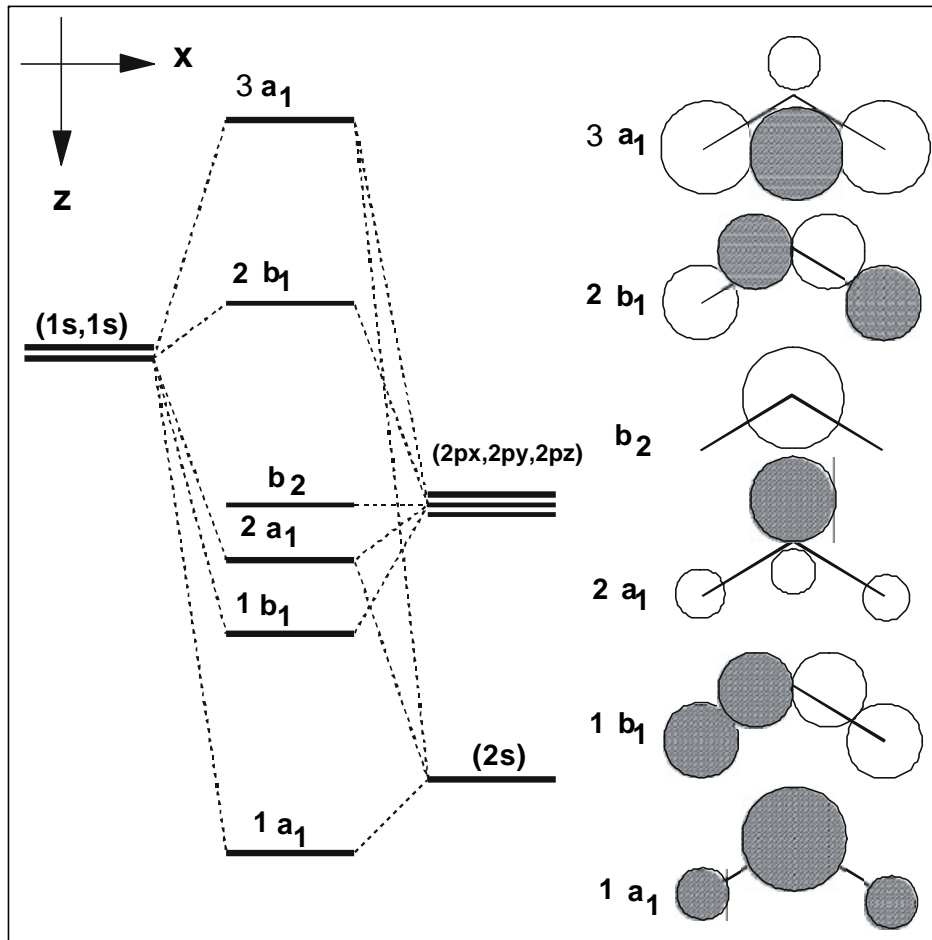
Figure 6.2: Correlation diagram of the water molecule.

DENSITY MATRIX $\qquad D_{r_k s_l} = \Sigma_i\, b_i c_{ir_k} c_{is_l}$

	2s	$2p_x$	$2p_y$	$2p_z$	1s	1s
O 1(S)	1.3732	.0000	.0000	-.4963	.2558	.2558
(X)	.0000	.8009	.0000	.0000	-.5283	.5283
(Y)	.0000	.0000	2.0000	.0000	.0000	.0000
(Z)	-.4963	.0000	.0000	1.6230	.2643	.2643
H 2(S)	.2558	-.5283	.0000	.2643	.4843	-.2126
H 3(S)	.2558	.5283	.0000	.2643	-.2126	.4843

OVERLAP POPULATION MATRIX FOR 8 ELECTRONS $\qquad S_{r_k s_l} = 2\,\Sigma_i\, b_i c_{ir_k} c_{is_l} S_{r_k s_l}$

	2s	$2p_x$	$2p_y$	$2p_z$	1s	1s
O 1(S)	1.3732	.0000	.0000	.0000	.2096	.2096
(X)	.0000	.8009	.0000	.0000	.3288	.3288
(Y)	.0000	.0000	2.0000	.0000	.0000	.0000
(Z)	.0000	.0000	.0000	1.6230	.1262	.1262
H 2(S)	.2096	.3288	.0000	.1262	.4843	-.0948
H 3(S)	.2096	.3288	.0000	.1262	-.0948	.4843

REDUCED OVERLAP POPULATION MATRIX, ATOM BY ATOM $\qquad P_{kl} = \Sigma_{r,s}\, P_{r_k s_l}$

	O	H	H
O 1	5.7971	.6646	.6646
H 2	.6646	.4843	-.0948
H 3	.6646	-.0948	.4843

COMPLETE CHARGE MATRIX FOR EACH MO, normalized to two electrons regardless of occupation

$$Q_{ir_k} = 2c_{ir_k}(c_{ir_k} + \Sigma_{l \neq k}\, c_{is_l} S_{r_k s_l})$$

	Ψ_1	Ψ_2 LUMO	Ψ_3 HOMO	Ψ_4	Ψ_5	Ψ_6
O 1(S)	.4172	.0000	.0000	.0627	.0000	1.5201
(X)	.0000	.8703	.0000	.0000	1.1297	.0000
(Y)	.0000	.0000	2.0000	.0000	.0000	.0000
(Z)	.2508	.0000	.0000	1.7533	.0000	-.0041
H 2(S)	.6660	.5649	.0000	.0920	.4351	.2420
H 3(S)	.6660	.5649	.0000	.0920	.4351	.2420

REDUCED CHARGE MATRIX, MOs in columns, atoms in rows, normalized to 2 electrons regardless of occupation

$$Q_{ri} = \Sigma_k\, Q_{ir_k}$$

	Ψ_1	Ψ_2 LUMO	Ψ_3 HOMO	Ψ_4	Ψ_5	Ψ_6
1	.6680	.8703	2.0000	1.8159	1.1297	1.5160
2	.6660	.5649	.0000	.0920	.4351	.2420
3	.6660	.5649	.0000	.0920	.4351	.2420

ATOM	NET CHARGE $Q_r = N_0(r) - \underset{occ}{\Sigma}\, Q_{ri}$	ATOMIC ORBITAL OCCUPATION FOR GIVEN MO OCCUPATION			
		s	p_x	p_y	p_z
O 1	-.46167	1.58278	1.12971	2.00000	1.74918
H 2	.23084	.76916			
H 3	.23084	.76916			

ENERGY MATRIX $\quad E_{r_k s_l} = a \Sigma_i\, b_i c_{ir_k} c_{is_l} h_{r_k s_l} \quad a = 1$ for $r_k = s_l$, $a = 2$ for $r_k \neq s_l$

	1	2	3	4	5	6
O 1(S)	-38.7241	.0000	.0000	.0000	-8.9947	-8.9947
(X)	.0000	-9.9313	.0000	.0000	-8.4284	-8.4284
(Y)	.0000	.0000	-24.8000	.0000	.0000	.0000
(Z)	.0000	.0000	.0000	-20.1249	-3.2351	-3.2351
H 2(S)	-8.9947	-8.4284	.0000	-3.2351	-6.5863	2.2959
H 3(S)	-8.9947	-8.4284	.0000	-3.2351	2.2959	-6.5863

REDUCED ENERGY MATRIX, ATOM BY ATOM $E_{kl} = \Sigma_{r,s}\, E_{r_k s_l}$

	1	2	3
1	-93.5803	-20.6582	-20.6582
2	-20.6582	-6.5863	2.2959
3	-20.6582	2.2959	-6.5863

ENERGY PARTITIONING

	1	2	3	4	5	6
O 1(S)	-44.6343	.0000	.0000	.0000	-4.6144	-4.6144
(X)	.0000	-14.0084	.0000	.0000	-4.1540	-4.1540
(Y)	.0000	.0000	-24.8000	.0000	.0000	.0000
(Z)	.0000	.0000	.0000	-21.6898	-1.5944	-1.5944
H 2(S)	-4.6144	-4.1540	.0000	-1.5944	-10.4606	1.0062
H 3(S)	-4.6144	-4.1540	.0000	-1.5944	1.0062	-10.4606

REDUCED ENERGY PARTITIONING, ATOM BY ATOM

	1	2	3
1	-105.1326	-10.3628	-10.3628
2	-10.3628	-10.4606	1.0062
3	-10.3628	1.0062	-10.4606

REPULSION ENERGY BETWEEN ATOM PAIRS

	1	2	3
1	.0000	1.8068	1.8068
2	1.8068	.0000	.0252

```
 3    1.8068  .0252  .0000
```

ICONC INPUT FILE H2OIT.GEN

```
   2   0   8   0
   2   0   8   0
Water molecule with charge iteration
  0  3 0 2 0 1FFFFFFFFF 2.00 .000 .000FFFFFFFFFFFFFFFFFFFFFFFF
        .350000
  1   2   -.96000  52.51000    .00000
  1   3   -.96000 -52.51000    .00000
 * * *
 O 6 22.5750-28.20 22.2750-12.40
 H 1 11.3000-13.60
 H 1 11.3000-13.60
    .10000   .10000   .00000   .10000   .00500   .50000 100   20    1    F
 3.4653860 22.8876600 32.3353300
 3.4641460 18.5667800 15.7957100
13.6185300 27.1775600 13.6011800
13.6185300 27.1775600 13.6011800
```

ICONC OUTPUT FILE H2O.OUT

Water with charge iteration d(O-H)=0.96, angle=105.2º
```
K IS CALCULATED WITH THE DISTANCE-DEPENDENT WEIGHTED FORMULA.
delta =     .3500,   1+kappa =    2.0000
```

INPUT

ATOM	X	Y	Z	S		P	
				N EXP	COUL	N EXP	COUL
O 1	.00000	.00000	.00000	2 2.5750	-28.2000	2 2.2750	-12.4000
H 2	-.76172	.00000	.58428	1 1.3000	-13.6000		
H 3	.76172	.00000	.58428	1 1.3000	-13.6000		

VSIE PARAMETERS $VSIE = A \cdot Q^2 + B \cdot Q + C$

ATOM	A	B	C	
O	3.46539	22.88766	32.33533	$2sVSIE(2s^2 2p^2) = 3.46Q^2(2s) + 22.88Q(2s) + 32.33$
	3.46415	18.56678	15.79571	$2pVSIE(2s^2 2p^2) = 3.46Q^2(2p) + 18.56Q(2p) + 15.79$
H	13.61853	27.17756	13.60118	$1sVSIE(1s^1) = 13.61Q^2(1s) + 27.17Q(1s) + 13.61$
H	13.61853	27.17756	13.60118	

DISTANCE MATRIX

	1	2	3
1	.0000	.9600	.9600
2	.9600	.0000	1.5234
3	.9600	1.5234	.0000

OVERLAP MATRIX

	1	2	3	4	5	6
O 1(S)	1.0000	.0000	.0000	.0000	.4096	.4096
(X)	.0000	1.0000	.0000	.0000	-.3112	.3112
(Y)	.0000	.0000	1.0000	.0000	.0000	.0000
(Z)	.0000	.0000	.0000	1.0000	.2387	.2387
H 2(S)	.4096	-.3112	.0000	.2387	1.0000	.2230
H 3(S)	.4096	.3112	.0000	.2387	.2230	1.0000

ICON-EDiT, Summer 2000   Gion Calzaferri

```
CYCLE NO. 1          ENERGY = -145.77337592    DENOM =    .48788938D+01
CYCLE NO. 2          ENERGY = -135.26170385    DENOM =    .98200931D+00
CYCLE NO. 14         ENERGY = -152.10166287    DENOM =    .47934261D-02
CONVERGENCE REACHED-FINAL CYCLE FOLLOWS
                     ENERGY = -152.11093359    DENOM =    .42521034D-02
```

$DENOM_k = MAX_r \left| Q_r^{output_k} - Q_r^{input_k} \right|$ stopping criterion: $DENOM_k < 0.005$

```
ATOM            NET CHG.-DAMPED        SUMMED ORBITAL OCCUPATIONS-DAMPED
                                           S        P
O 1               -.18429              1.52429   4.66000
H 2                .09215               .90785
H 3                .09215               .90785
```

ATOM   **CORRECTED H(I,I)'S**

```
                    S         X         Y         Z
O 1             -28.23506 -12.49169 -12.49169 -12.49169
H 2             -16.22109
H 3             -16.22109
```

ENERGY LEVELS (eV)

```
  E( 1) =       8.88134                .0000
  E( 2) =       3.38379                .0000
  E( 3) =     -12.49169               2.0000
  E( 4) =     -13.93605               2.0000
  E( 5) =     -17.85845               2.0000
  E( 6) =     -31.77184               2.0000
```

```
SUM OF ONE-ELECTRON ENERGIES =   -152.11606688 eV
ORBITAL STABILIZATION ENERGY =    -13.23702031 eV
CORE-CORE REPULSION ENERGY   =      3.63881174 eV
STABILIZATION + REPULSION    =     -9.59820857 eV
```

WAVE FUNCTIONS: MO'S IN COLUMNS, AO'S IN ROWS

```
                    1       2       3       4       5       6
O 1(S)           -.8812   .0000   .0000  -.3204   .0000   .7448
   (X)            .0000  1.0008   .0000   .0000   .5748   .0000
   (Y)            .0000   .0000  1.0000   .0000   .0000   .0000
   (Z)           -.6210   .0000   .0000   .8725   .0000  -.0199
H 2(S)            .7436   .8004   .0000   .1811  -.4654   .2466
H 3(S)            .7436  -.8004   .0000   .1811   .4654   .2466
```

REDUCED OVERLAP POPULATION MATRIX, ATOM BY ATOM

```
        1       2       3
1    5.4990   .6850   .6850
2     .6850   .6203  -.1097
3     .6850  -.1097   .6203
```

REDUCED CHARGE MATRIX, MO'S IN COLUMNS, ATOMS IN ROWS, NORMALIZED TO TWO
ELECTRONS REGARDLESS OF OCCUPATION

```
        1       2       3       4       5       6
1     .8099  1.0061  2.0000  1.7837   .9939  1.4064
2     .5950   .4970   .0000   .1081   .5030   .2968
3     .5950   .4970   .0000   .1081   .5030   .2968
```

ATOM   NET CHG.   ATOMIC ORBITAL OCCUPATION FOR GIVEN MO OCCUPATION

```
                           S         X         Y         Z
O 1      -.18397        1.52050   .99391   2.00000   1.66957
H 2       .09199         .90801
```

```
H 3       .09199             .90801
```

REDUCED ENERGY MATRIX, ATOM BY ATOM
```
          1        2        3
   1   -89.3889 -22.8846 -22.8846
   2   -22.8846 -10.0627   3.1674

   3   -22.8846   3.1674 -10.0627
```

Formaldehyde
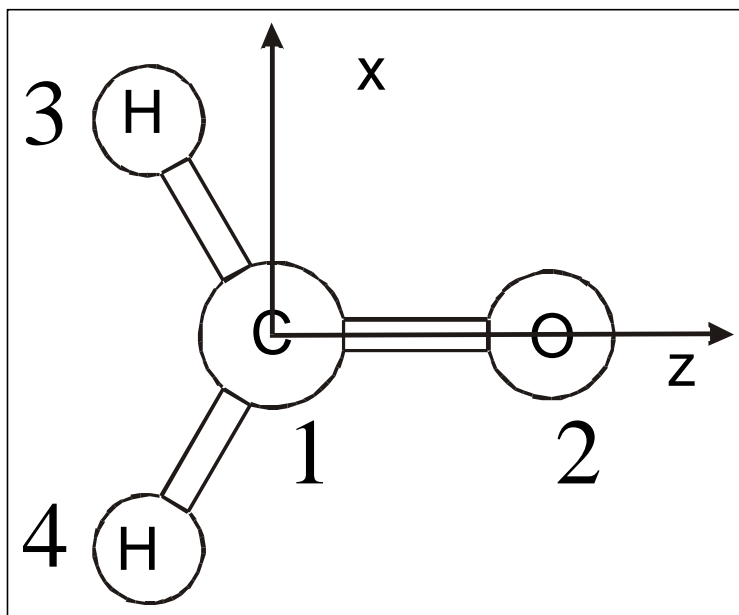
INPUT File Formal.gen
```
   3    5    3    0
   3    0    3    0
Formaldehyde standard geometry
  0   4 0 0 0 1FFFFFFFFF 2.00 .000 .000FFFFFFFFFFFFFFFFFFFFFFFFFFF
        .350000
  2    1   1.22000 180.00000     .00000
  2    3   1.08000  60.00000     .00000
  2    4   1.08000 300.00000     .00000
 * * * H
 O 6  22.5750 -28.20 2 2.2750 -12.40
 C 4  21.7100 -21.40 2 1.6250 -11.40
 H 1  11.3000 -13.60
  1    1  1    .010000
  1    2  1    .010000
  1 *  3  1    .010000
  1    2  2   1.000000
  1 *  3  2  -1.000000
```

This file can e.g. be used as an example for GOP.

OUTPUT File Formal.out

```
K IS CALCULATED WITH THE DISTANCE-DEPENDENT WEIGHTED FORMULA.
 delta =     .3500,   1+kappa =    2.0000


 ATOM      X             Y             Z        S                      P
                                            N  EXP     COUL   N  EXP     COUL
O 1     .00000        .00000       1.22000  2 2.5750 -28.2000 2 2.2750 -12.4000
C 2     .00000        .00000        .00000  2 1.7100 -21.4000 2 1.6250 -11.4000
H 3     .93531        .00000       -.54000  1 1.3000 -13.6000
H 4    -.93531        .00000       -.54000  1 1.3000 -13.6000


DISTANCE MATRIX
            1      2      3      4
    1     .0000 1.2200 1.9931 1.9931
    2    1.2200  .0000 1.0800 1.0800
    3    1.9931 1.0800  .0000 1.8706
    4    1.9931 1.0800 1.8706  .0000



OVERLAP MATRIX
              1       2       3       4       5       6       7       8       9      10
  O 1(S)  1.0000   .0000   .0000   .0000   .3128   .0000   .0000   .4300   .0557   .0557
     (X)   .0000  1.0000   .0000   .0000   .0000   .2146   .0000   .0000   .0364  -.0364
     (Y)   .0000   .0000  1.0000   .0000   .0000   .0000   .2146   .0000   .0000   .0000
     (Z)   .0000   .0000   .0000  1.0000  -.3125   .0000   .0000  -.3056  -.0685  -.0685
  C 2(S)   .3128   .0000   .0000  -.3125  1.0000   .0000   .0000   .0000   .4837   .4837
     (X)   .0000   .2146   .0000   .0000   .0000  1.0000   .0000   .0000   .4286  -.4286
     (Y)   .0000   .0000   .2146   .0000   .0000   .0000  1.0000   .0000   .0000   .0000
     (Z)   .4300   .0000   .0000  -.3056   .0000   .0000   .0000  1.0000  -.2474  -.2474
  H 3(S)   .0557   .0364   .0000  -.0685   .4837   .4286   .0000  -.2474  1.0000   .1276
  H 4(S)   .0557  -.0364   .0000  -.0685   .4837  -.4286   .0000  -.2474   .1276  1.0000


ENERGY LEVELS (eV)
  E( 1) =     32.49318                 .0000
  E( 2) =     17.80604                 .0000
  E( 3) =     14.69510                 .0000
  E( 4) =     -8.70760                 .0000     LUMO
  E( 5) =    -12.09823                2.0000     HOMO
  E( 6) =    -13.63979                2.0000
  E( 7) =    -13.98184                2.0000
  E( 8) =    -17.16724                2.0000
  E( 9) =    -23.09710                2.0000
  E( 10)=    -31.83152                2.0000


SUM OF ONE-ELECTRON ENERGIES    =    -223.63145705 eV
ORBITAL STABILIZATION ENERGY    =     -24.83145705 eV
CORE-CORE REPULSION ENERGY      =       5.72376737 eV
STABILIZATION + REPULSION       =     -19.10768967 eV



WAVE FUNCTIONS     MO'S IN COLUMNS, AO'S IN ROWS
             1        2        3        4        5        6        7        8        9       10
                                      LUMO     HOMO
  O 1(S)  -.5637    .6964    .0000    .0000    .0000   -.2379    .0000    .0000   -.3922    .7215
     (X)   .0000    .0000    .2896    .0000   -.9736    .0000    .0000   -.1738    .0000    .0000
     (Y)   .0000    .0000    .0000    .7315    .0000    .0000    .7164    .0000    .0000    .0000
     (Z)   .5739   -.5417    .0000    .0000    .0000   -.8454    .0000    .0000   -.1470    .0110
  C 2(S)  1.3521    .1494    .0000    .0000    .0000    .0703    .0000    .0000    .4808    .3778
     (X)   .0000    .0000  -1.2484    .0000    .0579    .0000    .0000   -.5165    .0000    .0000
```

ICON-EDiT, Summer 2000   Gion Calzaferri

```
  (Y) |  .0000 |   .0000 |   .0000 | -.8567 |  .0000 |  .0000 |  .5607 |  .0000 |  .0000 |  .0000 |
  (Z) |  .1709 | -1.2486 |   .0000 |  .0000 |  .0000 |  .2606 |  .0000 |  .0000 | -.2843 |  .1547 |
H 3(S)| -.7096 |  -.5638 |   .8879 |  .0000 |  .2172 | -.1588 |  .0000 | -.4090 |  .2854 |  .0575 |
H 4(S)| -.7096 |  -.5638 |  -.8879 |  .0000 | -.2172 | -.1588 |  .0000 |  .4090 |  .2854 |  .0575 |
```

REDUCED OVERLAP POPULATION MATRIX, ATOM BY ATOM

	1	2	3	4
1	5.9173	1.1086	-.0532	-.0532
2	1.1086	2.2721	.7821	.7821
3	-.0532	.7821	.6489	-.0533
4	-.0532	.7821	-.0533	.6489

REDUCED CHARGE MATRIX, MO'S IN COLUMNS, ATOMS IN ROWS, NORMALIZED TO TWO
ELECTRONS REGARDLESS OF OCCUPATION

	1	2	3	4	5	6	7	8	9	10
1	.3905	.3399	.0500	.8012	1.8407	1.6223	1.1988	.1093	.3340	1.3132
2	.8739	1.2572	1.0617	1.1988	.0041	.2730	.8012	.9343	.9663	.6295
3	.3678	.2014	.4442	.0000	.0776	.0524	.0000	.4782	.3498	.0286
4	.3678	.2014	.4442	.0000	.0776	.0524	.0000	.4782	.3498	.0286

ATOM	NET CHG.	ATOMIC ORBITAL OCCUPATION FOR GIVEN MO OCCUPATION			
		S	X	Y	Z
O 1	-.41834	1.63535	1.95001	1.19876	1.63423
C 2	.39158	1.16439	.93833	.80124	.70445
H 3	.13380	.98662			
H 4	.13380	.98662			

Oscillator Strength Calculation
Input File Formal.edi

TITLE Electronic Transitions in Formal
!Lines containing an exclamation mark are lines with comments and are not taken into account
!
! The files
KEYWRD OUTFILE=formal.edo
KEYWRD SPECFILE=formal.eds
!
! Output
KEYWRD OSCILLOUT
KEYWRD DIPLENOUT
!KEYWRD MATOUT
!
!KEYWRD FITONLY
!
! Method
KEYWRD MATRICE=ALL
!KEYWRD CUTOFF=10.0
!
! Polarization
KEYWRD POL = XYZ
KEYWRD CORRECT, TOLERANCE=0.0001
!
! Verbose output to log file
KEYWRD VERBOSE
!
[WAVERANGE]
! Change these numbers to something more reasonable :-)
START 4, 4
END 5, 7
!
[FIT_SPEC]
E_RANGE 20000.0, 40000.0
H_WIDTH 750.0

```
POINTS 20000
SPECS X, Y, Z, XYZ*
!
![DOT]
!E_RANGE 20000.0, 40000.0
!DELTA_E 10.0
! No changes should be necessary below here.
!------------------------------------------------------------------------
[ATOMS]
```

OUTPUT File Formal.edo

```
FORMALDEHYDE
Explanation of the keywords
```

* OUTFILE	- formal.edo will contain the chosen output data.
* SPECFILE	- formal.eds will contain the spectrum.
* OSCILLOUT	- The oscillator strengths will be printed out.
* DIPLENOUT	- The transition dipole lengths will be printed out.
* MATOUT	- The matrix elements will be printed out.
* FITONLY	- A spectrum will be fitted without a new oscillator strength calculation (to use this option the oscillator strength calculation has to be performed at least once before).
* MATRICE=ALL	- ALL transition elements are taken into account.
* CUTOFF=10.0	- Cutoff length for off block diagonal elements is 10.0 A.
* POL XYZ	- X, Y, and Z transitions will be considered.
* CORRECT	- We correct for degeneracies (TOL = .00001).
* VERBOSE	- Print verbose output to log file.
* WAVERANGE	- EDiT calculation will be performed in this waverange. The numbers correspond to the numbers of the energy levels in the ICONC-output file.
* E_RANGE	- The spectrum will be fitted within this energy range.
* H_ WIDTH	- The peaks of the single transitions will be fitted with this halfwidth.
* POINTS	- Amount of points the fitted spectrum contains.
* SPECS	- The spectrum contains these polarizations.
* [DOT]	- Density of transitions (DOT) will be printed out to the file FILENAME.EDD .

```
|_|_|(1)        |_|_|(1)   | deltaE/cm-1    f(x)        f(y)        f(z )       f(xyz)
  | (    5) <---   | (    4) |  27347.1    .000000     .000000     .000000     .000000
               corrected |          ( .000000) ( .000000) ( .000000) ( .000000)
                         |          D(x)        D(y)        D(z)        D(xyz)
               Angstroms |          .000000     .000000     .000000     .000000
               corrected |          ( .000000) ( .000000) ( .000000) ( .000000)
=================================================================================

|_|_|(1)        |_|_|(1)   | deltaE/cm-1    f(x)        f(y)        f(z)        f(xyz)
  | (    6) <---   | (    4) |  39780.5    .000000     .002607     .000000     .002607
               corrected |          ( .000000) ( .002607) ( .000000) ( .002607)
                         |          D(x)        D(y)        D(z)        D(xyz)
               Angstroms |          .000000    -.054954     .000000     .054954
               corrected |          ( .000000) (-.054954) ( .000000) ( .054954)
=================================================================================

|_|_|(1)        |_|_|(1)   | deltaE/cm-1    f(x)        f(y)        f(z)        f(xyz)
  | (    7) <---   | (    4) |  42539.3    .000000     .000000     .339823     .339823
               corrected |          ( .000000) ( .000000) ( .339823) ( .339823)
                         |          D(x)        D(y)        D(z)        D(xyz)
               Angstroms |          .000000     .000000     .606714     .606714
               corrected |          ( .000000) ( .000000) ( .606714) ( .606714)
=================================================================================
```

ICON-EDiT, Summer 2000   Gion Calzaferri

6.3 Resorufin

ResH   Res⁻

Gion Calzaferri
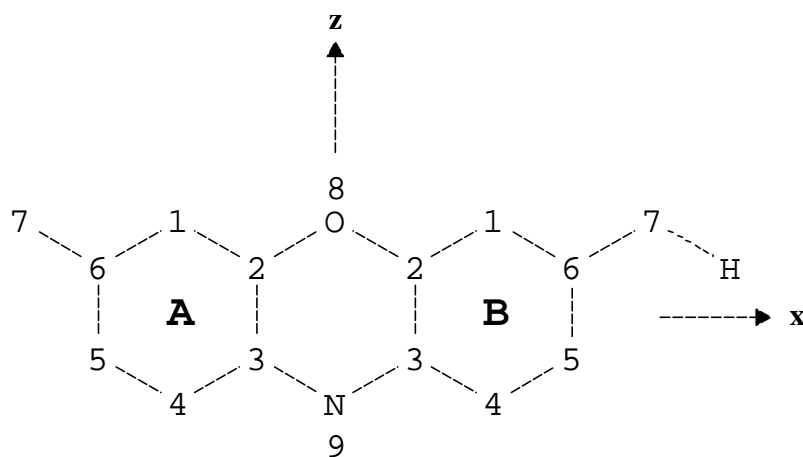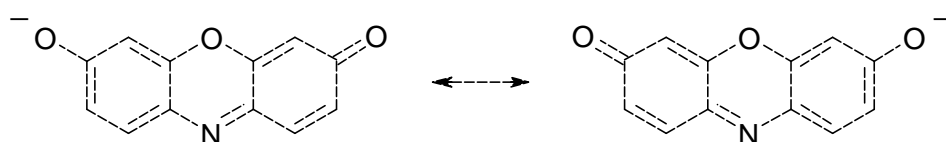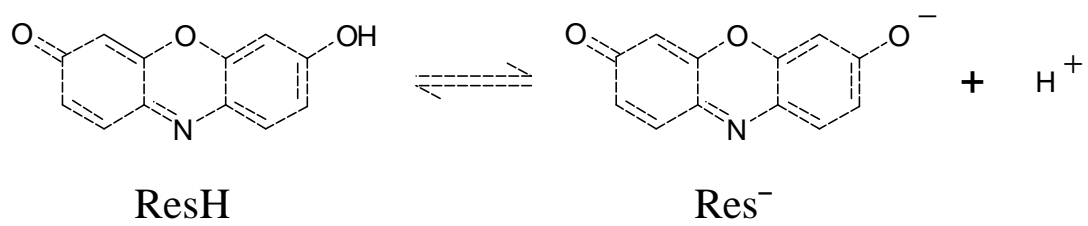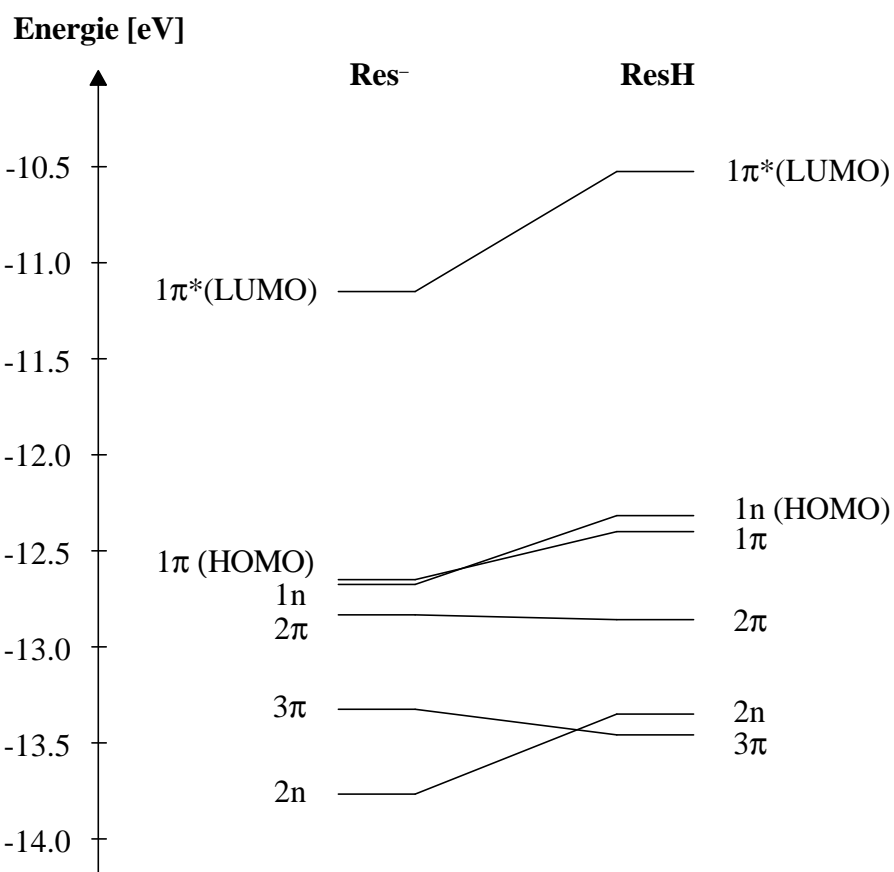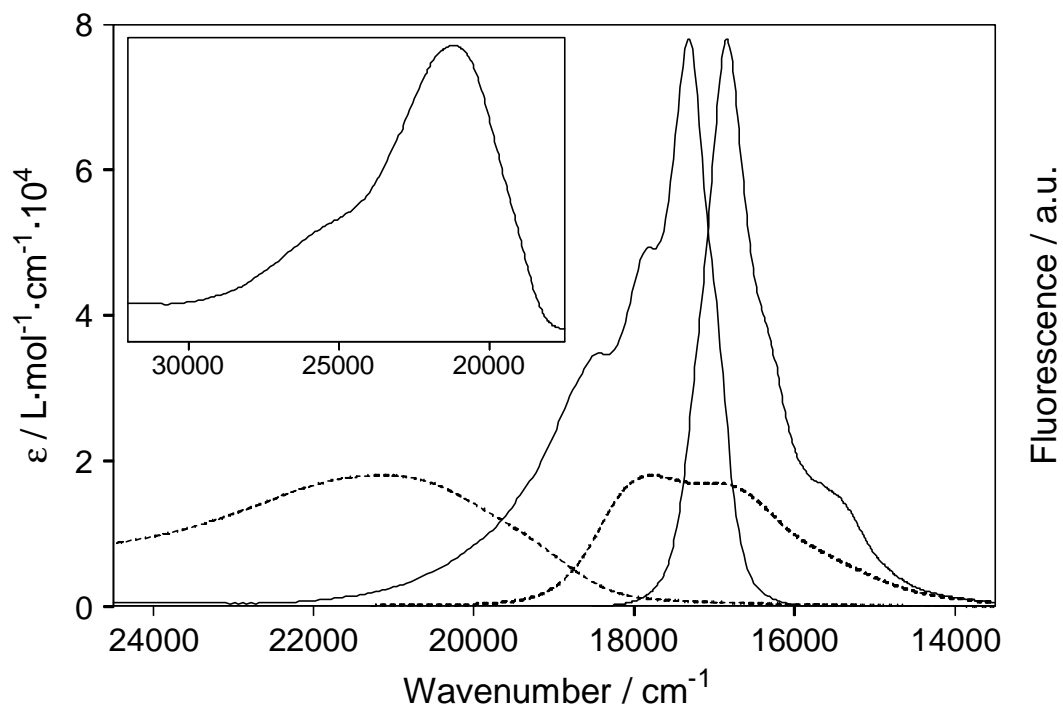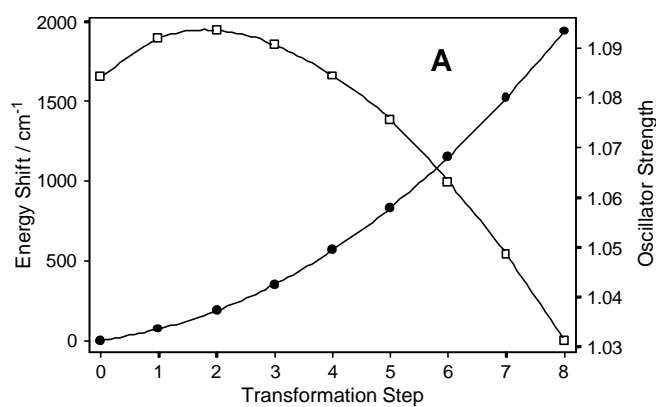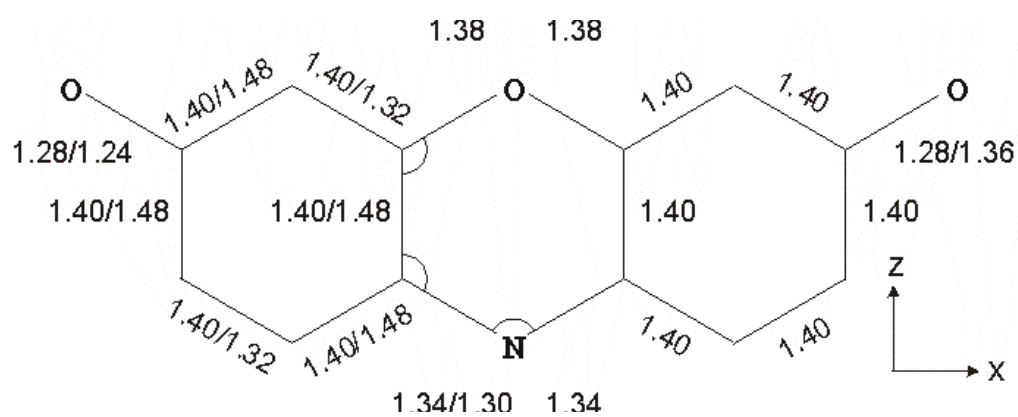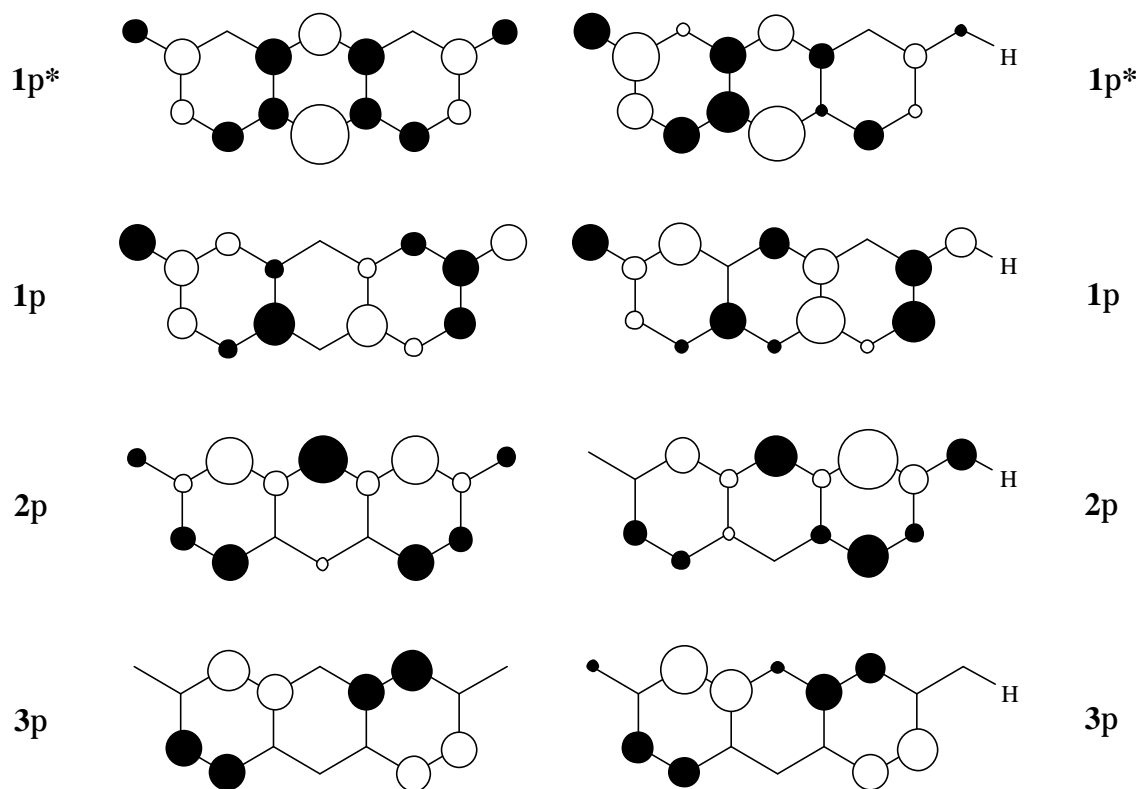
Input file for EHMO calculation (res0.gen):

```
 22   0   4   0
 22   1   4   0
Resorufin Anion (J. Phys. Chem. B 102 1998 2923)
  0 22 -1  0  0 1FFFFFFFFF 2.00  .000  .000FFFFFFFFFFFFFFFFFFFFFFFFF
         .350000
 23   1  1.50000 180.00000    .00000
  1   2  1.38000 301.50000    .00000
  2   3  1.40000 240.00000    .00000
  3   4  1.34000 236.79258    .00000
  4   5  1.34000 243.41484    .00000
  5   6  1.40000 236.79258    .00000
  2   7  1.40000 120.00000    .00000
  7   8  1.40000 240.00000    .00000
  8   9  1.40000 240.00000    .00000
  9  10  1.40000 240.00000    .00000
  6  11  1.40000 120.00000    .00000
 11  12  1.40000 120.00000    .00000
 12  13  1.40000 120.00000    .00000
 13  14  1.40000 120.00000    .00000
  7  15  1.08300 120.00000    .00000
  8  16  1.28000 120.00000    .00000
  9  17  1.08300 120.00000    .00000
 10  18  1.08300 120.00000    .00000
 11  19  1.08300 240.00000    .00000
 12  20  1.28000 240.00000    .00000
 13  21  1.08300 240.00000    .00000
 14  22  1.08300 240.00000    .00000
  * * C * C C C C C C C C C * O H H H O H H
  O  6  22.5750-32.30  22.2750-14.80
  C  4  21.7100-21.40  21.6250-11.40
  N  5  22.1400-26.00  21.9500-14.00
  H  1  11.3000-13.60
```

Input file for oscillator strength calculation (res0.edi):

```
TITLE Electronic Transitions in Res0
KEYWRD OUTFILE=res0.edo
KEYWRD SPECFILE=res0.eds
KEYWRD OSCILLOUT
KEYWRD DIPLENOUT
KEYWRD MATRICE=ALL
KEYWRD POL = XYZ
KEYWRD CORRECT, TOLERANCE=0.0001
KEYWRD VERBOSE
[WAVERANGE]
START 31, 31
END 32, 41
[FIT_SPEC]
E_RANGE 20000.0, 40000.0
H_WIDTH 750.0
POINTS 20000
SPECS X, Y, Z, XYZ*
```

Output file of EHMO calculation (res0.out):

```
          EXTENDED HUCKEL CALCULATION.

          K IS CALCULATED WITH THE DISTANCE-DEPENDENT WEIGHTED FORMULA.
          delta =    .3500,  1+kappa =   2.0000

     ATOM       X         Y         Z          S                    P
                                          N  EXP     COUL     N  EXP     COUL
     O   1    .00000    .00000   1.50000  2  2.5750 -32.3000  2  2.2750 -14.8000
     C   2  -1.17664    .00000    .77895  2  1.7100 -21.4000  2  1.6250 -11.4000
     C   3  -1.14000    .00000   -.62057  2  1.7100 -21.4000  2  1.6250 -11.4000
     N   4    .00000    .00000  -1.32485  2  2.1400 -26.0000  2  1.9500 -14.0000
     C   5   1.14000    .00000   -.62057  2  1.7100 -21.4000  2  1.6250 -11.4000
     C   6   1.17664    .00000    .77895  2  1.7100 -21.4000  2  1.6250 -11.4000
     C   7  -2.40699    .00000   1.44697  2  1.7100 -21.4000  2  1.6250 -11.4000
     C   8  -3.60068    .00000    .71548  2  1.7100 -21.4000  2  1.6250 -11.4000
     C   9  -3.56404    .00000   -.68404  2  1.7100 -21.4000  2  1.6250 -11.4000
     C  10  -2.33369    .00000  -1.35207  2  1.7100 -21.4000  2  1.6250 -11.4000
     C  11   2.40699    .00000   1.44697  2  1.7100 -21.4000  2  1.6250 -11.4000
     C  12   3.60068    .00000    .71547  2  1.7100 -21.4000  2  1.6250 -11.4000
     C  13   3.56404    .00000   -.68405  2  1.7100 -21.4000  2  1.6250 -11.4000
     C  14   2.33369    .00000  -1.35207  2  1.7100 -21.4000  2  1.6250 -11.4000
     H  15  -2.43534    .00000   2.52960  1  1.3000 -13.6000
     O  16  -4.72557    .00000   1.32624  2  2.5750 -32.3000  2  2.2750 -14.8000
     H  17  -4.48745    .00000  -1.24991  1  1.3000 -13.6000
     H  18  -2.30534    .00000  -2.43470  1  1.3000 -13.6000
     H  19   2.43534    .00000   2.52960  1  1.3000 -13.6000
     O  20   4.72557    .00000   1.32624  2  2.5750 -32.3000  2  2.2750 -14.8000
     H  21   4.48744    .00000  -1.24991  1  1.3000 -13.6000
     H  22   2.30534    .00000  -2.43470  1  1.3000 -13.6000

          CHARGE = -1       IPRINT =  0        IPUNCH =  1



   DISTANCE MATRIX

           1      2      3      4      5      6      7      8      9     10     11     12     13     14
     1   .0000 1.3800 2.4076 2.8248 2.4076 1.3800 2.4076 3.6852 4.1800 3.6852 2.4076 3.6852 4.1800 3.6852
     2  1.3800  .0000 1.4000 2.4105 2.7066 2.3533 1.4000 2.4249 2.8000 2.4249 3.6454 4.7777 4.9613 4.1065
     3  2.4076 1.4000  .0000 1.3400 2.2800 2.7066 2.4249 2.8000 2.4249 1.4000 4.1056 4.9253 4.7045 3.5499
     4  2.8248 2.4105 1.3400  .0000 1.3400 2.4105 3.6710 4.1386 3.6212 3.3339 3.6710 4.1386 3.6212 2.3338
     5  2.4076 2.7066 2.2800 1.3400  .0000 1.4000 4.1056 4.9253 4.7045 3.5499 2.4249 2.8000 2.4249 1.4000
     6  1.3800 2.3533 2.7066 2.4105 1.4000  .0000 3.6454 4.7777 4.9613 4.1065 1.4000 2.4249 2.8000 2.4249
     7  2.4076 1.4000 2.4249 3.6710 4.1056 3.6454  .0000 1.4000 2.4249 2.8000 4.8140 6.0520 6.3399 5.5053
     8  3.6852 2.4249 2.8000 4.1386 4.9253 4.7777 1.4000  .0000 1.4000 2.4249 6.0520 7.2014 7.3001 6.2842
     9  4.1800 2.8000 2.4249 3.6212 4.7045 4.9613 2.4249 1.4000  .0000 1.4000 6.3399 7.3001 7.1281 5.9354
    10  3.6852 2.4249 1.4000 2.3339 3.5499 4.1065 2.8000 2.4249 1.4000  .0000 5.5053 6.2842 5.9354 4.6674
    11  2.4076 3.6454 4.1056 3.6710 2.4249 1.4000 4.8140 6.0520 6.3399 5.5053  .0000 1.4000 2.4249 2.8000
    12  3.6852 4.7777 4.9253 4.1386 2.8000 2.4249 6.0520 7.2014 7.3001 6.2842 1.4000  .0000 1.4000 2.4249
    13  4.1800 4.9613 4.7045 3.6212 2.4249 2.8000 6.3399 7.3001 7.1281 5.9354 2.4249 1.4000  .0000 1.4000
    14  3.6852 4.1065 3.5499 2.3338 1.4000 2.4249 5.5053 6.2842 5.9354 4.6674 2.8000 2.4249 1.4000  .0000
    15  2.6440 2.1562 3.4061 4.5593 4.7651 4.0139 1.0830 2.1562 3.4061 3.8830 4.9619 6.3027 6.8059 6.1491
    16  4.7288 3.5909 4.0800 5.4184 6.1802 5.9275 2.3217 1.2800 2.3217 3.5909 7.1336 8.3486 8.5299 7.5503
    17  5.2630 3.8830 3.4061 4.4881 5.6625 6.0165 3.4061 2.1562 1.0830 2.1562 7.4031 8.3235 8.0713 6.8219
    18  4.5603 3.4061 2.1562 2.5586 3.8938 4.7383 3.8830 3.4061 2.1562 1.0830 6.1052 6.6936 6.1249 4.7637
    19  2.6440 4.0139 4.7651 4.5593 3.4061 2.1562 4.9619 6.3027 6.8059 6.1491 1.0830 2.1562 3.4061 3.8830
    20  4.7288 5.9275 6.1802 5.4184 4.0800 3.5909 7.1336 8.3486 8.5299 7.5503 2.3217 1.2800 2.3217 3.5909
    21  5.2630 6.0165 5.6625 4.4881 3.4061 3.8830 7.4031 8.3235 8.0713 6.8219 3.4061 2.1562 1.0830 2.1562
    22  4.5603 4.7383 3.8938 2.5586 2.1562 3.4061 6.1052 6.6936 6.1249 4.7637 3.8830 3.4061 2.1562 1.0830


          15     16     17     18     19     20     21     22
     1  2.6440 4.7288 5.2630 4.5603 2.6440 4.7288 5.2630 4.5603
     2  2.1562 3.5909 3.8830 3.4061 4.0139 5.9275 6.0165 4.7383
     3  3.4061 4.0800 3.4061 2.1562 4.7651 6.1802 5.6625 3.8938
     4  4.5593 5.4184 4.4881 2.5586 4.5593 5.4184 4.4881 2.5586
     5  4.7651 6.1802 5.6625 3.8938 3.4061 4.0800 3.4061 2.1562
     6  4.0139 5.9275 6.0165 4.7383 2.1562 3.5909 3.8830 3.4061
     7  1.0830 2.3217 3.4061 3.8830 4.9619 7.1336 7.4031 6.1052
     8  2.1562 1.2800 2.1562 3.4061 6.3027 8.3486 8.3235 6.6936
     9  3.4061 2.3217 1.0830 2.1562 6.8059 8.5299 8.0713 6.1249
    10  3.8830 3.5909 2.1562 1.0830 6.1491 7.5503 6.8219 4.7637
    11  4.9619 7.1336 7.4031 6.1052 1.0830 2.3217 3.4061 3.8830
    12  6.3027 8.3486 8.3235 6.6936 2.1562 1.2800 2.1562 3.4061
    13  6.8059 8.5299 8.0713 6.1249 3.4061 2.3217 1.0830 2.1562
    14  6.1491 7.5503 6.8219 4.7637 3.8830 3.5909 2.1562 1.0830
    15   .0000 2.5871 4.3007 4.9660 4.8707 7.2613 7.8873 6.8643
    16  2.5871  .0000 2.5871 4.4724 7.2613 9.4511 9.5664 7.9736
    17  4.3007 2.5871  .0000 2.4830 7.8873 9.5664 8.9749 6.8953
    18  4.9660 4.4724 2.4830  .0000 6.8643 7.9736 6.8953 4.6107
    19  4.8707 7.2613 7.8873 6.8643  .0000 2.5871 4.3007 4.9660
    20  7.2613 9.4511 9.5664 7.9736 2.5871  .0000 2.5871 4.4724
    21  7.8873 9.5664 8.9749 6.8953 4.3007 2.5871  .0000 2.4830
    22  6.8643 7.9736 6.8953 4.6107 4.9660 4.4724 2.4830  .0000




   RESULTS OF CALCULATION  Resorufin Anion
   ENERGY LEVELS (eV)
     E(  1) =   72.33803            .0000
     E(  2) =   71.98376            .0000
     E(  3) =   54.02704            .0000
     E(  4) =   52.43711            .0000
     E(  5) =   51.57781            .0000
     E(  6) =   50.03684            .0000
     E(  7) =   42.96307            .0000
     E(  8) =   40.55782            .0000
```

```
E(  9) =    39.40524                .0000
E( 10) =    39.35308                .0000
E( 11) =    29.33400                .0000
E( 12) =    23.14687                .0000
E( 13) =    22.44062                .0000
E( 14) =    22.35013                .0000
E( 15) =    21.54801                .0000
E( 16) =    17.44674                .0000
E( 17) =    16.92218                .0000
E( 18) =    15.12765                .0000
E( 19) =    12.50141                .0000
E( 20) =    10.68637                .0000
E( 21) =     8.62891                .0000
E( 22) =     7.14009                .0000
E( 23) =     6.21150                .0000
E( 24) =     1.35930                .0000
E( 25) =     -.98337                .0000
E( 26) =    -1.98380                .0000
E( 27) =    -5.41205                .0000
E( 28) =    -6.65542                .0000
E( 29) =    -7.08706                .0000
E( 30) =    -7.38091                .0000
E( 31) =   -10.96429                .0000
E( 32) =   -12.47194               2.0000
E( 33) =   -12.62357               2.0000
E( 34) =   -12.74578               2.0000
E( 35) =   -13.29711               2.0000
E( 36) =   -13.53886               2.0000
E( 37) =   -13.63185               2.0000
E( 38) =   -13.80177               2.0000
E( 39) =   -14.29553               2.0000
E( 40) =   -14.69362               2.0000
E( 41) =   -14.79409               2.0000
E( 42) =   -15.12414               2.0000
E( 43) =   -15.29695               2.0000
E( 44) =   -15.56349               2.0000
E( 45) =   -15.71705               2.0000
E( 46) =   -15.77366               2.0000
E( 47) =   -15.87651               2.0000
E( 48) =   -15.88454               2.0000
E( 49) =   -15.99019               2.0000
E( 50) =   -16.11764               2.0000
E( 51) =   -16.42967               2.0000
E( 52) =   -16.48311               2.0000
E( 53) =   -16.67962               2.0000
E( 54) =   -17.12910               2.0000
E( 55) =   -17.14701               2.0000
E( 56) =   -18.55356               2.0000
E( 57) =   -19.61019               2.0000
E( 58) =   -20.87992               2.0000
E( 59) =   -21.54090               2.0000
E( 60) =   -21.79976               2.0000
E( 61) =   -24.44548               2.0000
E( 62) =   -26.47127               2.0000
E( 63) =   -26.98930               2.0000
E( 64) =   -27.54581               2.0000
E( 65) =   -28.59602               2.0000
E( 66) =   -30.00026               2.0000
E( 67) =   -31.86777               2.0000
E( 68) =   -35.05459               2.0000
E( 69) =   -35.09651               2.0000
E( 70) =   -35.47212               2.0000


SUM OF ONE-ELECTRON ENERGIES =  -1530.06049126 eV
ORBITAL STABILIZATION ENERGY =   -195.86049126 eV
CORE-CORE REPULSION ENERGY   =     34.49260316 eV
BE CAREFUL TO INTERPRET REPULSION OF CHARGED MOLECULES
STABILIZATION + REPULSION    =   -161.36788809 eV



REDUCED OVERLAP POPULATION MATRIX, ATOM BY ATOM

          1       2       3       4       5       6       7       8       9      10      11      12      13      14
   1   5.8886   .6673  -.0455  -.0009  -.0455   .6673  -.0502   .0007   .0000   .0008  -.0502   .0007   .0000   .0008
   2    .6673  2.3358  1.0129  -.0727  -.0409  -.0964  1.0944  -.0574  -.0324  -.0805   .0013   .0000   .0000  -.0001
   3   -.0455  1.0129  2.3992   .9431  -.1199  -.0409  -.0838  -.0296  -.0771  1.0045   .0000   .0000   .0000   .0014
   4   -.0009  -.0727   .9431  4.8882   .9431  -.0727   .0009   .0000   .0011  -.0789   .0009   .0000   .0011  -.0789
   5   -.0455  -.0409  -.1199   .9431  2.3992  1.0129   .0000   .0000   .0000   .0014  -.0838  -.0296  -.0771  1.0045
   6    .6673  -.0964  -.0409  -.0727  1.0129  2.3358   .0013   .0000   .0000  -.0001  1.0944  -.0574  -.0324  -.0805
   7   -.0502  1.0944  -.0838   .0009   .0000   .0013  2.8744  1.0472  -.0901  -.0374   .0000   .0000   .0000   .0000
   8    .0007  -.0574  -.0296   .0000   .0000   .0000  1.0472  2.1357  1.0074  -.0670   .0000   .0000   .0000   .0000
   9    .0000  -.0324  -.0771   .0011   .0000   .0000  -.0901  1.0074  2.7693  1.1163   .0000   .0000   .0000   .0000
  10    .0008  -.0805  1.0045  -.0789   .0014  -.0001  -.0374  -.0670  1.1163  2.6889   .0000   .0000   .0000  -.0001
  11   -.0502   .0013   .0000   .0009  -.0838  1.0944   .0000   .0000   .0000   .0000  2.8744  1.0472  -.0901  -.0374
  12    .0007   .0000   .0000   .0000  -.0296  -.0574   .0000   .0000   .0000   .0000  1.0472  2.1357  1.0074  -.0670
  13    .0000   .0000   .0000   .0011  -.0771  -.0324   .0000   .0000   .0000   .0000  -.0901  1.0074  2.7693  1.1163
  14    .0008  -.0001   .0014  -.0789  1.0045  -.0805   .0000   .0000   .0000  -.0001  -.0374  -.0670  1.1163  2.6889
  15   -.0030  -.0570   .0017   .0000   .0000   .0000   .7928  -.0546   .0019   .0001   .0000   .0000   .0000   .0000
  16    .0000   .0005   .0001   .0000   .0000   .0000  -.0726   .7677  -.0702   .0007   .0000   .0000   .0000   .0000
  17    .0000   .0001   .0024   .0000   .0000   .0000   .0018  -.0560   .7972  -.0584   .0000   .0000   .0000   .0000
  18    .0000   .0016  -.0562  -.0083   .0000   .0000  -.0001   .0022  -.0601   .7994   .0000   .0000   .0000   .0000
  19   -.0030   .0000   .0000   .0000   .0017  -.0570   .0000   .0000   .0000   .0000   .7928  -.0546   .0019   .0001
  20    .0000   .0000   .0000   .0000   .0001   .0005   .0000   .0000   .0000   .0000  -.0726   .7677  -.0702   .0007
  21    .0000   .0000   .0000   .0000   .0024   .0001   .0000   .0000   .0000   .0000   .0018  -.0560   .7972  -.0584
  22    .0000   .0000   .0000  -.0083  -.0562   .0016   .0000   .0000   .0000   .0000  -.0001   .0022  -.0601   .7994

         15      16      17      18      19      20      21      22
```

```
 1    -.0030    .0000    .0000    .0000   -.0030    .0000    .0000    .0000
 2    -.0570    .0005    .0016    .0000    .0000    .0000    .0000    .0000
 3     .0017    .0001    .0024   -.0562    .0000    .0000    .0000    .0000
 4     .0000    .0000    .0000   -.0083    .0000    .0000    .0000   -.0083
 5     .0000    .0000    .0000    .0000    .0017    .0001    .0024   -.0562
 6     .0000    .0000    .0000    .0000   -.0570    .0005    .0001    .0016
 7     .7928   -.0726    .0018   -.0001    .0000    .0000    .0000    .0000
 8    -.0546    .7677   -.0560    .0022    .0000    .0000    .0000    .0000
 9     .0019   -.0702    .7972   -.0601    .0000    .0000    .0000    .0000
10     .0001    .0007   -.0584    .7994    .0000    .0000    .0000    .0000
11     .0000    .0000    .0000    .0000    .7928   -.0726    .0018   -.0001
12     .0000    .0000    .0000    .0000   -.0546    .7677   -.0560    .0022
13     .0000    .0000    .0000    .0000    .0019   -.0702    .7972   -.0601
14     .0000    .0000    .0000    .0000    .0001    .0007   -.0584    .7994
15     .6379   -.0037   -.0001    .0000    .0000    .0000    .0000    .0000
16    -.0037   6.8766   -.0036    .0000    .0000    .0000    .0000    .0000
17    -.0001   -.0036    .6425   -.0084    .0000    .0000    .0000    .0000
18     .0000    .0000   -.0084    .6467    .0000    .0000    .0000    .0000
19     .0000    .0000    .0000    .0000    .6379   -.0037   -.0001    .0000
20     .0000    .0000    .0000    .0000   -.0037   6.8766   -.0036    .0000
21     .0000    .0000    .0000    .0000   -.0001   -.0036    .6425   -.0084
22     .0000    .0000    .0000    .0000    .0000    .0000   -.0084    .6467
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REDUCED CHARGE MATRIX, MO'S IN COLUMNS, ATOMS IN ROWS, NORMALIZED TO TWO ELECTRONS REGARDLESS OF OCCUPATION

```
         1       2       3       4       5       6       7       8       9      10      11      12      13      14
 1    -.0011   .0007   .0072   .0067   .0040   .0049   .0017   .0104   .0167   .0290   .0460   .0233  -.0001   .0056
 2     .1652   .1504   .1285   .1364   .1609   .1548   .0837   .1625   .1145   .0993   .1302   .1250   .0737   .0189
 3     .1637   .1690   .1532   .3019   .0724   .1665   .1800   .2542   .0619   .2623   .3062   .0914   .0793   .0447
 4    -.0004   .0093   .0509   .2063   .0153   .0387   .1777   .0017   .0832   .0483   .2016   .0622   .0023   .0102
 5     .1639   .1688   .1532   .3019   .0724   .1665   .1800   .2542   .0621   .2621   .3062   .0914   .0792   .0447
 6     .1654   .1502   .1285   .1364   .1609   .1548   .0837   .1625   .1145   .0993   .1302   .1250   .0737   .0189
 7     .1648   .1531   .2371   .1044   .1539   .0471   .0912   .1199   .1832   .1752   .0828   .1884   .0871   .0901
 8     .1621   .1595   .1208   .1313   .1185   .1873   .1911   .1525   .1526   .1557   .0241   .1882   .3053   .4151
 9     .1659   .1706   .0653   .0468   .2236   .2395   .2118   .0654   .1850   .0338   .0737   .1638   .1690   .1261
10     .1697   .1831   .1932   .1324   .1734   .1215   .0601   .0849   .1517   .1087   .1313   .0804   .0673   .0100
11     .1650   .1530   .2371   .1044   .1539   .0471   .0912   .1199   .1835   .1748   .0828   .1884   .0871   .0901
12     .1622   .1593   .1208   .1313   .1185   .1873   .1911   .1525   .1528   .1554   .0241   .1882   .3051   .4151
13     .1660   .1704   .0653   .0468   .2236   .2395   .2118   .0654   .1849   .0338   .0737   .1638   .1689   .1261
14     .1699   .1829   .1932   .1324   .1733   .1215   .0601   .0849   .1519   .1086   .1313   .0805   .0673   .0100
15     .0026   .0025   .0355   .0193   .0241   .0018   .0141   .0631   .0059   .0322   .0397   .0326   .0418   .0634
16     .0002   .0002   .0035   .0063   .0012   .0093   .0401   .0019   .0575   .0113   .0130   .0256   .0825   .1328
17     .0029   .0029   .0035   .0048   .0432   .0504   .0039   .0270   .0167   .0354   .0472   .0580   .0734   .0816
18     .0032   .0043   .0305   .0101   .0192   .0000   .0344   .0625   .0206   .0480   .0278   .0036   .0196   .0092
19     .0026   .0025   .0355   .0193   .0241   .0018   .0141   .0631   .0059   .0322   .0397   .0326   .0418   .0634
20     .0002   .0002   .0035   .0063   .0012   .0093   .0401   .0019   .0576   .0112   .0130   .0256   .0824   .1328
21     .0029   .0029   .0035   .0048   .0432   .0504   .0039   .0270   .0167   .0353   .0472   .0580   .0734   .0816
22     .0032   .0043   .0305   .0101   .0192   .0000   .0344   .0625   .0206   .0480   .0278   .0036   .0196   .0092
```

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        15      16      17      18      19      20      21      22      23      24      25      26      27      28
 1     .0062   .0684   .0000   .0071   .1813   .1261   .0501   .0360   .1249   .4956   .0365   .0000   .0127   .0000
 2     .1638   .1457   .0058   .0451   .2370   .1506   .1388   .0837   .2395   .4389   .1984   .1579   .0413   .1122
 3     .1458   .0035   .0843   .2600   .0209   .0792   .0598   .1220   .0739   .0697   .2657   .1521   .2318   .3323
 4     .0084  -.0001   .0459   .3079   .0302   .0050   .0397   .1647   .0123   .0802   .1067   .0000   .1647   .0000
 5     .1458   .0035   .0843   .2600   .0209   .0792   .0598   .1220   .0739   .0697   .2657   .1521   .2318   .3323
 6     .1638   .1457   .0058   .0451   .2370   .1506   .1388   .0837   .2395   .4389   .1984   .1579   .0413   .1122
 7     .1828   .2013   .1697   .1040   .0198   .0242   .0931   .1279   .1272   .0323   .1189   .1662   .0771   .0388
 8     .1701   .0060   .0531   .1561   .0483   .0548   .1854   .1263   .0936   .0452   .1155   .2101   .3738   .3308
 9     .1604   .0943   .0635   .0125   .1213   .2259   .1398   .0996   .0842   .0207   .0943   .1565   .1395   .0560
10     .1607   .2109   .2976   .0287   .1086   .0979   .1423   .1138   .0863   .0629   .1273   .1403   .0037   .0828
11     .1828   .2013   .1697   .1040   .0198   .0242   .0931   .1279   .1272   .0323   .1189   .1662   .0771   .0388
12     .1701   .0060   .0531   .1561   .0483   .0548   .1854   .1263   .0936   .0452   .1155   .2101   .3738   .3308
13     .1603   .0943   .0635   .0125   .1213   .2259   .1398   .0996   .0842   .0207   .0943   .1565   .1395   .0560
14     .1607   .2109   .2976   .0287   .1086   .0979   .1423   .1138   .0863   .0629   .1273   .1403   .0037   .0828
15     .0019   .1369   .0945   .1027   .0299   .0041   .0399   .1131   .1070   .0143   .0000   .0000   .0000   .0000
16     .0054   .0012   .0079   .0654   .0310   .0176   .0668   .0402   .0061   .0041   .0085   .0168   .0441   .0473
17     .0018   .0397   .0297   .0285   .1372   .1951   .0528   .0009   .0594   .0240   .0000   .0000   .0000   .0000
18     .0001   .1265   .1710   .0396   .1401   .0850   .0364   .0722   .0542   .0000   .0000   .0000   .0000   .0000
19     .0019   .1368   .0945   .1027   .0299   .0041   .0399   .1131   .1070   .0143   .0000   .0000   .0000   .0000
20     .0054   .0012   .0079   .0654   .0310   .0176   .0668   .0402   .0061   .0041   .0085   .0168   .0441   .0473
21     .0018   .0397   .0297   .0285   .1372   .1952   .0528   .0009   .0594   .0240   .0000   .0000   .0000   .0000
22     .0001   .1265   .1710   .0396   .1401   .0850   .0364   .0722   .0542   .0000   .0000   .0000   .0000   .0000
```

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        29      30      31      32      33      34      35      36      37      38      39      40      41      42
 1     .0893   .0000   .1525   .0000   .3342   .2791   .0000   .0697   .0017   .0376   .0945   .0000   .0041   .0033
 2     .2389   .2452   .1472   .0448   .1660   .0898   .2450   .0108   .0069   .0039   .0149   .1741   .2328   .0206
 3     .0214   .0021   .1133   .2656   .1321   .0000   .0000   .0053   .0008  -.0003   .1892   .2352   .1860   .0045
 4     .0170   .0000   .4372   .0000   .8228   .0058   .0000   .0020   .0081   .2140   .2889   .0000   .0028   .0392
 5     .0214   .0021   .1133   .2656   .1321   .0000   .0000   .0053   .0008  -.0003   .1892   .2352   .1860   .0045
 6     .2389   .2452   .1472   .0448   .1660   .0898   .2450   .0108   .0069   .0039   .0149   .1741   .2328   .0206
 7     .2162   .2456   .0001   .1193   .0378   .4416   .2895   .1423   .1199   .0568   .0311   .0691   .1381   .0551
 8     .0011   .0002   .1498   .1838   .0014   .0349   .0006   .1209   .1124   .0486   .0103  -.0001   .0339   .0944
 9     .1945   .2380   .0927   .1690   .0025   .0868   .2256   .1258   .1478   .3209   .1598   .0823   .0247   .1145
10     .2746   .2689   .1357   .0312   .0445   .1607   .2380   .0124   .0181   .2136   .2660   .2160   .0906   .1185
11     .2162   .2456   .0001   .1193   .0378   .4416   .2895   .1423   .1199   .0568   .0311   .0691   .1381   .0551
12     .0011   .0002   .1498   .1838   .0014   .0349   .0006   .1209   .1124   .0486   .0103  -.0001   .0339   .0944
13     .1945   .2380   .0927   .1690   .0025   .0868   .2256   .1258   .1478   .3209   .1598   .0823   .0247   .1145
14     .2746   .2689   .1357   .0312   .0445   .1607   .2380   .0124   .0181   .2136   .2660   .2160   .0906   .1185
15     .0000   .0000   .0000   .0000   .0191   .0000   .0000   .0158   .0165   .0000   .0014   .0000   .0485  -.0001
16     .0002   .0000   .0662   .1863   .0019   .0436   .0013   .4933   .5424   .2307   .0922   .2234   .1711   .5248
17     .0000   .0000   .0000   .0000   .0041   .0000   .0000   .0223   .0160   .0000   .0433   .0000   .0144   .0128
18     .0000   .0000   .0000   .0000   .0118   .0000   .0000   .0155   .0144   .0000   .0002   .0000   .0564   .0335
19     .0000   .0000   .0000   .0000   .0191   .0000   .0000   .0158   .0165   .0000   .0014   .0000   .0485  -.0001
20     .0002   .0000   .0662   .1863   .0019   .0436   .0013   .4932   .5425   .2307   .0922   .2234   .1711   .5248
21     .0000   .0000   .0000   .0000   .0041   .0000   .0000   .0223   .0160   .0000   .0433   .0000   .0144   .0128
22     .0000   .0000   .0000   .0000   .0118   .0000   .0000   .0155   .0144   .0000   .0002   .0000   .0564   .0335
```

	43	44	45	46	47	48	49	50	51	52	53	54	55	56
1	.9836	.9799	.0087	.2470	.1547	.0218	.0000	.0296	.1950	.3906	.1734	.0447	.4018	.1021
2	.0246	.0883	.0593	.0262	.0753	.0036	.0208	.0075	.0946	.1887	.1420	.0725	.1619	.0266
3	.0760	.0985	.0940	.0610	.0052	.0351	.0126	.0410	.0364	.2346	.0689	.0796	.1529	.0521
4	.6789	.5003	.1602	.0348	.0004	.1246	.0000	.0210	.0023	.4296	.1619	.0572	.2315	.1613
5	.0760	.0985	.0940	.0610	.0052	.0351	.0126	.0410	.0364	.2346	.0689	.0796	.1529	.0521
6	.0246	.0883	.0593	.0262	.0753	.0036	.0208	.0075	.0946	.1887	.1420	.0725	.1619	.0266
7	.0011	.0134	.1325	.0652	.0855	.0324	.0716	.0744	.0791	.0435	.1396	.2167	.0150	.1544
8	.0014	.0018	.1035	.0870	.1538	.2425	.2747	.1341	.0438	.0320	.0580	.0035	.0177	.0522
9	.0067	.0109	.0061	.1582	.0887	.0423	.0726	.1688	.1879	.0180	.0839	.0047	.0608	.1375
10	.0306	.0383	.0019	.0692	.0591	.0000	.0228	.1617	.1723	.0460	.0925	.2494	.1310	.0342
11	.0011	.0134	.1325	.0652	.0855	.0324	.0716	.0744	.0791	.0435	.1396	.2167	.0150	.1544
12	.0014	.0018	.1035	.0870	.1538	.2425	.2747	.1341	.0438	.0320	.0580	.0035	.0177	.0522
13	.0067	.0109	.0061	.1582	.0887	.0423	.0726	.1688	.1879	.0180	.0839	.0047	.0608	.1375
14	.0306	.0383	.0019	.0692	.0591	.0000	.0228	.1617	.1723	.0460	.0925	.2493	.1310	.0342
15	.0002	.0000	.0778	.0545	.0010	.0000	.0000	.0263	.0443	.0000	.0319	.1432	.0029	.1564
16	.0129	.0086	.4403	.1943	.4218	.5708	.5250	.3264	.0404	.0272	.1154	.0094	.0685	.0619
17	.0059	.0000	.0001	.1371	.0051	.0000	.0000	.0188	.1068	.0000	.0429	.0006	.0124	.1405
18	.0092	.0000	.0000	.0063	.0271	.0000	.0000	.0156	.0959	.0000	.0573	.1695	.0602	.0525
19	.0002	.0000	.0778	.0545	.0010	.0000	.0000	.0263	.0443	.0000	.0319	.1432	.0029	.1564
20	.0129	.0086	.4403	.1943	.4218	.5708	.5250	.3264	.0404	.0272	.1154	.0094	.0685	.0619
21	.0059	.0000	.0001	.1371	.0051	.0000	.0000	.0188	.1068	.0000	.0429	.0006	.0124	.1405
22	.0092	.0000	.0000	.0063	.0271	.0000	.0000	.0156	.0959	.0000	.0573	.1695	.0602	.0525

	57	58	59	60	61	62	63	64	65	66	67	68	69	70
1	.0042	.1149	.0679	.0847	.0484	.0085	.0671	.0251	.0139	.0084	.0846	.1294	.0000	1.2441
2	.0518	.1240	.1646	.1258	.1312	.0830	.1430	.1933	.0204	.1630	.0314	.0197	.0014	.2522
3	.0432	.1280	.1651	.0989	.2171	.2316	.0217	.0321	.0445	.1974	.3864	.0006	.0003	.0222
4	.0249	.2097	.0696	-.0007	.2671	.0710	.0032	.0005	.1978	.0182	.8522	.0005	.0000	.0112
5	.0432	.1280	.1651	.0989	.2171	.2316	.0217	.0321	.0445	.1974	.3864	.0006	.0003	.0222
6	.0518	.1240	.1646	.1258	.1312	.0830	.1430	.1933	.0204	.1630	.0314	.0197	.0014	.2522
7	.1708	.1115	.1042	.1376	.0306	.0889	.3596	.2721	.1090	.1207	.0014	.0069	.0170	.0212
8	.1457	.1217	.0615	.0847	.1236	.2060	.0741	.0396	.1591	.0690	.0017	.2185	.2412	.0223
9	.1959	.1043	.0908	.1257	.1165	.1743	.1032	.1640	.2926	.1429	.0156	.0144	.0170	.0022
10	.0619	.1165	.1347	.1477	.1301	.0709	.1519	.1946	.1519	.2181	.0883	.0004	.0015	.0020
11	.1708	.1115	.1042	.1376	.0306	.0889	.3596	.2721	.1090	.1207	.0014	.0069	.0170	.0212
12	.1457	.1217	.0615	.0847	.1236	.2060	.0741	.0396	.1591	.0690	.0017	.2185	.2412	.0223
13	.1959	.1043	.0908	.1257	.1165	.1743	.1032	.1640	.2926	.1429	.0156	.0144	.0170	.0022
14	.0619	.1165	.1347	.1477	.1301	.0709	.1519	.1946	.1519	.2181	.0883	.0004	.0015	.0020
15	.0646	.0084	.0649	.0732	.0000	.0121	.0587	.0392	.0098	.0072	-.0001	.0000	-.0001	-.0006
16	.1154	.0636	.0031	.0036	.0328	.0584	.0105	.0016	.0651	.0460	.0045	.6746	.7220	.0510
17	.1362	.0174	.0437	.0669	.0270	.0298	.0162	.0229	.0287	.0083	.0002	.0000	-.0001	-.0001
18	.0000	.0423	.0986	.0939	.0334	.0053	.0260	.0277	.0129	.0140	.0023	.0000	.0000	-.0002
19	.0646	.0084	.0649	.0732	.0000	.0121	.0587	.0392	.0098	.0072	-.0001	.0000	-.0001	-.0006
20	.1154	.0636	.0031	.0036	.0328	.0584	.0105	.0016	.0651	.0460	.0045	.6747	.7219	.0510
21	.1362	.0174	.0437	.0669	.0270	.0298	.0162	.0229	.0287	.0083	.0002	.0000	-.0001	-.0001
22	.0000	.0423	.0986	.0939	.0334	.0053	.0260	.0277	.0129	.0140	.0023	.0000	.0000	-.0002

ATOM	NET CHG.	ATOMIC ORBITAL OCCUPATION FOR GIVEN MO OCCUPATION			
		S	X	Y	Z
O 1	-.45831	1.63727	1.27209	1.70894	1.84001
C 2	.49395	1.12394	.68511	.85898	.83801
C 3	.34435	1.11301	.79754	.88133	.86375
N 4	-.67287	1.44599	1.14795	1.27435	1.80458
C 5	.34435	1.11301	.79754	.88134	.86375
C 6	.49395	1.12394	.68511	.85898	.83801
C 7	-.17653	1.16743	.94692	1.13711	.92507
C 8	.58403	1.08870	.67221	.81884	.83622
C 9	-.06636	1.17004	.92565	1.02852	.94216
C 10	.01082	1.17167	.92870	.96668	.92213
C 11	-.17653	1.16743	.94692	1.13711	.92507
C 12	.58403	1.08870	.67221	.81884	.83622
C 13	-.06636	1.17004	.92565	1.02852	.94216
C 14	.01082	1.17167	.92870	.96668	.92213
H 15	.02313	.97687			
O 16	-1.18604	1.71247	1.74791	1.81688	1.90878
H 17	.01997	.98003			
H 18	.01828	.98172			
H 19	.02313	.97687			
O 20	-1.18604	1.71247	1.74791	1.81688	1.90878
H 21	.01997	.98003			
H 22	.01828	.98172			

Output file of oscillator strength calculation (res0.edo):

```
|_|_|(1)            |_|_|(1)   | deltaE/cm-1      f(x)         f(y)         f(z)        f(xyz)
 | ( 32) <---        | ( 31) |   12159.9       1.084278     .000000      .000000     1.084278
                     corrected |              (1.084278) ( .000000) ( .000000) (1.084278)
                               |               D(x)         D(y)         D(z)         D(xyz)
                     Angstroms |              ********     .000000     -.000001     2.027016
                     corrected |              (********) ( .000000) (-.000001) (2.027016)
==========================================================================================

|_|_|(1)            |_|_|(1)   | deltaE/cm-1      f(x)         f(y)         f(z)        f(xyz)
 | ( 33) <---        | ( 31) |   13382.9        .000000      .000088      .000000      .000088
                     corrected |              ( .000000) ( .000088) ( .000000) ( .000088)
```

ICON-EDiT, Summer 2000   Gion Calzaferri

```
                              |                D(x)       D(y)       D(z)       D(xyz)
                   Angstroms  |               .000000    .017399    .000000    .017399
                   corrected  |             ( .000000) ( .017399) ( .000000) ( .017399)
================================================================================================

|_|_|(1)           |_|_|(1)  | deltaE/cm-1     f(x)       f(y)       f(z)       f(xyz)
  |  ( 34) <---      |  ( 31) |  14368.6       .000000    .000000    .024571    .024571
                   corrected  |             ( .000000) ( .000000) ( .024571) ( .024571)
                              |                D(x)       D(y)       D(z)       D(xyz)
                   Angstroms  |              -.000009    .000000    .280710    .280710
                   corrected  |             (-.000009) ( .000000) ( .280710) ( .280710)
================================================================================================

|_|_|(1)           |_|_|(1)  | deltaE/cm-1     f(x)       f(y)       f(z)       f(xyz)
  |  ( 35) <---      |  ( 31) |  18815.3       .022124    .000000    .000000    .022124
                   corrected  |             ( .022124) ( .000000) ( .000000) ( .022124)
                              |                D(x)       D(y)       D(z)       D(xyz)
                   Angstroms  |              -.232769    .000000   -.000001    .232769
                   corrected  |             (-.232769) ( .000000) (-.000001) ( .232769)
================================================================================================

|_|_|(1)           |_|_|(1)  | deltaE/cm-1     f(x)       f(y)       f(z)       f(xyz)
  |  ( 36) <---      |  ( 31) |  20765.1       .000000    .000000    .000000    .000000
                   corrected  |             ( .000000) ( .000000) ( .000000) ( .000000)
                              |                D(x)       D(y)       D(z)       D(xyz)
                   Angstroms  |               .000000    .000000    .000000    .000000
                   corrected  |             ( .000000) ( .000000) ( .000000) ( .000000)
================================================================================================

|_|_|(1)           |_|_|(1)  | deltaE/cm-1     f(x)       f(y)       f(z)       f(xyz)
  |  ( 37) <---      |  ( 31) |  21515.1       .000000    .000007    .000000    .000007
                   corrected  |             ( .000000) ( .000007) ( .000000) ( .000007)
                              |                D(x)       D(y)       D(z)       D(xyz)
                   Angstroms  |               .000000    .003873    .000000    .003873
                   corrected  |             ( .000000) ( .003873) ( .000000) ( .003873)
================================================================================================

|_|_|(1)           |_|_|(1)  | deltaE/cm-1     f(x)       f(y)       f(z)       f(xyz)
  |  ( 38) <---      |  ( 31) |  22885.7       .000000    .000000    .108208    .108208
                   corrected  |             ( .000000) ( .000000) ( .108208) ( .108208)
                              |                D(x)       D(y)       D(z)       D(xyz)
                   Angstroms  |               .000004    .000000   -.466769    .466769
                   corrected  |             ( .000004) ( .000000) (-.466769) ( .466769)
================================================================================================

|_|_|(1)           |_|_|(1)  | deltaE/cm-1     f(x)       f(y)       f(z)       f(xyz)
  |  ( 39) <---      |  ( 31) |  26868.1       .000000    .000000    .000000    .000000
                   corrected  |             ( .000000) ( .000000) ( .000000) ( .000000)
                              |                D(x)       D(y)       D(z)       D(xyz)
                   Angstroms  |               .000000    .000000    .000000    .000000
                   corrected  |             ( .000000) ( .000000) ( .000000) ( .000000)
================================================================================================

|_|_|(1)           |_|_|(1)  | deltaE/cm-1     f(x)       f(y)       f(z)       f(xyz)
  |  ( 40) <---      |  ( 31) |  30078.9       .011978    .000000    .000000    .011978
                   corrected  |             ( .011978) ( .000000) ( .000000) ( .011978)
                              |                D(x)       D(y)       D(z)       D(xyz)
                   Angstroms  |               .135464    .000000    .000001    .135464
                   corrected  |             ( .135464) ( .000000) ( .000001) ( .135464)
================================================================================================

|_|_|(1)           |_|_|(1)  | deltaE/cm-1     f(x)       f(y)       f(z)       f(xyz)
  |  ( 41) <---      |  ( 31) |  30889.2       .000000    .000000    .000000    .000000
                   corrected  |             ( .000000) ( .000000) ( .000000) ( .000000)
                              |                D(x)       D(y)       D(z)       D(xyz)
                   Angstroms  |               .000000    .000000    .000000    .000000
                   corrected  |             ( .000000) ( .000000) ( .000000) ( .000000)
================================================================================================
```

6.4 FMO Example: Propene H₂C=CH–CH₃, Hyperconjugation

```
     8    0    2    3
     8    0    2    0
Propene, approximately experimental geometry
 0  9 0 0 0 1FFFFFTFFF 2.00 0.000 0.000FFFFFFFFFFFFFFFFFFFFFFFFF
        0.350000
   1    2    1.33600 180.00000    0.00000
   2    3    1.50100 124.30000    0.00000
   1    4    1.09000  60.00000    0.00000
   1    5    1.09000 -60.00000    0.00000
   2    6    1.09000-120.00000    0.00000
   3    7    1.09000 111.20000    0.00000
   3    8    1.09000 109.50000 120.00000
   3    9    1.09000 109.50000-120.00000
 * C  C  * H H H H H
 C 4 21.7100-21.40 21.6250-11.40
 H 1 11.3000-13.60
112111222                 (FRAGMENT-Definition)
  0 0 0 0 0 0 0 0 0       (Charge of the FRAGMENTS)
FFFFFFF                   (Output options)
```
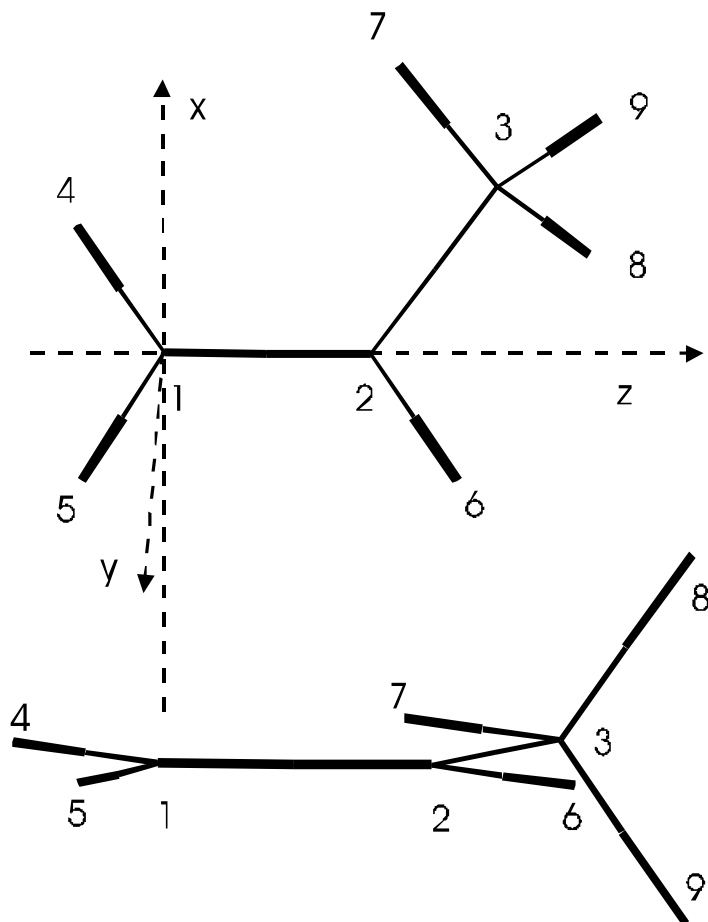
EXTENDED HUCKEL FMO CALCULATION, complete molecule

K IS CALCULATED WITH THE DISTANCE-DEPENDENT WEIGHTED FORMULA.
delta =   .3500,   1+kappa =   2.0000

ATOM	X	Y	Z	S		P	
				N EXP	COUL	N EXP	COUL
C 1	.00000	.00000	.00000	2 1.7100	-21.4000	2 1.6250	-11.4000
C 2	.00000	.00000	1.33600	2 1.7100	-21.4000	2 1.6250	-11.4000
C 3	1.23997	.00000	2.18185	2 1.7100	-21.4000	2 1.6250	-11.4000
H 4	.94397	.00000	-.54500	1 1.3000	-13.6000		
H 5	-.94397	.00000	-.54500	1 1.3000	-13.6000		
H 6	-.94397	.00000	1.88100	1 1.3000	-13.6000		
H 7	2.13827	.00000	1.56447	1 1.3000	-13.6000		
H 8	1.25104	.88982	2.81129	1 1.3000	-13.6000		
H 9	1.25104	-.88982	2.81129	1 1.3000	-13.6000		

DISTANCE MATRIX

	1	2	3	4	5	6	7	8	9
1	.0000	1.3360	2.5096	1.0900	1.0900	2.1046	2.6495	3.2032	3.2032
2	1.3360	.0000	1.5010	2.1046	2.1046	1.0900	2.1504	2.1292	2.1292
3	2.5096	1.5010	.0000	2.7429	3.4936	2.2046	1.0900	1.0900	1.0900
4	1.0900	2.1046	2.7429	.0000	1.8879	3.0740	2.4241	3.4858	3.4858
5	1.0900	2.1046	3.4936	1.8879	.0000	2.4260	3.7350	4.1079	4.1079
6	2.1046	1.0900	2.2046	3.0740	2.4260	.0000	3.0984	2.5447	2.5447
7	2.6495	2.1504	1.0900	2.4241	3.7350	3.0984	.0000	1.7702	1.7702
8	3.2032	2.1292	1.0900	3.4858	4.1079	2.5447	1.7702	.0000	1.7796
9	3.2032	2.1292	1.0900	3.4858	4.1079	2.5447	1.7702	1.7796	.0000

OVERLAP MATRIX

|	1	2	3	4	5	6	7	8	9	10	11	12	13	14
C 1(S)	1.0000	.0000	.0000	.0000	.4036	.0000	.0000	-.4356	.0583	-.0443	.0000	-.0779	.4779	.4779
(X)	.0000	1.0000	.0000	.0000	.0000	.2718	.0000	.0000	.0443	-.0089	.0000	-.0654	.4256	-.4256
(Y)	.0000	.0000	1.0000	.0000	.0000	.0000	.2718	.0000	.0000	.0000	.0283	.0000	.0000	.0000
(Z)	.0000	.0000	.0000	1.0000	.4356	.0000	.0000	-.3244	.0779	-.0654	.0000	-.0868	-.2457	-.2457
C 2(S)	.4036	.0000	.0000	.4356	1.0000	.0000	.0000	.0000	.3231	-.3102	.0000	-.2116	.1027	.1027
(X)	.0000	.2718	.0000	.0000	.0000	1.0000	.0000	.0000	.3102	-.1610	.0000	-.2500	.0644	-.0644
(Y)	.0000	.0000	.2718	.0000	.0000	.0000	1.0000	.0000	.0000	.0000	.2055	.0000	.0000	.0000
(Z)	-.4356	.0000	.0000	-.3244	.0000	.0000	.0000	1.0000	.2116	-.2500	.0000	.0350	-.1283	-.1283
C 3(S)	.0583	.0443	.0000	.0779	.3231	.3102	.0000	.2116	1.0000	.0000	.0000	.0000	.0314	.0069
(X)	-.0443	-.0089	.0000	-.0654	-.3102	-.1610	.0000	-.2500	.0000	1.0000	.0000	.0000	-.0052	-.0073
(Y)	.0000	.0000	.0283	.0000	.0000	.0000	.2055	.0000	.0000	.0000	1.0000	.0000	.0000	.0000
(Z)	-.0779	-.0654	.0000	-.0868	-.2116	-.2500	.0000	.0350	.0000	.0000	.0000	1.0000	-.0483	-.0091
H 4(S)	.4779	.4256	.0000	-.2457	.1027	.0644	.0000	-.1283	.0314	-.0052	.0000	-.0483	1.0000	.1240
H 5(S)	.4779	-.4256	.0000	-.2457	.1027	-.0644	.0000	-.1283	.0069	-.0073	.0000	-.0091	.1240	1.0000
H 6(S)	.1027	-.0644	.0000	.1283	.4779	-.4256	.0000	.2457	.0860	-.1214	.0000	-.0167	.0145	.0485
H 7(S)	.0376	.0464	.0000	.0339	.0947	.1328	.0000	.0142	.4779	.4050	.0000	-.2784	.0487	.0040
H 8(S)	.0126	.0080	.0057	.0180	.0984	.0812	.0577	.0957	.4779	.0050	.4012	.2838	.0065	.0019
H 9(S)	.0126	.0080	-.0057	.0180	.0984	.0812	.0577	.0957	.4779	.0050	.4012	.2838	.0065	.0019

	15	16	17	18
C 1(S)	.1027	.0376	.0126	.0126
(X)	-.0644	.0464	.0080	.0080
(Y)	.0000	.0000	.0057	-.0057
(Z)	.1283	.0339	.0180	.0180
C 2(S)	.4779	.0947	.0984	.0984
(X)	-.4256	.1328	.0812	.0812
(Y)	.0000	.0000	.0577	-.0577
(Z)	.2457	.0142	.0957	.0957
C 3(S)	.0860	.4779	.4779	.4779
(X)	-.1214	.4050	.0050	.0050
(Y)	.0000	.0000	.4012	-.4012
(Z)	-.0167	-.2784	.2838	.2838
H 4(S)	.0145	.0487	.0065	.0065
H 5(S)	.0485	.0040	.0019	.0019
H 6(S)	1.0000	.0138	.0391	.0391
H 7(S)	.0138	1.0000	.1506	.1506
H 8(S)	.0391	.1506	1.0000	.1483
H 9(S)	.0391	.1506	.1483	1.0000

Gion Calzaferri
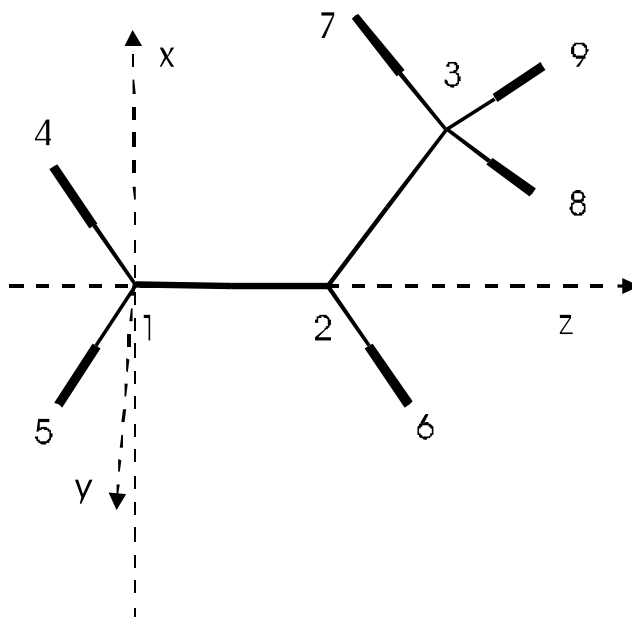
ENERGY LEVELS (eV)

```
E( 1) =      62.85095              .0000
E( 2) =      46.41573              .0000
E( 3) =      25.72215              .0000
E( 4) =      18.29330              .0000
E( 5) =      13.85685              .0000
E( 6) =      10.63028              .0000
E( 7) =       8.10562              .0000
E( 8) =       5.22319              .0000
E( 9) =      -7.00648              .0000    LUMO
E( 10) =    -13.59232             2.0000    HOMO
E( 11) =    -14.93929             2.0000
E( 12) =    -15.66521             2.0000
E( 13) =    -16.74145             2.0000
E( 14) =    -16.85475             2.0000
E( 15) =    -17.37493             2.0000
E( 16) =    -21.53021             2.0000
E( 17) =    -25.82475             2.0000
E( 18) =    -29.15800             2.0000
```

```
SUM OF ONE-ELECTRON ENERGIES =   -343.36181766 eV
ORBITAL STABILIZATION ENERGY =    -64.96181766 eV
CORE-CORE REPULSION ENERGY   =     10.75302452 eV
STABILIZATION + REPULSION    =    -54.20879314 eV
```

WAVE FUNCTIONS, MO'S IN COLUMNS, AO'S IN ROWS

```
                 1       2       3       4       5       6       7       8       9      10      11      12      13      14
                                                                              LUMO    HOMO
  C 1(S)    -1.2994   .4137  -.6318  -.2803   .2032   .0000   .0047  -.0077   .0000   .0000  -.0452  -.0472   .0087   .0000
     (X)     -.0111  -.1913  -.3439   .9284   .5323   .0000  -.0805   .5351   .0000   .0000  -.1372   .1454   .2643   .0000
     (Y)      .0000   .0000   .0000   .0000   .0000   .0687   .0000   .0000   .8061  -.6508   .0000   .0000   .0000  -.0519
     (Z)     -.7864   .0838   .4895   .5088  -.6434   .0000  -.5055   .0040   .0000   .0000  -.2738  -.3562  -.1345   .0000

  C 2(S)     1.3306   .2247  -.7118  -.1560  -.1770   .0000  -.1364   .0710   .0000   .0000   .0399  -.0527  -.0126   .0000
     (X)      .0473   .4480   .4967  -.7122  -.0578   .0000  -.1370   .7788   .0000   .0000   .3696  -.2879   .0000   .0000
     (Y)      .0000   .0000   .0000   .0000   .0000  -.2447   .0000   .0000  -.8366  -.5883   .0000   .0000   .0000  -.1553
     (Z)     -.7740   .5434  -.4592   .2245  -.6993   .0000  -.5214   .0887   .0000   .0000   .3424   .3287   .1486   .0000

  C 3(S)     -.3481 -1.4932  -.1654  -.1448  -.0386   .0000   .0259  -.0766   .0000   .0000   .0651  -.0139  -.0035   .0000
     (X)      .0837   .0521  -.4242  -.2203  -.7626   .0000   .1200   .7406   .0000   .0000  -.3827   .2161  -.2932   .0000
     (Y)      .0000   .0000   .0000   .0000   .0000  1.1761   .0000   .0000  -.0067   .1069   .0000   .0000   .0000  -.5252
     (Z)      .2276  -.0374  -.0210  -.4559   .2595   .0000  -.9842   .2328   .0000   .0000  -.3296  -.1321   .3432   .0000

  H 4(S)      .2848  -.0828   .7261  -.2023  -.8249   .0000  -.1699  -.4740   .0000   .0000  -.0493   .3027   .2969   .0000
  H 5(S)      .2789  -.2390   .3428   .9860  -.0610   .0000  -.3218   .5066   .0000   .0000   .2853  -.0145  -.1399   .0000
  H 6(S)     -.2791  -.0404   .8483  -.4327   .3840   .0000   .2905   .6047   .0000   .0000  -.1296   .4139   .0610   .0000
  H 7(S)      .1533   .6029   .2911   .0404   .6829   .0000  -.6577  -.4402   .0000   .0000  -.0690   .2801  -.4275   .0000
  H 8(S)      .0643   .6388   .1184   .3015  -.0778  -.8518   .5332  -.0663   .1626   .1483  -.1456  -.1107   .1816  -.4147
  H 9(S)      .0643   .6388   .1184   .3015  -.0778   .8518   .5332  -.0663  -.1626  -.1483  -.1456  -.1107   .1816   .4147

                15      16      17      18
  C 1(S)      .0106   .2718   .3919   .3950
     (X)     -.4048   .0083   .0052  -.0026
     (Y)      .0000   .0000   .0000   .0000
     (Z)     -.1297  -.2289   .0048   .0478

  C 2(S)     -.0586  -.3975   .0454   .4723
     (X)     -.2346   .1006  -.0593   .0185
     (Y)      .0000   .0000   .0000   .0000
     (Z)      .0899  -.1226  -.1233  -.0301

  C 3(S)      .0119   .1685  -.4991   .3094
     (X)     -.0051   .1438  -.0138  -.0285
     (Y)      .0000   .0000   .0000   .0000
     (Z)      .2290   .0872  -.0048  -.0147

  H 4(S)     -.2444   .2189   .1418   .0720
  H 5(S)      .3806   .2122   .1379   .0735
  H 6(S)      .1511  -.3189   .0201   .0879
  H 7(S)     -.1114   .1342  -.1721   .0516
  H 8(S)      .1375   .1230  -.1698   .0541
  H 9(S)      .1375   .1230  -.1698   .0541
```


ICON-EDiT, Summer 2000   Gion Calzaferri
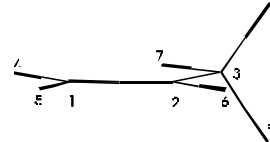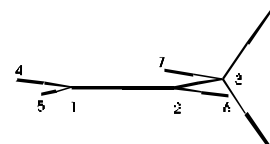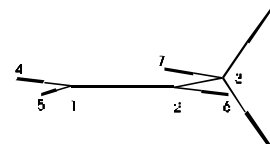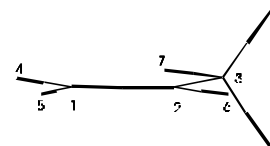
REDUCED OVERLAP POPULATION MATRIX, ATOM BY ATOM

|	1	2	3	4	5	6	7	8	9
1	2.7590	1.3055	-.0754	.7899	.7881	-.0627	-.0123	-.0009	-.0009
2	1.3055	2.6728	.7579	-.0606	-.0616	.7978	-.0456	-.0479	-.0479
3	-.0754	.7579	2.5402	-.0111	.0030	-.0527	.7944	.7850	.7850
4	.7899	-.0606	-.0111	.6304	-.0405	.0030	-.0005	.0000	.0000
5	.7881	-.0616	.0030	-.0405	.6310	-.0102	.0000	.0000	.0000
6	-.0627	.7978	-.0527	.0030	-.0102	.6489	.0022	-.0052	-.0052
7	-.0123	-.0456	.7944	-.0005	.0000	.0022	.6574	-.0394	-.0394
8	-.0009	-.0479	.7850	.0000	.0000	-.0052	-.0394	.6525	-.0366
9	-.0009	-.0479	.7850	.0000	.0000	-.0052	-.0394	-.0366	.6525

REDUCED CHARGE MATRIX, MO'S IN COLUMNS, ATOMS IN ROWS, NORMALIZED TO TWO ELECTRONS REGARDLESS OF OCCUPATION

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	.8438	.0626	.3829	.7510	.4668	.0035	.1680	.2610	.9356	1.0490	.2584	.4158	.2803	.0118
2	.8668	.3427	.4557	.2918	.2813	.0405	.2220	.5236	.8544	.6842	.5255	.0884	.1010	
2	.8668	.3427	.4557	.2918	.2813	.0405	.2220	.5236	.8544	.6842	.5255	.0884	.1010	
3	.0948	.7579	.1381	.1823	.4474	1.0449	.7976	.5033	.0003	.0185	.7085	.1678	.6725	.9363
4	.0614	.0071	.3541	.0066	.4202	.0000	.0159	.1641	.0000	.0000	.0029	.2329	.2234	.0000
5	.0593	.0352	.1068	.5777	.0043	.0000	.0635	.1828	.0000	.0000	.1818	-.0005	.0554	.0000
6	.0593	.0011	.4783	.0704	.0995	.0000	.0668	.2422	.0000	.0000	.0405	.4186	.0114	.0000
7	.0102	.2480	.0577	.0025	.2744	.0000	.2984	.1217	.0000	.0000	.0148	.1899	.4832	.0000
8	.0022	.2727	.0132	.0588	.0030	.4555	.1839	.0006	.0300	.0390	.0544	.0250	.0927	.4755
9	.0022	.2727	.0132	.0588	.0030	.4555	.1839	.0006	.0300	.0390	.0544	.0250	.0927	.4755

	15	16	17	18
1	.6728	.4183	.4387	.5796
2	.2709	.4954	.1496	.8021
3	.2086	.2065	.7446	.3702
4	.1845	.1839	.0959	.0469
5	.4282	.1593	.0993	.0469
6	.0839	.3592	.0012	.0677
7	.0438	.0724	.1543	.0285
8	.0536	.0525	.1582	.0290
9	.0536	.0525	.1582	.0290

ATOM	NET CHG.	ATOMIC ORBITAL OCCUPATION FOR GIVEN MO OCCUPATION			
		S	X	Y	Z
C 1	-.12469	1.18577	.93042	1.06083	.94767
C 2	.02843	1.17887	.91732	.95544	.91995
C 3	-.03328	1.17337	.94467	.95476	.96048
H 4	.02948	.97052			
H 5	.02961	.97039			
H 6	.01751	.98249			
H 7	.01293	.98707			
H 8	.02001	.97999			
H 9	.02001	.97999			

REDUCED ENERGY MATRIX, ATOM BY ATOM

	1	2	3	4	5	6	7	8	9
1	-39.2124	-37.5109	1.8414	-22.3421	-22.2980	1.5330	.2735	.0155	.0155
2	-37.5109	-38.2904	-21.4889	1.4824	1.4960	-22.5616	1.1022	1.1567	1.1567
3	1.8414	-21.4889	-36.5136	.2390	-.0572	1.2500	-22.1500	-21.8976	-21.8976
4	-22.3421	1.4824	.2390	-8.5739	.9295	-.0598	.0117	-.0004	-.0004
5	-22.2980	1.4960	-.0572	.9295	-8.5813	.2171	-.0007	.0009	.0009
6	1.5330	-22.5616	1.2500	-.0598	.2171	-8.8252	-.0438	.1084	.1084
7	.2735	1.1022	-22.1500	.0117	-.0007	-.0438	-8.9403	.9195	.9195
8	.0155	1.1567	-21.8976	-.0004	.0009	.1084	.9195	-8.8739	.8539
9	.0155	1.1567	-21.8976	-.0004	.0009	.1084	.9195	.8539	-8.8739
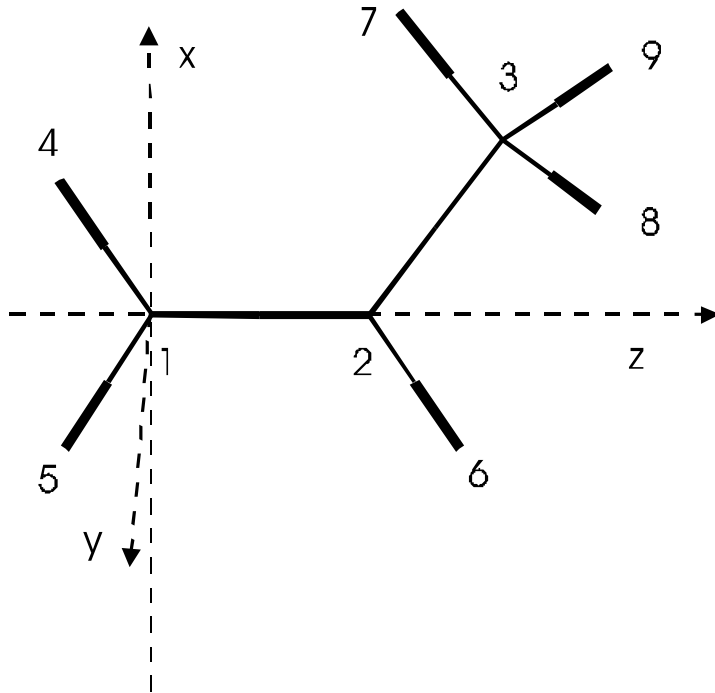
*****FRAGMENT 1*****
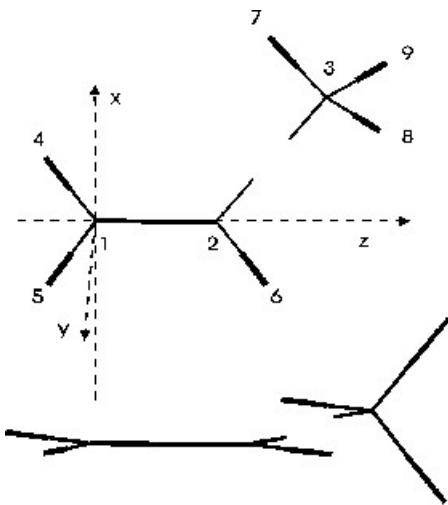
FRAGMENT 1   FRAGMENT 2

ATOM	X	Y	Z	N EXP	S COUL	N EXP	P COUL
C 1	.00000	.00000	.00000	2 1.7100	-21.4000	2 1.6250	-11.4000
C 2	.00000	.00000	1.33600	2 1.7100	-21.4000	2 1.6250	-11.4000
H 3	.94397	.00000	-.54500	1 1.3000	-13.6000		
H 4	-.94397	.00000	-.54500	1 1.3000	-13.6000		
H 5	-.94397	.00000	1.88100	1 1.3000	-13.6000		

DISTANCE MATRIX

	1	2	3	4	5
1	.0000	1.3360	1.0900	1.0900	2.1046
2	1.3360	.0000	2.1046	2.1046	1.0900
3	1.0900	2.1046	.0000	1.8879	3.0740
4	1.0900	2.1046	1.8879	.0000	2.4260
5	2.1046	1.0900	3.0740	2.4260	.0000

ENERGY LEVELS (eV)

```
E( 1) =    59.97940          .0000
E( 2) =    24.01856          .0000
E( 3) =    16.47236          .0000
E( 4) =     9.55473          .0000
E( 5) =    -7.19547          .0000 LUMO
```
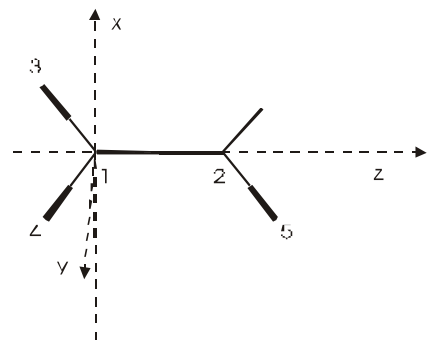

FRAGMENT 1
"be aware of the new numbers of the atoms"

```
  E( 6) =   -11.70088                1.0000 SOMO
  E( 7) =   -13.80766                2.0000
  E( 8) =   -15.89625                2.0000
  E( 9) =   -17.25357                2.0000
  E( 10) =   -21.92741                2.0000
  E( 11) =   -28.40937                2.0000


SUM OF ONE-ELECTRON ENERGIES =   -206.28938984 eV
ORBITAL STABILIZATION ENERGY =    -34.28938984 eV
CORE-CORE REPULSION ENERGY   =      4.74798623 eV
STABILIZATION + REPULSION    =    -29.54140361 eV


WAVE FUNCTIONS
MO'S IN COLUMNS, AO'S IN ROWS
              1       2       3       4       5       6       7       8       9      10      11
                                             LUMO    SOMO
  C 1(S)   -1.3782  -.6169   .2965  -.0543   .0000   .0442   .0000  -.0413   .0031   .3377   .5132
     (X)     .0521  -.4942  -.8936  -.7360   .0000   .0678   .0000   .1730  -.4832  -.0007   .0021
     (Y)     .0000   .0000   .0000   .0000  -.8286   .0000   .6270   .0000   .0000   .0000   .0000
     (Z)    -.7890   .5774  -.7805   .4876   .0000   .1008   .0000  -.4313  -.1207  -.2439   .0659


  C 2(S)    1.1819  -.6337   .1611   .2294   .0000  -.2606   .0000  -.0582  -.0641  -.4416   .4851
     (X)    -.1583   .6330   .4696  -.3717   .0000  -.7610   .0000  -.2307  -.2169   .0404   .0095
     (Y)     .0000   .0000   .0000   .0000   .8286   .0000   .6270   .0000   .0000   .0000   .0000
     (Z)    -.9079  -.2928  -.4414   .6289   .0000  -.4929   .0000   .4142   .0592  -.1792  -.0565


  H 3(S)     .2955   .8644   .0567   .8618   .0000   .1122   .0000   .3611  -.3260   .2417   .1152
  H 4(S)     .3415   .2904 -1.1230  -.3001   .0000  -.3066   .0000   .0152   .4307   .2422   .1146
  H 5(S)    -.2869   .8551   .3657  -.8121   .0000   .1220   .0000   .3824   .1112  -.3295   .1122



REDUCED OVERLAP POPULATION MATRIX, ATOM BY ATOM
          1       2       3       4       5
  1    2.6170  1.3287   .7838   .7480  -.0750
  2    1.3287  3.1767  -.0655  -.0538   .7712
  3     .7838  -.0655   .6293  -.0398   .0024
  4     .7480  -.0538  -.0398   .6090  -.0062
  5    -.0750   .7712   .0024  -.0062   .5743



REDUCED CHARGE MATRIX, MO'S IN COLUMNS, ATOMS IN ROWS, NORMALIZED TO TWO ELECTRONS REGARDLESS OF OCCUPATION
          1       2       3       4       5       6       7       8       9      10      11
                                                  SOMO
  1     .9098   .5182   .9653   .5704  1.0000   .0532  1.0000   .6299   .8854   .5568   .9110
  2     .8753   .4367   .2201   .4335  1.0000  1.7347  1.0000   .6660   .2124   .6132   .8080
  3     .0702   .4823  -.0023   .4702   .0000   .0199   .0000   .3282   .3088   .2263   .0965
  4     .0856   .0839   .7668   .0590   .0000   .1434   .0000   .0014   .5446   .2194   .0960
  5     .0591   .4789   .0502   .4669   .0000   .0488   .0000   .3745   .0488   .3843   .0885

ATOM    NET CHG.           ATOMIC ORBITAL OCCUPATION FOR GIVEN MO OCCUPATION
                              S        X        Y        Z
  C 1    -.00970           1.17688   .92469  1.00000   .90812
  C 2    -.16699           1.28641   .94010  1.00000   .94048
  H 3     .03028            .96972
  H 4     .06694            .93306
```

*****FRAGMENT 2*****

```
    ATOM        X          Y          Z                    S                 P
                                           N EXP    COUL     N EXP    COUL
    C 1      1.23997     .00000     2.18185 2 1.7100 -21.4000 2 1.6250 -11.4000
    H 2      2.13827     .00000     1.56447 1 1.3000 -13.6000
    H 3      1.25104     .88982     2.81129 1 1.3000 -13.6000
    H 4      1.25104    -.88982     2.81129 1 1.3000 -13.6000
```

```
DISTANCE MATRIX
          1      2      3      4
    1    .0000 1.0900 1.0900 1.0900
    2   1.0900  .0000 1.7702 1.7702
    3   1.0900 1.7702  .0000 1.7796
    4   1.0900 1.7702 1.7796  .0000
```

```
ENERGY LEVELS (eV)

  E( 1) =   36.35951              .0000
  E( 2) =    9.57776              .0000
  E( 3) =    9.35041              .0000 LUMO
  E( 4) =  -11.82479             1.0000 SOMO
  E( 5) =  -16.69124             2.0000
  E( 6) =  -16.72382             2.0000
  E( 7) =  -26.00333             2.0000

SUM OF ONE-ELECTRON ENERGIES =   -130.66158242 eV
ORBITAL STABILIZATION ENERGY =    -24.26158242 eV
CORE-CORE REPULSION ENERGY   =      1.72799065 eV
STABILIZATION + REPULSION    =    -22.53359176 eV
```



```
WAVE FUNCTIONS
MO'S IN COLUMNS, AO'S IN ROWS

                 1       2       3       4       5       6       7
               π*(CH₃)  LUMO    SOMO                   π(CH₃)
  C 1(S)     -1.3551   .0000  -.0047   .2164   .0012   .0000   .6419
     (X)      -.4073   .0000   .6598  -.7802  -.3157   .0000  -.0065
     (Y)       .0000  1.1461   .0000   .0000   .0000  -.5424   .0000
     (Z)      -.2795   .0000  -.9305  -.5554   .4433   .0000  -.0045

  H 2(S)       .7645   .0000  -.9977  -.0608  -.5052   .0000   .2188
  H 3(S)       .7585  -.8676   .5022  -.0615   .2523  -.4371   .2189
  H 4(S)       .7585   .8676   .5022  -.0615   .2523   .4371   .2189
```

```
REDUCED OVERLAP POPULATION MATRIX, ATOM BY ATOM

            1       2       3       4

    1    2.9691   .7810   .7810   .7810
    2     .7810   .6098  -.0468  -.0468
    3     .7810  -.0468   .6089  -.0460
    4     .7810  -.0468  -.0460   .6089
```



```
REDUCED CHARGE MATRIX, MO'S IN COLUMNS, ATOMS IN ROWS,
NORMALIZED TO TWO ELECTRONS REGARDLESS OF OCCUPATION

            1       2       3       4       5       6       7

    1    .8252  1.0312  1.0283  1.9494   .9717   .9688  1.2254
    2    .3947   .0000   .6434   .0167   .6869   .0000   .2583
    3    .3900   .4844   .1642   .0169   .1707   .5156   .2582
    4    .3900   .4844   .1642   .0169   .1707   .5156   .2582
```

```
ATOM      NET CHG.          ATOMIC ORBITAL OCCUPATION FOR GIVEN MO OCCUPAT
                            S         X         Y         Z

  C 1     -.14050         1.25482   .95420   .96876   .96271
  H 2      .04646          .95354
  H 3      .04702          .95298
  H 4      .04702          .95298
```


Gion Calzaferri
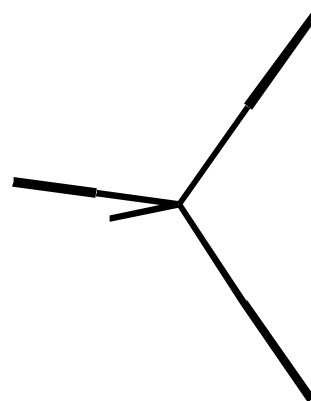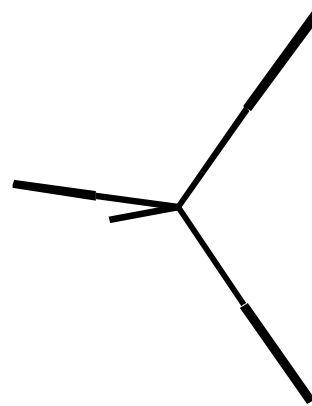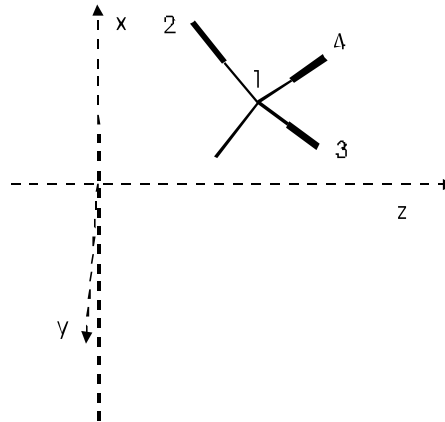
********** FMO **********

OVERLAP MATRIX (FOR FRAGMENT MOLECULAR ORBITALS)

```
                  1       2       3       4       5       6       7       8       9      10      11      12      13      14
                                                          SOMO
FRAG 1( 1)  1.0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0025   .0000   .0588
     ( 2)    .0000  1.0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0061   .0000   .0433
     ( 3)    .0000   .0000  1.0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000  -.0195   .0000   .0429
     ( 4)    .0000   .0000   .0000  1.0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000  -.0064   .0000  -.0737
     ( 5)    .0000   .0000   .0000   .0000  1.0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0935   .0000
     ( 6)    .0000   .0000   .0000   .0000   .0000  1.0000   .0000   .0000   .0000   .0000   .0000   .0764   .0000   .0012
     ( 7)    .0000   .0000   .0000   .0000   .0000   .0000  1.0000   .0000   .0000   .0000   .0000   .0000   .0990   .0000
     ( 8)    .0000   .0000   .0000   .0000   .0000   .0000   .0000  1.0000   .0000   .0000   .0000   .0117   .0000  -.0875
     ( 9)    .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000  1.0000   .0000   .0000   .0035   .0000  -.0367
     ( 10)   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000  1.0000   .0000   .0242   .0000   .0401
     ( 11)   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000   .0000  1.0000  -.0055   .0000   .0112

FRAG 2( 1)   .0025   .0061  -.0195  -.0064   .0000   .0764   .0000   .0117   .0035   .0242  -.0055  1.0000   .0000   .0000
     ( 2)    .0000   .0000   .0000   .0000   .0935   .0000   .0990   .0000   .0000   .0000   .0000   .0000  1.0000   .0000
     ( 3)    .0588   .0433   .0429  -.0737   .0000   .0012   .0000  -.0875  -.0367   .0401   .0112   .0000   .0000  1.0000
     ( 4)    .0229  -.0038   .0475   .0537   .0000  -.4159   .0000   .0040  -.1120  -.2322   .2612   .0000   .0000   .0000
     ( 5)   -.0643  -.0689  -.0314   .0714   .0000  -.0089   .0000   .0822   .0683  -.0605  -.0244   .0000   .0000   .0000
     ( 6)    .0000   .0000   .0000   .0000  -.1173   .0000  -.1143   .0000   .0000   .0000   .0000   .0000   .0000   .0000
     ( 7)   -.0146   .0228   .0372   .0424   .0000  -.3407   .0000   .0164  -.0927  -.1571   .1694   .0000   .0000   .0000

                 15      16      17      18

FRAG 1( 1)   .0229  -.0643   .0000  -.0146
     ( 2)   -.0038  -.0689   .0000   .0228
     ( 3)    .0475  -.0314   .0000   .0372
     ( 4)    .0537   .0714   .0000   .0424
     ( 5)    .0000   .0000  -.1173   .0000
     ( 6)   -.4159  -.0089   .0000  -.3407
     ( 7)    .0000   .0000  -.1143   .0000
     ( 8)    .0040   .0822   .0000   .0164
     ( 9)   -.1120   .0683   .0000  -.0927
     ( 10)  -.2322  -.0605   .0000  -.1571
     ( 11)   .2612  -.0244   .0000   .1694

FRAG 2( 1)   .0000   .0000   .0000   .0000
     ( 2)    .0000   .0000   .0000   .0000
     ( 3)    .0000   .0000   .0000   .0000
     ( 4)   1.0000   .0000   .0000   .0000
     ( 5)    .0000  1.0000   .0000   .0000
     ( 6)    .0000   .0000  1.0000   .0000
     ( 7)    .0000   .0000   .0000  1.0000
```
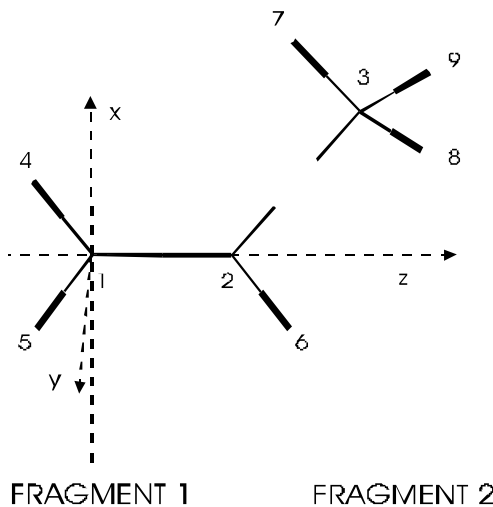

FRAGMENT 1   FRAGMENT 2

WAVEFUNCTIONS
MOLECULE MOLECULAR ORBITALS IN COLUMNS, FRAGMENT MOLECULAR ORBITALS IN ROWS

```
                  1       2       3       4       5       6       7       8       9      10      11      12      13      14

FRAG 1( 1)   .9697  -.2219   .0316   .0674   .0304   .0000   .0764  -.0725   .0000   .0000   .0293  -.0057   .0019   .0000
     ( 2)   -.0093  -.0961   .9387  -.1557  -.2536   .0000  -.0462   .1539   .0000   .0000  -.0386   .0116  -.0071   .0000
     ( 3)    .0651   .1657  -.0427  -.9094   .1477   .0000   .3136  -.1703   .0000   .0000   .0248   .0010  -.0082   .0000
     ( 4)    .0277   .1323  -.1196  -.0674  -.7478   .0000  -.2540  -.5989   .0000   .0000   .0231  -.0130   .0130   .0000
     ( 5)    .0000   .0000   .0000   .0000   .0000  -.1891   .0000   .0000  -.9912   .0377   .0000   .0000   .0000  -.0624
     ( 6)   -.2277  -.5637   .1579   .2424   .3295   .0000   .3921  -.6749   .0000   .0000  -.6201   .1075  -.0189   .0000
     ( 7)    .0000   .0000   .0000   .0000   .0000  -.1403   .0000   .0000  -.0243 - .9881   .0000   .0000   .0000  -.1652
     ( 8)   -.0125   .0041  -.0280   .0191  -.0687   .0000   .0798   .0262   .0000   .0000   .1605   .8992   .3972   .0000
     ( 9)   -.0613  -.1141   .0279   .0698   .0479   .0000   .1118  -.1293   .0000   .0000   .2150   .0419  -.4046   .0000
     ( 10)  -.0994  -.2426   .0895   .1018   .1687   .0000   .1271  -.2649   .0000   .0000   .2177  -.0829   .0732   .0000
     ( 11)   .1108   .2223  -.0806  -.1208  -.1369   .0000  -.1609   .2459   .0000   .0000  -.1459   .0219   .0074   .0000

FRAG 2( 1)   .1432   .8770   .2193   .2518   .1991   .0000   .1475  -.2085   .0000   .0000  -.0551   .0078  -.0109   .0000
     ( 2)    .0000   .0000   .0000   .0000   .0000  1.0047   .0000   .0000  -.0938  -.0347   .0000   .0000   .0000  -.0047
     ( 3)   -.0898   .0440  -.1578   .1959  -.5398   .0000   .7795   .2279   .0000   .0000  -.0040  -.0215  -.0054   .0000
     ( 4)   -.2815  -.4714   .2599   .3316   .3882   .0000   .4143  -.6612   .0000   .0000   .5552  -.1080   .0475   .0000
     ( 5)    .0612  -.0331   .0864  -.0410   .0666   .0000   .0303   .0401   .0000   .0000  -.0932  -.4733   .8150   .0000
     ( 6)    .0000   .0000   .0000   .0000   .0000  -.0454   .0000   .0000  -.1859  -.2705   .0000   .0000   .0000   .9583
     ( 7)   -.1459  -.3155   .1163   .1956   .2253   .0000   .2179  -.3351   .0000   .0000  -.2019   .0319  -.0460   .0000

                 15      16      17      18

FRAG 1( 1)  -.0049   .0014  -.0230   .0143
     ( 2)    .0053  -.0013   .0277  -.0168
     ( 3)   -.0068   .0036  -.0166   .0085
     ( 4)    .0013   .0040  -.0158   .0074
     ( 5)    .0000   .0000   .0000   .0000
     ( 6)    .0257  -.0753   .1129  -.0295
```

```
( 7)   .0000   .0000   .0000   .0000
( 8)   .1025   .0014   .0099  -.0060
( 9)   .8829  -.0399   .0344  -.0054
(10)  -.0152   .8989   .2990  -.0685
(11)   .0286  -.0547   .5372   .8309

FRAG 2( 1)   .0251   .0350   .0019  -.0373
      ( 2)   .0000   .0000   .0000   .0000
      ( 3)  -.0047   .0021  -.0011  -.0014
      ( 4)  -.1482  -.1965   .0201   .0491
      ( 5)   .3380  -.0189   .0053   .0059
      ( 6)   .0000   .0000   .0000   .0000
      ( 7)   .1208   .4026  -.7802   .3867
```

OVERLAP POPULATION MATRIX FOR 18 ELECTRONS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
FRAG 1(1)	.0033	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
(2)	.0000	.0055	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0001	.0000	.0000
(3)	.0000	.0000	.0022	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0001	.0000	.0000
(4)	.0000	.0000	.0000	.0024	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
(5)	.0000	.0000	.0000	.0000	.0106	.0000	.0000	.0000	.0000	.0000	.0000	.0000	-.0004	.0000
(6)	.0000	.0000	.0000	.0000	.0000	.8328	.0000	.0000	.0000	.0000	.0000	.0106	.0000	.0000
(7)	.0000	.0000	.0000	.0000	.0000	.0000	2.0073	.0000	.0000	.0000	.0000	.0000	.0139	.0000
(8)	.0000	.0000	.0000	.0000	.0000	.0000	.0000	2.0055	.0000	.0000	.0000	-.0002	.0000	.0079
(9)	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	1.9879	.0000	.0000	.0002	.0000	.0006
(10)	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	1.9240	.0000	.0020	.0000	.0004
(11)	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	2.0093	.0005	.0000	-.0001
FRAG 2(1)	.0000	.0001	.0001	.0000	.0000	.0106	.0000	-.0002	.0002	.0020	.0005	.0129	.0000	.0000
(2)	.0000	.0000	.0000	.0000	-.0004	.0000	.0139	.0000	.0000	.0000	-.0001	.0000	.0025	.0000
(3)	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0079	.0006	.0004	-.0001	.0000	.0000	.0011
(4)	.0016	.0004	.0026	.0030	.0000	.5740	.0000	-.0001	.0121	.0356	-.0260	.0000	.0000	.0000
(5)	.0001	.0016	.0015	.0043	.0000	-.0001	.0000	-.0270	-.0192	-.0140	-.0027	.0000	.0000	.0000
(6)	.0000	.0000	.0000	.0000	.0329	.0000	-.0498	.0000	.0000	.0000	.0000	.0000	.0000	.0000
(7)	-.0010	-.0018	.0018	.0019	.0000	-.0038	.0000	-.0012	-.0141	-.0316	-.0587	.0000	.0000	.0000

	15	16	17	18
FRAG 1(1)	.0016	.0001	.0000	-.0010
(2)	.0004	.0016	.0000	-.0018
(3)	.0026	.0015	.0000	.0018
(4)	.0030	.0043	.0000	.0019
(5)	.0000	.0000	.0329	.0000
(6)	.5740	-.0001	.0000	-.0038
(7)	.0000	.0000	-.0498	.0000
(8)	-.0001	-.0270	.0000	-.0012
(9)	.0121	-.0192	.0000	-.0141
(10)	.0356	-.0140	.0000	-.0316
(11)	-.0260	-.0027	.0000	-.0587
FRAG 2(1)	.0000	.0000	.0000	.0000
(2)	.0000	.0000	.0000	.0000
(3)	.0000	.0000	.0000	.0000
(4)	.7712	.0000	.0000	.0000
(5)	.0000	2.0231	.0000	.0000
(6)	.0000	.0000	1.9830	.0000
(7)	.0000	.0000	.0000	1.9577
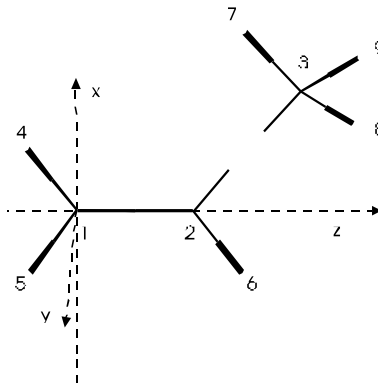
FRAGMENT 1   FRAGMENT 2

REDUCED OVERLAP POPULATION MATRIX,
FRAGMENT BY FRAGMENT

```
            1        2
FRAG 1   10.7908    .4577
FRAG 2    .4577    6.7515
```

COMPLETE CHARGE MATRIX FOR EACH MO, NORMALIZED TO TWO ELECTRONS REGARDLESS OF OCCUPATION

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
FRAG 1(1)	1.8553	.0981	.0014	.0117	.0000	.0000	.0194	.0105	.0000	.0000	.0030	-.0002	-.0002	.0000
(2)	.0003	.0177	1.7440	.0435	.1404	.0000	.0009	.0476	.0000	.0000	.0030	.0010	.0009	.0000
(3)	.0049	.0389	.0034	1.6033	.0429	.0000	.2327	.0687	.0000	.0000	.0023	.0000	.0005	.0000
(4)	.0009	.0218	.0202	.0081	1.0083	.0000	.1416	.7921	.0000	.0000	.0018	.0013	.0019	.0000
(5)	.0000	.0000	.0000	.0000	.0000	.0340	.0000	.0000	1.9391	.0050	.0000	.0000	.0000	.0219
(6)	.0231	.2174	.0082	.0280	.0693	.0000	.1235	.4074	.0000	.0000	.9744	.0315	.0012	.0000
(7)	.0000	.0000	.0000	.0000	.0000	.0100	.0000	.0000	.0006	1.8984	.0000	.0000	.0000	.0909
(8)	.0000	.0000	.0001	.0002	.0012	.0000	.0034	-.0001	.0000	.0000	.0486	1.5509	.3686	.0000
(9)	.0010	.0075	.0000	.0008	.0008	.0000	.0043	.0079	.0000	.0000	.0710	.0016	.2832	.0000
(10)	.0030	.0284	.0008	.0021	.0075	.0000	.0076	.0303	.0000	.0000	.0543	.0058	.0029	.0000
(11)	.0021	.0188	-.0003	-.0002	.0017	.0000	.0028	.0094	.0000	.0000	.0095	.0005	-.0001	.0000
FRAG 2(1)	.0353	1.4404	.1058	.1467	.0912	.0000	.0526	.1085	.0000	.0000	.0104	.0004	.0002	.0000
(2)	.0000	.0000	.0000	.0000	.0000	1.9553	.0000	.0000	.0354	.0090	.0000	.0000	.0000	.0003
(3)	.0058	.0018	.0328	.0619	.5157	.0000	1.2577	.1189	.0000	.0000	.0002	.0045	.0003	.0000
(4)	.0569	.0938	.0716	.0817	.1080	.0000	.1414	.3738	.0000	.0000	.7821	.0280	.0083	.0000
(5)	-.0001	.0001	.0013	.0008	.0016	.0000	.0005	.0005	.0000	.0000	.0126	.3734	1.3319	.0000
(6)	.0000	.0000	.0000	.0000	.0000	.0007	.0000	.0000	.0248	.0876	.0000	.0000	.0000	1.8869
(7)	.0115	.0153	.0107	.0114	.0114	.0000	.0117	.0246	.0000	.0000	.0268	.0015	.0005	.0000

	15	16	17	18
FRAG 1(1)	.0003	.0000	.0005	.0003
(2)	-.0002	.0000	.0005	.0003
(3)	.0003	.0001	.0015	.0004
(4)	.0001	.0001	.0015	.0004
(5)	.0000	.0000	.0000	.0000

```
         ( 6)     .0023    .0193    .0836    .0109
         ( 7)     .0000    .0000    .0000    .0000
         ( 8)     .0271    .0000    .0000    .0000
         ( 9)    1.6096    .0045    .0072    .0005
         (10)     .0006   1.5881    .2492    .0194
         (11)     .0001    .0041    .4407   1.5110

 FRAG 2( 1)     .0015    .0036    .0001    .0034
         ( 2)     .0000    .0000    .0000    .0000
         ( 3)     .0004    .0002    .0000    .0000
         ( 4)     .0732    .1506    .0015    .0291
         ( 5)     .2751    .0028   -.0003   -.0001
         ( 6)     .0000    .0000    .0000    .0000
         ( 7)     .0095    .2268   1.2140    .4244
```

```
REDUCED CHARGE MATRIX, MO'S IN COLUMNS, FRAGMENTS IN ROWS

             1       2       3       4       5       6       7       8       9      10      11      12      13      14
                                                                             LUMO    HOMO
FRAG 1   1.8906   .4487  1.7778  1.6975  1.2721   .0440   .5361  1.3737  1.9397  1.9034  1.1679  1.5923   .6588   .1128
FRAG 2    .1094  1.5513   .2222   .3025   .7279  1.9560  1.4639   .6263   .0603   .0966   .8321   .4077  1.3412  1.8872

            15      16      17      18
FRAG 1   1.6403  1.6161   .7847  1.5432
FRAG 2    .3597   .3839  1.2153   .4568
```
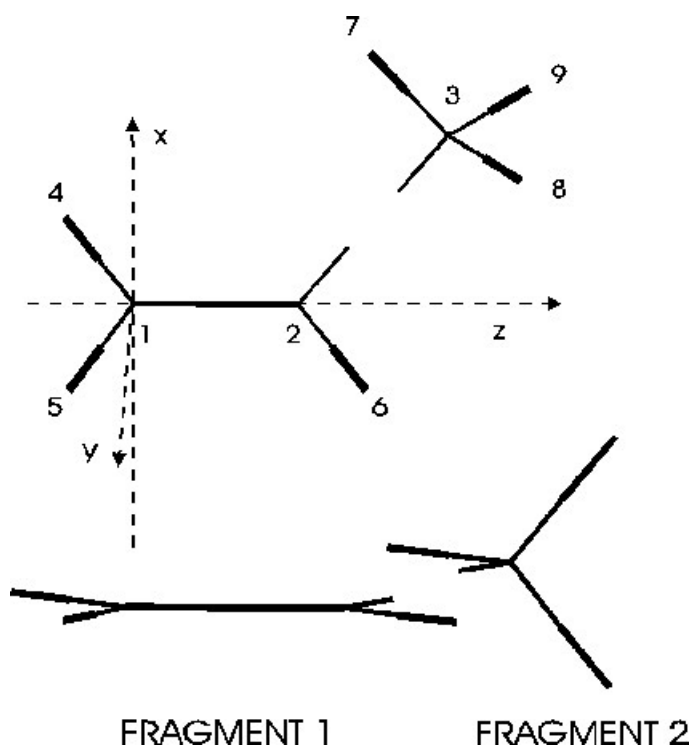
```
ATOM          NET CHG.          FRAGMENT MO OCCUPATION FOR GIVEN MOLECULAR MO OCCUPATION

FRAGMENT 1:    -.01966    .00363    .00563    .00519    .00698    .02688   1.12309   1.98939   1.99517   1.97768   1.92025   1.96577
FRAGMENT 2:     .01966    .01959    .00922    .00543   1.07279   1.99539   1.97452   1.90340
```

The total charge shift is small!

Overview:

FRAGMENT 1   FRAGMENT 2

Propene			Fragment 1			Fragment 2		
E(1) =	62.85095	.0000						
E(2) =	46.41573	.0000						
E(3) =	25.72215	.0000						
E(4) =	18.29330	.0000						
E(5) =	13.85685	.0000	E(1) =	59.97940	.0000			
E(6)$\mathbf{p}_2$* =	**10.63028**	**.0000**	E(2) =	24.01856	.0000	E(1) =	36.35951	.0000
E(7) =	8.10562	.0000	E(3) =	16.47236	.0000	**E(2)$\mathbf{p}$* =**	**9.57776**	**.0000**
E(8) =	5.22319	.0000	E(4) =	9.55473	.0000	E(3) =	9.35041	.0000
E(9)$\mathbf{p}_1$* =	**−7.00648**	**.0000**	**E(5)$\mathbf{p}$* =**	**−7.19547**	**.0000**			
E(10)$\mathbf{p}_1$ =	**−13.59232**	**2.0000**	E(6) =	−11.70088	1.0000	E(4) =	−11.82479	1.0000
E(11) =	−14.93929	2.0000	**E(7)$\mathbf{p}$ =**	**−13.80766**	**2.0000**			
E(12) =	−15.66521	2.0000	E(8) =	−15.89625	2.0000			
E(13) =	−16.74145	2.0000				E(5) =	−16.69124	2.0000
E(14)$\mathbf{p}_2$ =	**−16.85475**	**2.0000**				**E(6)$\mathbf{p}$ =**	**−16.72382**	**2.0000**
E(15) =	−17.37493	2.0000	E(9) =	−17.25357	2.0000			
E(16) =	−21.53021	2.0000	E(10) =	−21.92741	2.0000			
E(17) =	−25.82475	2.0000				E(7) =	−26.00333	2.0000
E(18) =	−29.15800	2.0000	E(11) =	−28.40937	2.0000			

Exercise: Draw the correlation diagram between the two fragments and propene.

7 PARAMETERS

For a discussion of Slater exponents and coefficients we refer to [11], [18-31].

Below we give a table of references in which extended-Hückel parameters for the corresponding elements are reported. The references are not complete, they can, however, be used as a guide. We recommend in every case to check the parameters.

Element	Reference	Element	Reference	Element	Reference
Ac	32	He	46	Pd	57
Ag	33	Hf	32	Pt	40
Al	33, 10	Hg	47, 79	Rb	65
As	34	I	48	Re	58
Au	36	In	44	Rh	40, 59
B	10	Ir	49	Ru	45, 60, 80
Be	35	K	38	S	8
Bi	37	La	50	Sb	62
Br	38	Li (Li$_2$)	10	Sc	
C	1, 8	Li(metal)	51	Se	63, 66
Ca	39	Mg	52	Si	7, 9, 33, 67
Cd	79	Mn	12, 40	Sm	32
Ce	32	Mn(metal)	41	Sn	65
Cl	40	Mo	40	Sr	65
Co	40, 5	N	8	Ta	68
Co(metal)	41	Na (Na$_2$)	10	Tc	69
Cr	40	Na(metal)	51	Te	70, 79
Cr(metal)	40	Ne	46	Th	71
Cs	38	Nb	40	Tl(metal)	41
Cu	43	Ni	54	U	71
F (F$_2$)	10	Ni(metal)	41	V	73
Fe	40, 42	O	8	V(metal)	41
Fe(metal)	41	Os	80	W	58
Ga	44	P	40	Yb	74
Gd	32	Pa	32	Zn	76
Ge	45	Pb	56, 79	Zr	75
H	1				

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