

Extended Hückel Molecular Orbitals and Oscillator Strength Calculations

ICON-EDiT
Manual written by
Gion Calzaferri, Stephan Glaus, Dominik Brühwiler

ICON-EDiT
Program written by
Ruedi Rytz, Stephan Glaus, Martin Brändle,
Dominik Brühwiler and Gion Calzaferri

Department of Chemistry and Biochemistry
University of Berne, Freiestrasse 3, CH-3012 Bern

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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 electronic dipole-induced transitions (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.

A set of additional programs, useful for more advanced users of **ICON-EDiT** is provided in **Q-TOOLS**. A description of these is included in this document.

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 separately 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:\SOME PATH\ 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 ICONC.EXE EDiT.EXE GOP.EXE <i>ATOMDEF.DAT</i> FOI.DAT VOI.DAT	INPUTC (DIR) ICONC (DIR) EDiT (DIR) GOP (DIR) containing the sources	2-H2O_GOP.GEN 2H2OAG_ANGLE.GEN 2H2OAG_DISTANCE.GEN BENZENE.GEN BENZENE.OUT BENZENE1.PGR.GOP 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 PROOPEN_F.GEN PROOPEN_F.OUT	Q-TOOLS.EXE SAMPLES(DIR) Containing some examples. Refer to the description of Q-TOOLS

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 $\pm 180^\circ$ 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.

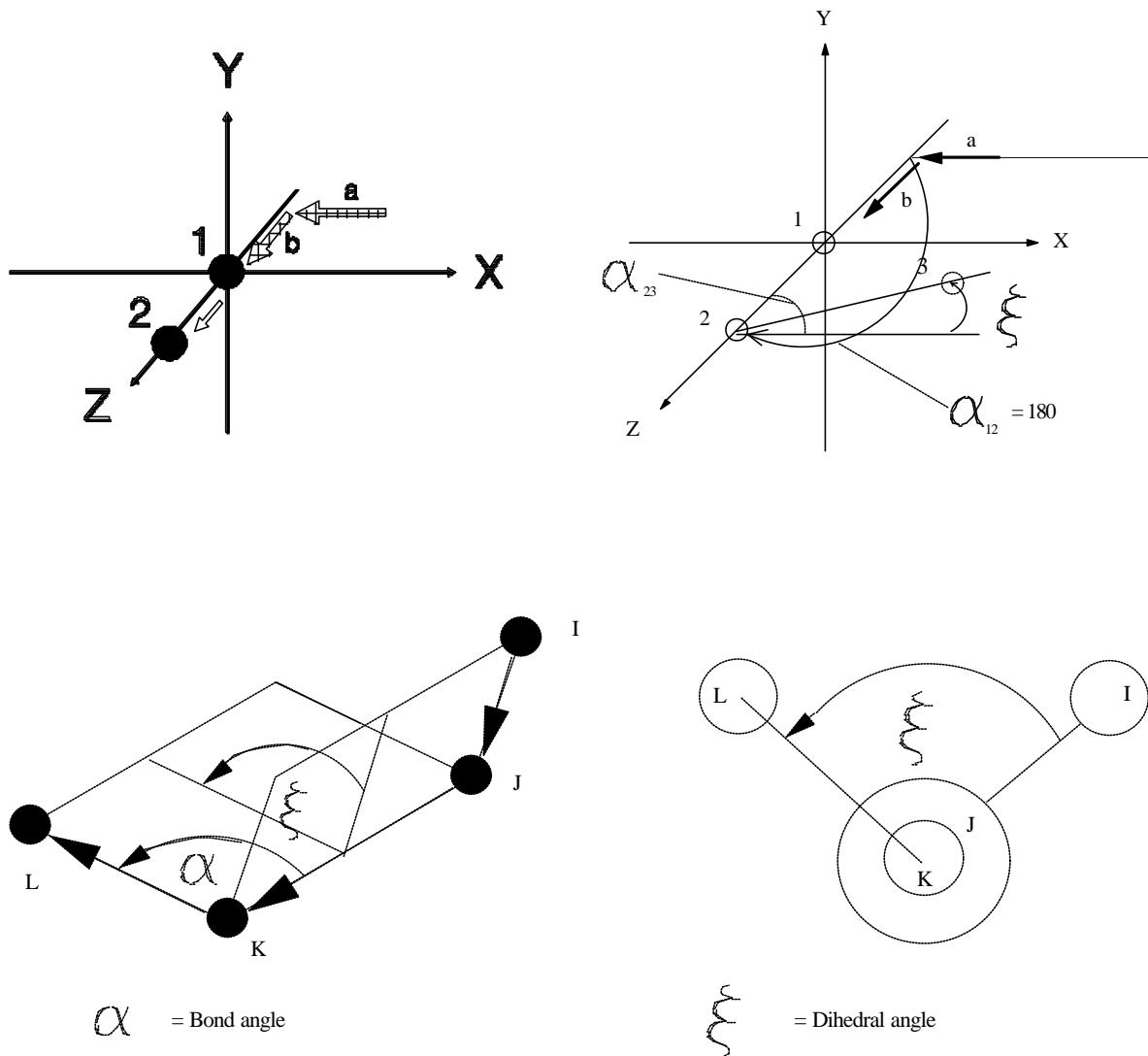
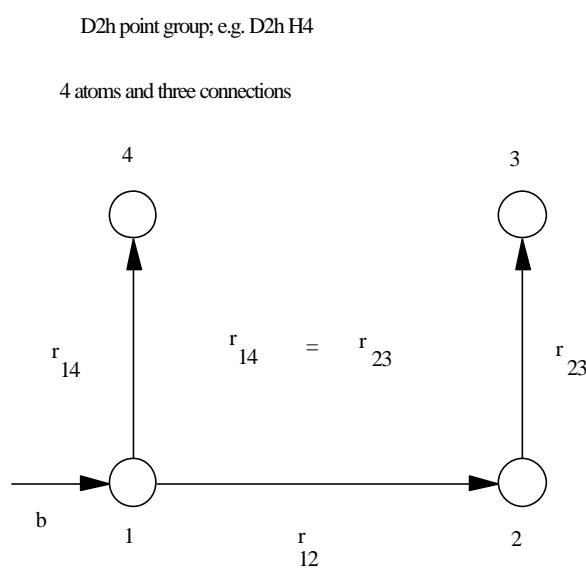


Figure 1: Definition of the bond angle α and the dihedral angle ξ . In case of atoms 1 and 2 in the upper scheme **K** corresponds to atom 1.

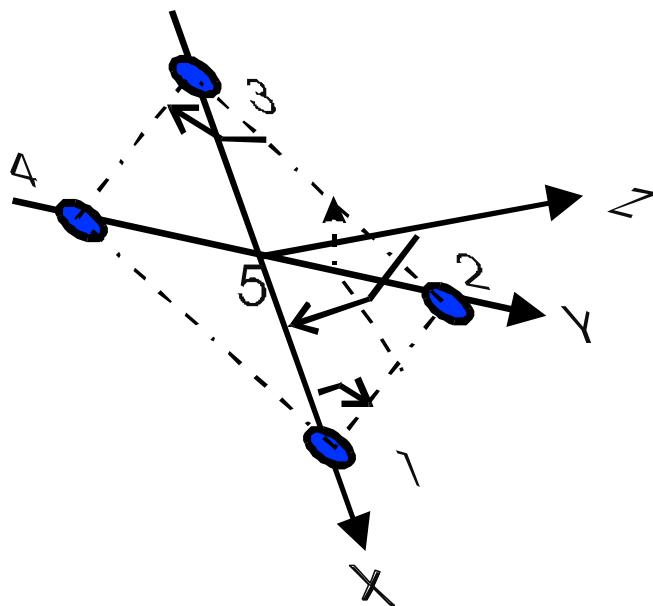
Figure 2: EXAMPLE 1, D_{2h} H₄

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



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 C₄ axis, the following input will do it:



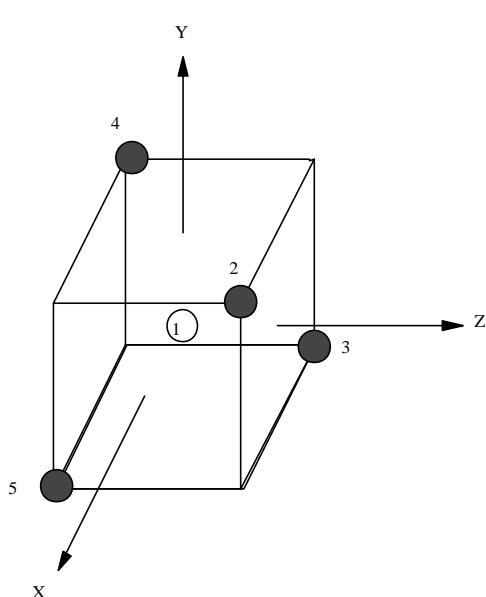
vector	distance	α	ξ
5 1	0,707107	90	0
1 2	1	45	90
2 3	1	90	0
3 4	1	90	0
atom	x	y	z
1	0,7071	0	0
2	0	0,7071	0
3	-0,7071	0	0
4	0	-0,7071	0
5=dummy	0	0	0

The following input places the four atoms into the y,z plane, so that the x axis coincides with the C₄ 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 CH₄

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	0	0
3	-a	0	0
4	-a	0	0
5	a	0	0
			a=0.6293

Figure 4: 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

```

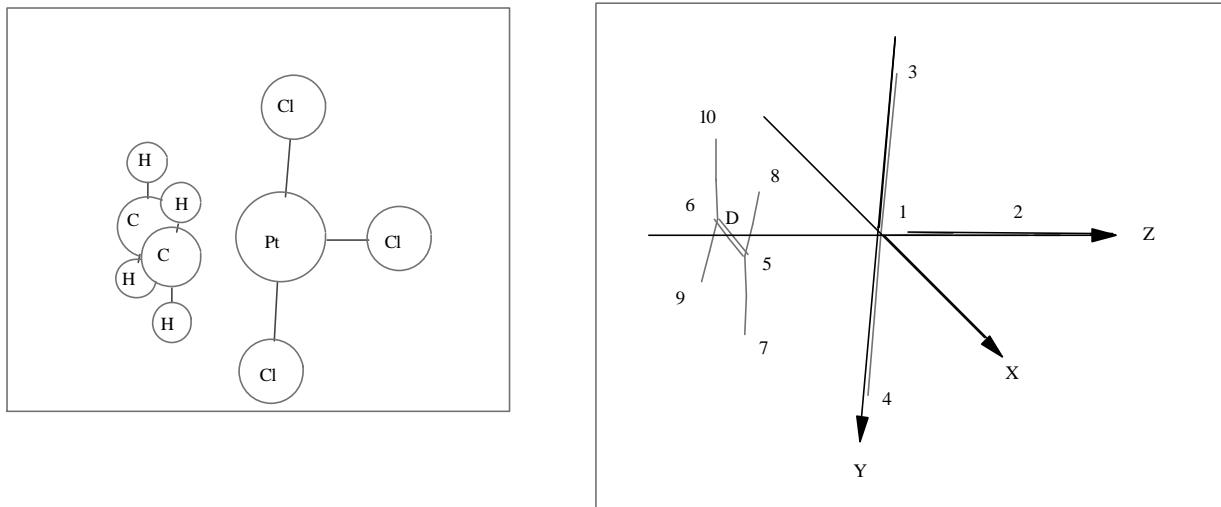
Resulting cartesian coordinates:

```

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

```

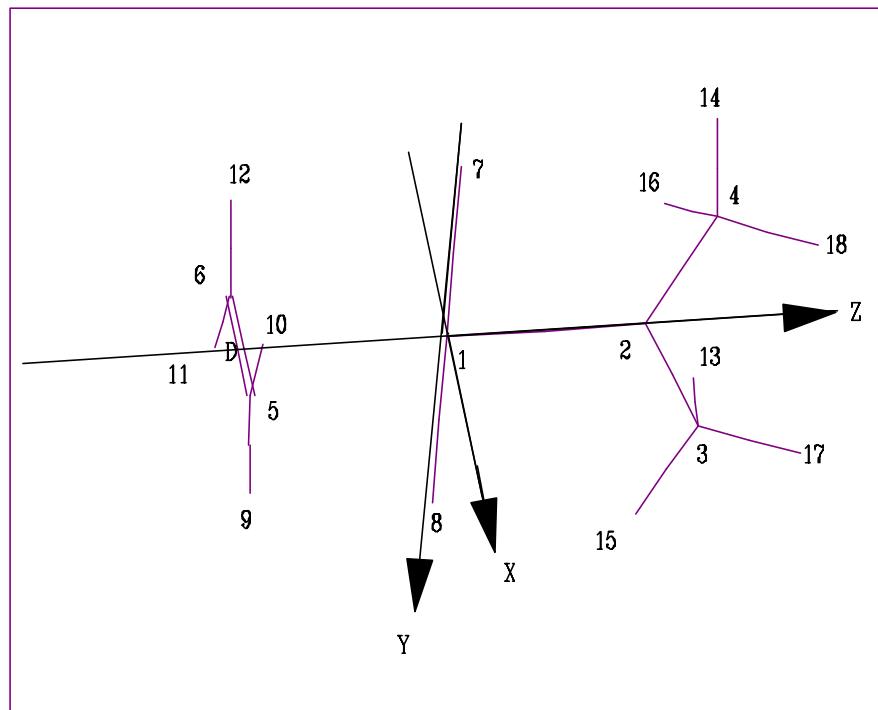
Figure 5: EXAMPLE 4, Zeise-Salt ($(\text{H}_2\text{C} = \text{CH}_2)$ PtCl_3), try ZEISE.GEN.



number of atoms	10
number of dummy atoms D	1
number of vectors	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, ($\text{H}_2\text{C} = \text{CH}_2$) $\text{PtCl}_2\text{N}(\text{CH}_3)_2$, try CHNCLPT.GEN.

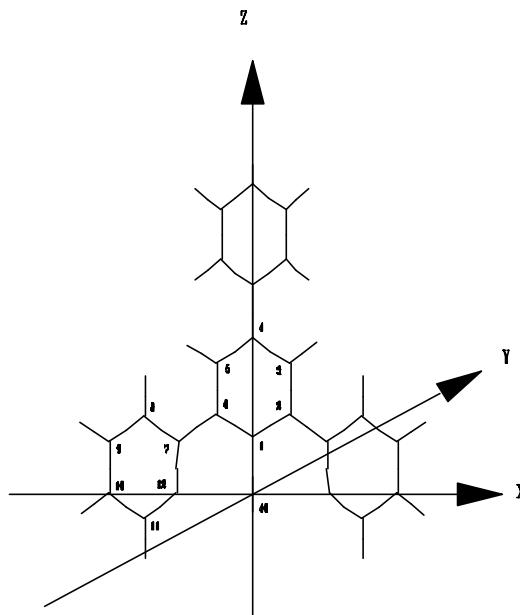


number of atoms 18

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

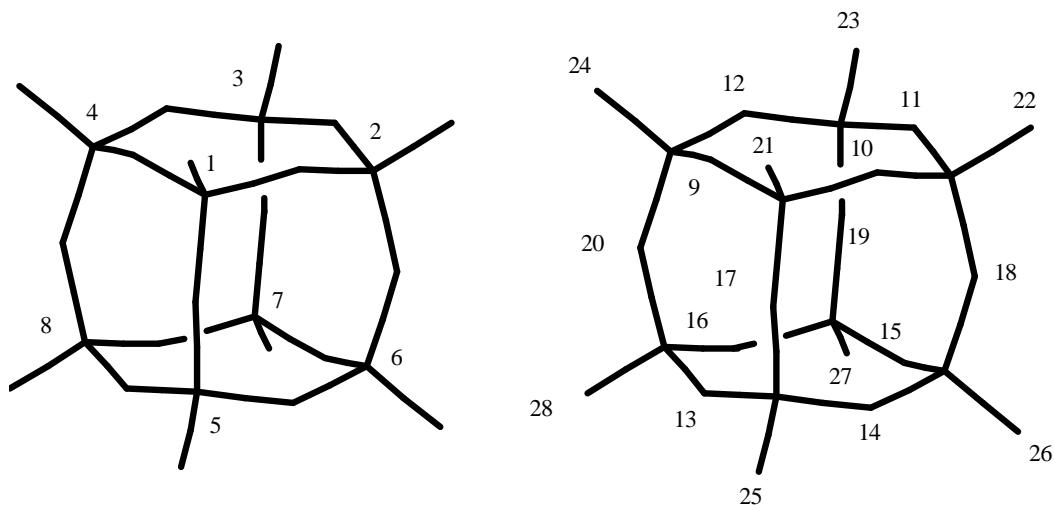
Figure 7: EXAMPLE 6, 4' -Phenylterpyridine, try PTPY.GEN.

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, H₈Si₈O₁₂, 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:

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

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

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

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

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 *CO₂*. 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 iterated 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 standard 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 C₃ 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

EDiT <filename.EDI>filename.EDO

The *filename.EDI* is the EDiT input file that has to be created separately 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 the EDiT program
!
! Any line containing an exclamation mark is treated as
! a comment.
Hence, this line is a comment, too!

! Blank lines are skipped
! We start the input file with a title that will be written
! to the output to help us keeping track of input and output
! files. The title card has to be preceded by TITLE.
!
TITLE First Electronic Transition in Permanganate
!
! We then define the names of the MO (MOBY) and the GEN files.
! The extensions .mo and .gen will be automatically appended
! to the base-name. We read the Cartesian coordinates of the
! molecule as well as the wave functions from the mno4-.mo
! file. The mno4-.gen file is needed to extract the Slater
! exponents.

KEYWRD MOFILE=mno4
KEYWRD GENFILE=mno4

! The polarization is given by the KEYWRD POL. In this case we
! chose x, y and z polarized transitions. Any combination and
! order are allowed.

KEYWRD POL=XYZ

! Now we have to chose between BDIAG and ALL (KEYWRD MATRICE).
! BDIAG only accounts for the transitions at the SAME atom.
! This means that off block diagonal elements of the transition
! matrix are skipped. Indeed you shouldn't use this feature
! unless you exactly know what you are doing.
! For further information refer to G. Calzaferri and R. Rytz,
! J. Phys. Chem., 99 (1995) 12141.

KEYWRD MATRICE=ALL

! For degenerate MOs we will have to correct the oscillator
! strength for the degeneracy of the initial MOs (see eq. 9 in
! our reference). Of course the sum in the nominator of eq. 9
! will have to be carried out by hand.
! The TOLERANCE is the value in eV within two NEIGHBORING MOs
! are considered degenerate.

KEYWRD CORRECT
KEYWRD TOLERANCE=0.00001
```

```

! SPECOUT initiates the printing of a file called mno4-.eds.
! It contains five columns the first of which displays the wave
! numbers of the calculated transitions sorted from low to high
! energy. It is followed by the projected oscillator strengths
! in x, y and z direction. The last column shows the total
! oscillator strengths. Only the contributions specified by the
! KEYWRD POL are taken into account. Correction for degeneracies are
! done regardless of the specification of the KEYWORD CORRECT.
! If not stated otherwise (KEYWRD TOLERANCE) a tolerance of
! 1.0D-5 is assumed.

```

KEYWRD SPECOUT

```

! releases the printing of transitions between a given initial
! and final wave function. The transition energy and the
! calculated oscillator strengths (see KEYWRD POL) are output
! to stdout.

```

KEYWRD TRANSOUT

```

! gives the numbers of the initial and final wave functions in
! MOBY notation. Unfortunately MOBY and ICONC follow different
! conventions in enumerating the wave functions. MOBY starts
! counting with the lowest energy; ICONC does the opposite.
! This should be no problem but has to be born in mind.

```

[WAVERANGE]

```

START 14 16
END   17 18

```

```

! Run this file by typing at the command line
!
!     EDiT < mno4-.edi > mno4-.edo
!
! (Be careful not to overwrite the mno4-.edo and mno4-.eds
! files provided with this distribution. You might want to keep
! them for comparison.) The output should agree with Table 4 in
! our reference. Try to substitute lines 75 to 77 with
!
! [WAVERANGE]
! START 17 18
! END   14 16
! Compare the two mno4-.eds!

```

As you may have already noted EDiT needs to read information from two files, namely *filename.GEN* and *filename.MO*, which should be located in the same directory as the program itself. The *.GEN files are needed to read the Slater exponents while the geometry information as well as the final and initial wave functions are read from the respective *.MO file. The *.MO files are written on request by ICONC. Hence, in order to calculate oscillator strengths of electronic dipole-induced transitions you will first have to set up the appropriate *.GEN file with INPUTC. Do not forget to select MOBY output by choosing option 2 „Controlling output options” and then picking option 22 „Moby output”. After running the ICONC calculation as described above you should make sure that the *filename.MO* was written. You can then set up an *.EDI file by using *MNO4-.EDI* as a template.

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 .000FFFFFFFFFFFFFFFFFF
    .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 must 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 computer's 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 $1+\kappa$ 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

```
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

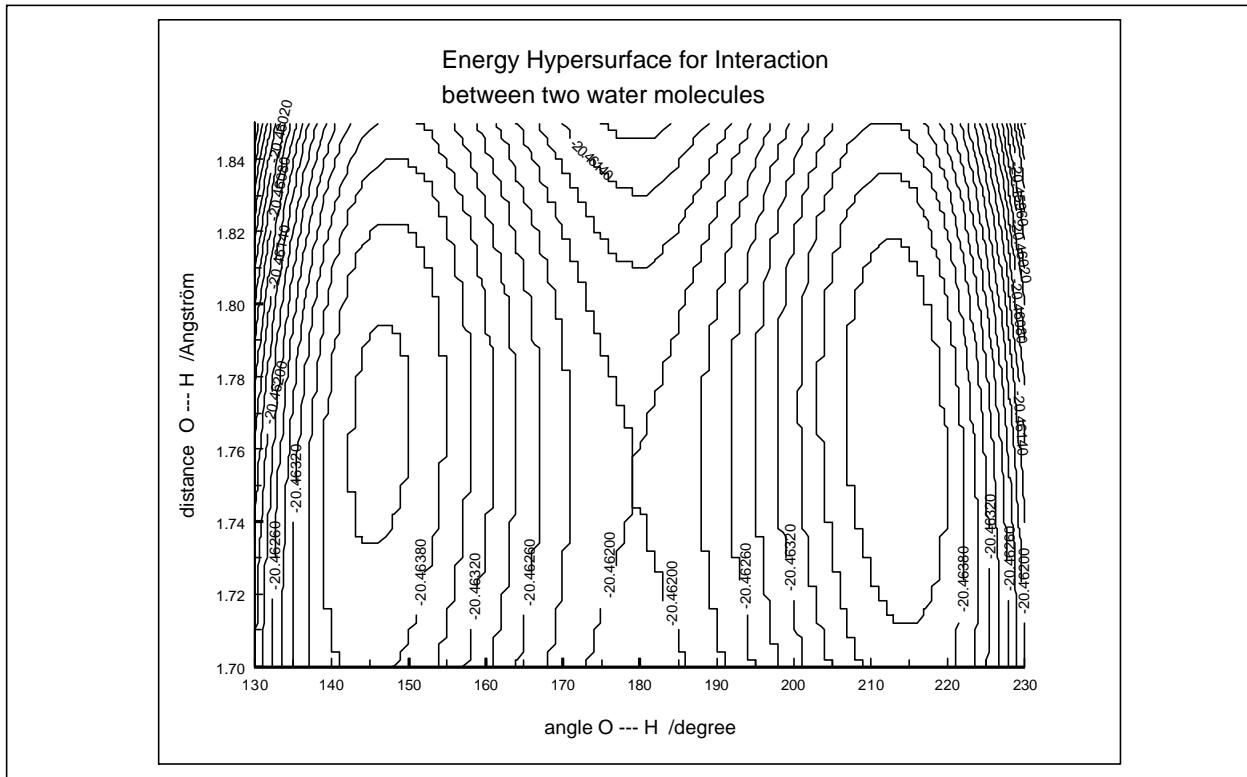
The algorithm finds four different minimums for various starting values.

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:



We can see clearly the same minimums as found with GOP. Note that $360^\circ - 146.5^\circ = 213.5^\circ$.

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. no.	vector [1-3]	new 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 Q-TOOLS

a) Introduction

a1) About Q-Tools

Q-TOOLS is currently version 1.1a. Mainly, the changes made to version 1.0 are:

Version 1.0 ...

- sometimes counted the number of variations wrongly.
- could not handle .gen files containing FMO specifications, charge iterations, ommittings from core-core repulsion or orbital occupation.
- sometimes created unusable temporary .gen files.

These problems have been solved.

Up to now, Q-TOOLS mainly can do two things:

- Create an energy/variation matrix: Q-TOOLS takes the information ICONC stores in the enerot.dat file and rearranges it to a matrix which can easily be used to make a plot. See section b) for further information.
- Vary 1+kappa and delta values: Q-TOOLS lets you specify which 1+kappa and/or delta values you want to vary. For each set of values, Q-TOOLS makes a call to INPUTC and ICONC and stores the error of the ICONC calculations. See section c) for further information.

a2) How to use Q-Tools

Before you start:

Q-TOOLS must be located in the same directory as INPUTC and ICONC. Also in this directory you should place the .gen files you want to make calculations on. Be sure you know the name and approximate content of your .gen files.

Start Q-TOOLS from the command prompt. It will prompt you for every entry you have to make:

- If you make a wrong entry, you won't be able to correct it. The only thing you can do is to stop execution by pressing CTRL+C, but this will work only if the execution of INPUTC and ICONC has not started yet.
- The first thing the program will ask for is the name of the .gen file you want to make calculations on. THIS CAN BE ANY NAME EXCEPT *temp*. The program will copy your .gen file to a file *temp.gen*, and then modify only this file. If you have any .gen file called *temp.gen*, please rename it before starting the program.
- If you have to specify any output file names (refer to sections b) and c) for more information), please make sure you don't use names of existing files. The program won't notice the existing files and overwrite them.
- After the program has finished a calculation, it will ask you if you want to make another one. It is not recommended to make too many or too big calculations, because the program may cause your system to halt.

b) Energy/variation matrices

Idea:

Sometimes, you may want to see the results of a single ICONC calculation as a graph. For example, you may want a graph of how the total energy in a water molecule changes if you change the size of the angle (H-O-H). The output ICONC provides, however, isn't of much use for this problem and it is annoying to sort it by hand. Q-TOOLS can sort the output of ICONC for you, so that afterwards a graph can easily be created.

How it works:

Start Q-TOOLS from the command prompt. The program will ask you for the name of your .gen file. Please make sure that the .gen file doesn't contain superfluous information, i.e.: If you want to make a two dimensional graph, therefore plot the energy dependent on one variation, your .gen file should contain only one uncoupled variation. For a three dimensional graph (energy dependent on two variations), your .gen file should contain two uncoupled variations. Otherwise, the output of Q-TOOLS may be redundant or even unusable. If you have specified the name of the .gen file, the main menu will appear. Choose option number 1 (make an energy/variation matrix). The menu 'Energy/Variation Matrix' will appear. If you want to create a two dimensional graph (with a one dimensional function), choose option one. For a three dimensional graph (with a two dimensional function), choose option 2. Refer to sections b1) and b2) for informations on this choice.

When you have ended Q-TOOLS, you will find the output files in the same directory in which Q-TOOLS is located. In addition to these, Q-TOOLS creates the following files which you may delete:

- notext. xx : temporary file used for data storage
- call. xx : temporary file used to make a call to INPUTC
- temp.gen : temporary .gen file Q-TOOLS uses for calculations
- temp.out : ICONC output file

b1) Two dimensional (energy against one variation) matrices

If you have chosen option #1 from the 'Energy/Variation Matrix' menu, the next thing the program will ask for is the name of the output files. The extensions will be added by the program. After you have typed in the name and pressed ENTER, the program will call INPUTC and ICONC. You will see some output of these programs on the screen. When the calculations of ICONC are finished (it may take some seconds up to minutes, depending on your computer), the program will sort out the information you need for a plot from the enertot.dat file.

It then creates the following output files (*filename* will be the name you have specified):

- filename.ene*: In this file you will find a column containing the (STAB.+REP.) energy values from the enertot.dat file.
- filename.var*: The values of the variation in your .gen file corresponding to the energies.
- filename.all*: The two columns of values (from the .ene and the .var file) combined in one file.

When calculations and output are terminated, the program will beep and print out a success message. See \samples\2dmatr\2-h2o_8a.mcd for a mathcad sample file.

b2) Three dimensional (energy against two variations) matrices

If you have chosen option #2 from the ‘Energy/Variation Matrix’ menu, the next thing the program will ask for is the name of the output files. The extensions will be added by the program. After you have typed in the name and pressed ENTER, the program will call INPUTC and ICONC.

You will see some output of these programs on the screen. When the calculations of ICONC are finished (it may take some seconds up to minutes, depending on your computer), the program will sort out the information you need for a plot from the enertot.dat file. The program detects automatically your two variations and creates a matrix out of the energy values, the first variation being the vertical, the second the horizontal axis of this matrix.

Two output files are created (*filename* will be the name you have specified):

<i>filename.enm:</i>	Contains the energy matrix.
<i>filename.cor:</i>	Contains the ‘coordinates’ of this matrix, i.e. the values of the two variations.

When calculations and output are terminated, the program will beep and print out a success message. See \samples\3dmatr\dis_angl.mcd for a mathcad sample file.

c) Variation of 1+kappa and d values

Idea:

Often you don’t know the exact values of the $1+\kappa$ and δ parameters in a specific molecule. Q-TOOLS varies these parameters for you. The program lets you optimize up to four values (κ or δ) at one time; if you want to vary only one or two parameters, you can use the output to make a two or three dimensional plot.

How it works:

Refer to section c1).

c1) General

What Q-TOOLS does:

Q-Tools starts INPUTC and ICONC for each set of $1+\kappa$ and/or delta values. Each time, it extracts the minimal (STAB.+REP.) energy with the corresponding variations from the enertot.dat file. To let you find out how good the ICONC calculation for each set of $1+\kappa$ and/or delta values is, Q-TOOLS calculates the $(\text{SIGMA})^2$ value, comparing the variations it has found in enertot.dat with literature values you can specify. $(\text{SIGMA})^2$ is calculated according to the following formula:

$$(\text{SIGMA})^2 = 0.5 * \{ [(\text{VAR1(LIT)} - \text{VAR1(CALC)})/\text{VAR1(LIT)}]^2 + [(\text{VAR2(LIT)} - \text{VAR2(CALC)})/\text{VAR2(LIT)}]^2 \}$$

LIT stands for literature value, CALC for calculated value.

VAR1 and VAR2 stand for 1st and 2nd variation.

If your .gen file contains only one variation, the formula will alter accordingly.

The calculations Q-TOOLS makes won’t let you optimize more than two (uncoupled) variations at a time.

Depending on your choice, Q-TOOLS makes one of two things with the $(\text{SIGMA})^2$ and the other values:

- If you want to vary only one or two $1+\kappa$ and/or delta parameters, Q-TOOLS can make matrix output files which you can later use to create surface or contour plots.

- Else, if you choose ‘Vary up to four 1+kappa and delta values (output only for minimal SIGMA)²’ from the ‘Variation of 1+kappa and delta’ menu (option #4), Q-TOOLS will only save the (SIGMA)² values that lie below a certain value you can specify.

Refer to sections c2), c3), c4) and c5) for details.

What you have to do:

Start Q-TOOLS from the command prompt. The program will ask you for the name of your .gen file. Please make sure your .gen file contains a maximum of two uncoupled variations! More variations won’t bother the program, but increase calculation time immensely!

If you have specified the name of the .gen file, the main menu will appear. Choose option #2 (Vary 1+kappa and delta) and press ENTER. The following menu, ‘Variation of 1+kappa and delta’, will appear:

```
***** VARIATION OF 1+KAPPA AND DELTA ****
*
* 1 Vary global values
* 2 Vary a set of individual values
* 3 Vary a global and an individual value or
*      two individual values
* 4 Vary up to four 1+kappa and delta values
*      (output only for minimal (SIGMA)2)
*
*****
```

For the choices you have, please refer to the following chapters:

- Option #1: section c2)
- #2: section c3)
- #3: section c4)
- #4: section c5)

See \samples\k_d_01\h2oco01a.mcd for a mathcad sample file.

c2) Variation of global values

If you have chosen option #1 from the ‘Variation of 1+kappa and delta’ menu, the first thing the program will ask you for is the name you want for your output files.

Afterwards, it will ask for the literature value of your first variation, and, if you have got one, of your second variation. Please make sure you don’t confuse first and second variation.

Then the program will ask for the starting, ending and increment value for both 1+kappa and delta. All values must be positive!

If you want to vary only either 1+kappa or delta, set starting and ending value of the other parameter at the same value and the increment value > 0.

Afterwards calculations will start. Depending on your choices and the ability of your computer, the calculations can take a few minutes up to hours.

Q-TOOLS will create the following output files (‘filename’ will be the name you have specified):

- filename.mat: Contains a matrix of the (SIGMA²) values (cf. section c1).
- filename.ene: Contains a matrix with the minimal energy values.
- filename.va1: Contains a matrix with the first variations at the minimal energy levels.
- filename.va2: Same for 2nd variations (this file will only be created if your .gen file

contains two variations).

- filename.cor: Contains the ‘coordinates’ of the matrix files, i.e. the 1+kappa and delta values at which the calculations took place.

When calculations and output are terminated, the program will beep and print out a success message.

c3) Variation of a set of individual values

If you have chosen option #2 from the ‘Variation of 1+kappa and delta’ menu, the first thing the program will ask you for is the name you want for your output files.

Afterwards, it will ask for the literature value of your first variation, and, if you have got one, of your second variation. Please make sure you don’t confuse first and second variation.

If your .gen file contains more than one set of individual 1+kappa and delta values, the program will display them and ask which one you want to vary. Then the program will ask for the starting, ending and increment value for both 1+kappa and delta. All values must be positive!

If you want to vary only either 1+kappa or delta, set starting and ending value of the other parameter at the same value and the increment value > 0.

Afterwards, calculations will start. Depending on your choices and the ability of your computer, the calculations can take a few minutes up to hours.

Q-TOOLS will create the following output files (*filename* will be the name you have specified):

- filename.mat: Contains a matrix of the (SIGMA²) values (cf. section c1).
- filename.ene: Contains a matrix with the minimal energy values.
- filename.va1: Contains a matrix with the first variations at the minimal energy levels.
- filename.va2: Same for 2nd variations (this file will only be created if your .gen file contains two variations).
- filename.cor: Contains the ‘coordinates’ of the matrix files, i.e. the 1+kappa and delta values at which the calculations took place.

When calculations and output are terminated, the program will beep and print out a success message.

c4) Variation of a global and an individual value or of two individual values

If you have chosen option #3 from the ‘Variation of 1+kappa and delta’ menu, the first thing the program will ask you for is the name you want for your output files.

Afterwards, it will ask for the literature value of your first variation, and, if you have got one, of your second variation. Please make sure you don’t confuse first and second variation.

Then the program will scan your .gen file for individual 1+kappa and delta parameters. It will display all the parameters you can vary and ask you to choose two of them. After you have made your choice, the program will ask for the starting, ending and increment value for both parameters. All values must be positive!

Afterwards, calculations will start. Depending on your choices and the ability of your computer, the calculations can take a few minutes up to hours.

Q-TOOLS will create the following output files (*filename* will be the name you have specified):

- filename.mat: Contains a matrix of the (SIGMA²) values (cf. section c1).
- filename.ene: Contains a matrix with the minimal energy values.
- filename.va1: Contains a matrix with the first variations at the minimal energy levels.
- filename.va2: Same for 2nd variations (this file will only be created if your .gen file contains two variations).
- filename.cor: Contains the ‘coordinates’ of the matrix files, i.e. the 1+kappa and delta values at which the calculations took place.

When calculations and output are terminated, the program will beep and print out a success message.

c5) Variation of one to four values (without matrix output)

If you have chosen option #4 from the ‘Variation of 1+kappa and delta’ menu, the first thing the program will ask you for is the name you want for your output file.

Then it will ask you how many parameters you want to vary. If your .gen file contains individual 1+kappa and delta values, you can choose up to four, otherwise up to two parameters.

Then the program will display all the parameters you can vary and ask you to choose as much of them as you have specified. After you have made your choice, the program will ask for the starting, ending and increment value for all parameters. These values must be positive! Afterwards, it will ask for the literature value of your first variation, and, if you have got one, of your second variation. Please make sure you don’t confuse first and second variation.

At last, the program will ask for the tolerance for $(\text{SIGMA})^2$. It will save only the $(\text{SIGMA})^2$ values that are smaller than this tolerance.

Afterwards, calculations will start. Depending on your choices and the ability of your computer, the calculations can take a few minutes up to hours.

Q-TOOLS will create one output file, called *filename.min* (where *filename* is the name you have specified for your output file). This file will contain several entries of the following structure:

```
Good enough sigmasquare found at:  
global δ = 0.4  
1+κ between atom 2 and atom 3 = 1.1  
δ between atom 2 and atom 3 = 0.35  
1st variation = 0.87  
2nd variation = 101.5  
 $(\text{SIGMA})^2 = 0.0072546$ 
```

Note that the program will only write $(\text{SIGMA})^2$ values (with the corresponding parameter) to the file that are smaller than the tolerance you have specified. If the file should contain nothing, you may have to increase your tolerance.

Note also that the number of calculations is multiplied with every parameter you vary.

2.7 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	<i>filename</i> .OUT, ENERTOT.DAT, ENERNI.DAT, <i>filename</i> .MO
	EDiT	<i>filename</i> .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

2.8 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) ₃ Al-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 ₂ C=CH ₂][N-(CH ₃) ₂]Pt = <i>trans</i> -Dichloromethyl-aminoethyleneplatinum(II). Internal coordinates with variation of the [H ₂ C = 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 ₃ C-CH ₃ molecule at equilibrium geometry. Internal coordinates with variation along the C-C and the C-H bonds.
ETHENE.GEN	Input example, H ₂ C-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 ₂ O molecule at equilibrium geometry.
H2OIT.KAR	Input example, H ₂ O molecule at equilibrium geometry. Charge iteration on all atoms.
H2OFA1.GEN	Input example, H ₂ O molecule. Internal coordinates with variation along the totally symmetric A ₁ stretching and bending modes: 0.9 Å ≤ r ₁ , r ₂ ≤ 1.1 Å and 100° ≤ φ ≤ 160°.
H2OFB1.GEN	Input example, H ₂ O molecule. Internal coordinates with variation along the asymmetric stretching mode B ₁ : 0.9 Å ≤ r ₁ , r ₂ ≤ 1.1 Å and α = 105°.
MNO4-.KAR	Input example, permanganate at equilibrium geometry. Charge iteration on Mn only.
PROOPEN_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 ₂ C = 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 < FORMAL.EDI > FORMAL.EDO
```

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							
<u>a</u>	10	2	4	0			
	10	1	4	0			
<u>b</u>	ZEISE-SALT						
<u>c</u>	0	10	-1	0	0	1FFFFFFF	2.00 .000 .000FFFFFFFFFFFFFFFFFF
<u>d</u>	.350000						
<u>e</u>	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		
<u>f</u>	*	*CLCL	*C	*	H H H		
<u>g</u>	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			
<u>m</u>	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 (I), FMO specifications (i), individual $1 + \kappa, \delta$ 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	FFFFFFFFFFFFFFFFFF
NH	NA	KA	ME	IP	IU	F1-F9	CON	PEEP	COULH	PRT(I) I01 , 22

FORMAT(6I3,9L1,F5.2,2F6.3,22L1)

NH = not used
 NA = number of atoms
 KA = charge of the molecule
 ME = METH calculation method. 0 = without, 2 = with charge iteration
 .GEN files do not allow METH = 2
 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**, etc. having code number **I**. Moby output is an exception here. If PRT(22) = .TRUE., Moby output will be performed.

CODE NUMBER I	PRINT-OPTION TABLE	IPRINT						
		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	x
3	Distance matrix	x	x	x	x	x	x	x
4	Overlap matrix	x	x	x	x	x	x	x
5	Madelung parameters	x	x	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	x	x
9	Total energy	x	x	x	x	x	x	x
10	Wavefunctions	x	x	x	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 (yes if T)							

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		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	EXPDI	COULD	C1	EXPDI2	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

COULS	s electron H_{ii}^*
EXPP	p electron exponent
COULP	p electron H_{ii}^*
ND	d electron principal quantum number
EXPDI	d electron first exponent
COULD	d electron H_{ii}^*
C ₁	coefficient of EXPDI
EXPD ₂	d electron exponent 2
C ₂	coefficient of EXPD ₂

C₁, EXPD₂ and C₂ are required if double ζ orbitals are used:

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

* 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 1 + k, δ . If $\delta = 0.0$, 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 = r, 2 = a, and 3 = 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 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 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:

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

where ρ is the summed orbital occupation of a given type, s , p , or d , indexed by r on the k^{th} 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

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

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, $\text{ADJUST} = \text{DENOM}^k$ (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, $\text{ADJUST} = \text{DAMP1} * \text{DENOM}^k$. $0 < \text{DAMP1} \leq \lambda$. DAMP1 is usually set to 0.10, but can be increased if the initial guess is known to be particularly good.
3. $\text{ADJUST} = \text{DAMP2} * \text{DENOM}^k$ is used whenever λ becomes equal to or greater than λ' . $0 < \text{DAMP2} \leq \lambda'$. DAMP2 should be nearly equal to λ' as possible.
4. Whenever $\max[(\rho_r^{output_k} - \rho_r^{input_k})]$ is of different sign than $\max[(\rho_r^{output_{k-1}} - \rho_r^{input_{k-1}})]$, two options are possible:
 - a) $\text{DAMP3} \neq 0$. $\text{ADJUST} = \text{DAMP3} * \text{ADJUST}$ where $0 < \text{DAMP3} \leq 1.0$
 - b) $\text{DAMP3} = 0$. 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 $\text{DENOM}^k < \text{DELTAC}$ 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 **Linear Combination of Atomic Orbitals to Molecular Orbitals** – 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.

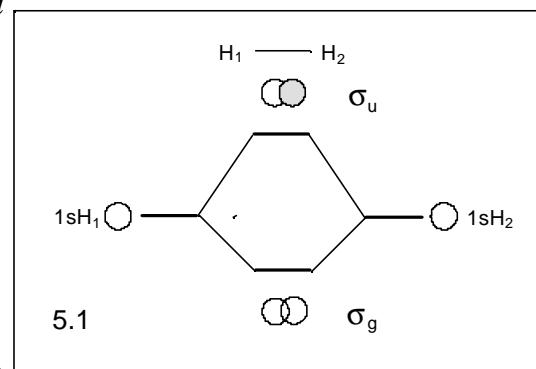
This limitation can be dropped when required.

This rule can be illustrated with the H₂ molecule.

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

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

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



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.

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

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

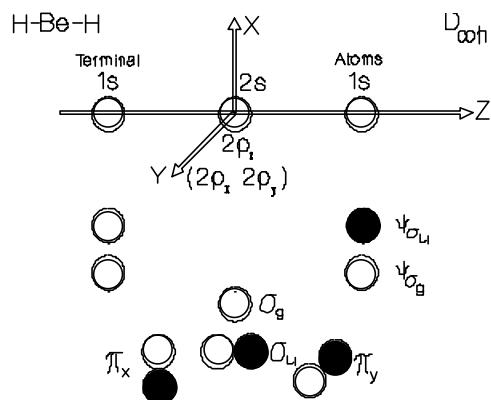
$$\langle \Psi_{\sigma_u} | \Psi_{\sigma_u} \rangle = \langle (1s(H_1) - 1s(H_2))(1s(H_1) - 1s(H_2)) \rangle \cdot \frac{1}{2(1-S)} \quad (5.3)$$

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

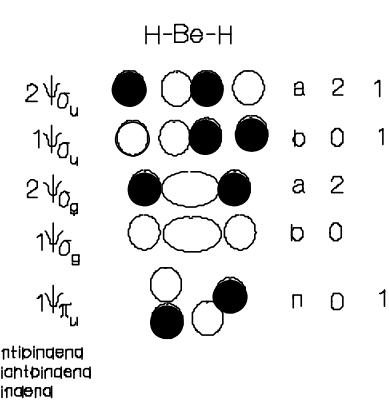
$$\langle \Psi_{\sigma_u} | \Psi_{\sigma_u} \rangle = (1 + 1 - 2S) \cdot \frac{1}{2(1-S)} = 1 \quad (5.5)$$

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 stands 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 antibonding 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.

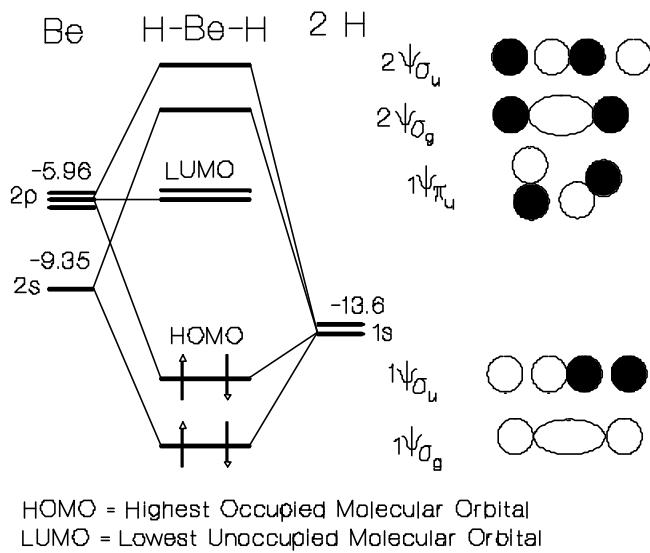


Figure 5.1: Qualitative MO-diagram of the linear $H—Be—H$ molecule. For orbitals with the same symmetry, the MO's are numbered advancing from low energy towards higher energy. The determination of the 1s orbitals of H and of the 2s and the 2p orbitals of Be on the basis of the experimental ionization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

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

$$(1\Psi_{\sigma_g})^2 (1\Psi_{\sigma_u})^2 \quad (5.6)$$

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 :

$$\begin{aligned} IP_1: & (1s)^2 (\Psi_{\sigma_g})^2 (\Psi_{\sigma_u})^1 \leftarrow (1s)^2 (\Psi_{\sigma_g})^2 (\Psi_{\sigma_u})^2 \\ IP_2: & (1s)^2 (\Psi_{\sigma_g})^1 (\Psi_{\sigma_u})^2 \leftarrow (1s)^2 (\Psi_{\sigma_g})^2 (\Psi_{\sigma_u})^2 \\ IP_3: & (1s)^1 (\Psi_{\sigma_g})^2 (\Psi_{\sigma_u})^2 \leftarrow (1s)^2 (\Psi_{\sigma_g})^2 (\Psi_{\sigma_u})^2 \end{aligned} \quad (5.7)$$

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:

$$a_0 := 0.529$$

$$Z := 1$$

$$\zeta := \frac{Z}{a_0}$$

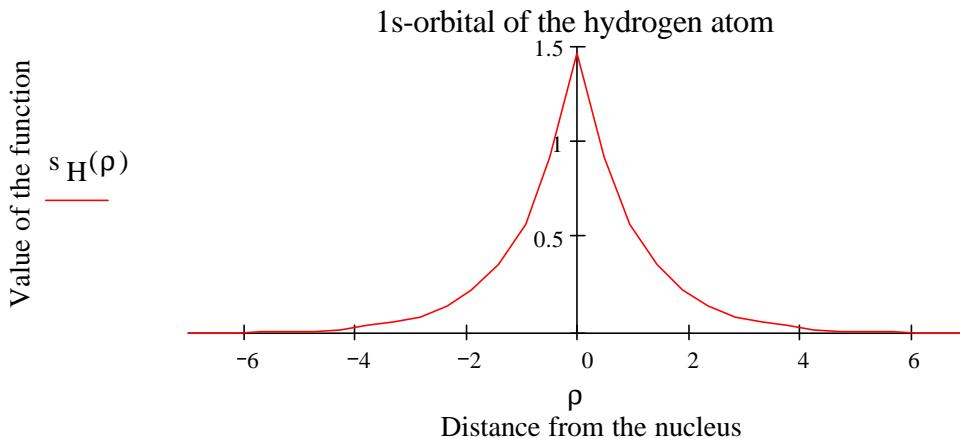
Distance $\rho = r \cdot (Z/a_0)$:

$$\rho := -7 \cdot \zeta, -6.75 \cdot \zeta, \dots, 7 \cdot \zeta$$

1s orbital:

$$N_H := \sqrt{\frac{1}{4 \cdot \pi}} \cdot 2 \cdot \zeta^{\frac{3}{2}}$$

$$s_H(\rho) := N_H \cdot e^{-|\rho|}$$



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 :

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

The negative linear combination results in the antibonding interactions:

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

For the following we need some definitions:

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

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

Orbitals of the two H atoms:

$$s_{H1}(\rho) := N_H \cdot e^{-|\rho_i + \rho_e|} \quad s_{H2}(\rho) := N_H \cdot e^{-|\rho_i - \rho_e|}$$

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

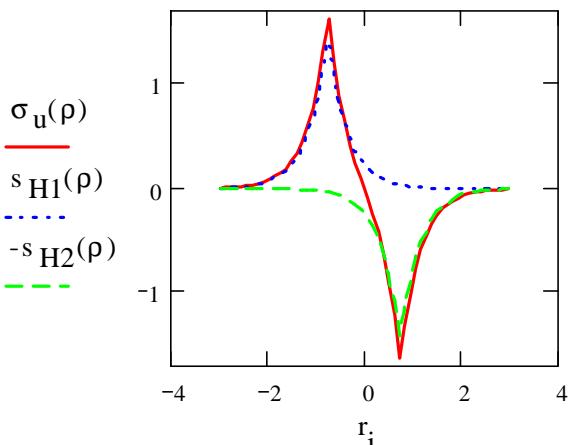
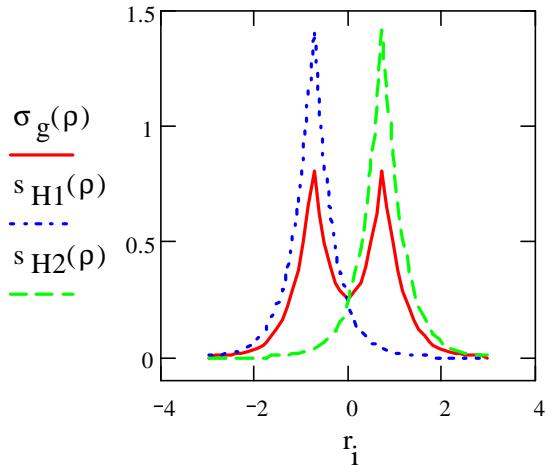
$$S_e := \left(1 + \rho_e + \frac{\rho_e^2}{3} \right) \cdot e^{-\rho_e}$$

Bonding linear combination:

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

Antibonding linear combination:

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

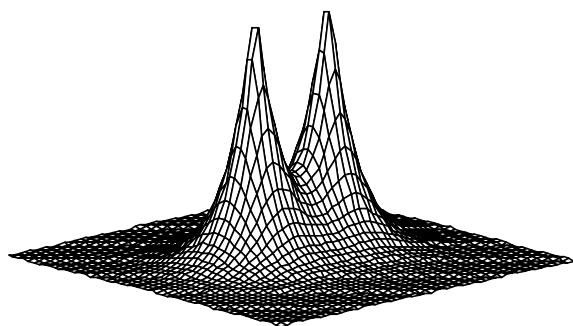


3-dimensional illustration:

$$s_1(x, y) := N_H \cdot e^{-[(x + \rho_e)^2 + y^2]^{0.5}} \quad s_2(x, y) := N_H \cdot e^{-[(x - \rho_e)^2 + y^2]^{0.5}}$$

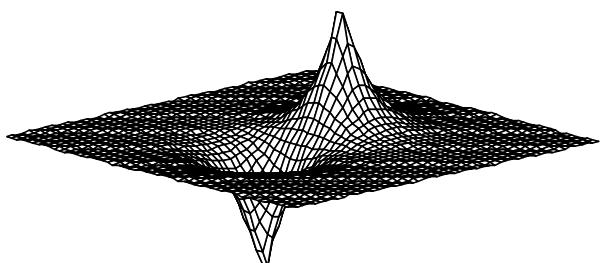
$$\sigma_{g_{i,j}} := (s_1(x_i, y_j) + s_2(x_i, y_j)) \cdot \frac{1}{\sqrt{2 \cdot (1 + S_e)}} \quad \sigma_{u_{i,j}} := (s_1(x_i, y_j) - s_2(x_i, y_j)) \cdot \frac{1}{\sqrt{2 \cdot (1 - S_e)}}$$

Bonding MO



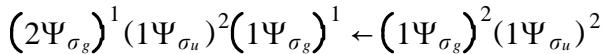
σ_g

Antibonding MO



σ_u

The electronic absorption spectrum of BeH₂ is described by the following two transitions:



If one tries to bend BeH₂, the 1Ψ_{σ_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 BeH₂ 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 BeH₂ is of hydridic nature. During the reaction from n × BeH₂ to (BeH₂)_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.

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

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

$$\hat{H} = \hat{H}_{EHMO} + \hat{H}_{rep} \quad (5.10)$$

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:

$$\Phi(1, 2, 3, \dots, N_A + N_B) = \quad (5.11)$$

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

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

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

with

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

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:

$$\Psi_i = \sum_{r_k} c_{ir_k} \chi_{r_k} + \sum_{s_l} c_{is_l} \chi_{s_l} \quad (5.14)$$

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:

$$\Psi(c_A, c_B) = c_A \chi_A + c_B \chi_B \quad (5.15)$$

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

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

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

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:

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

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

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

$$\Phi(1, 2) = \Psi_1(1) \cdot \Psi_2(2) \quad (5.19)$$

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

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

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

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

$$\begin{aligned} \langle \Phi(1, 2) | \hat{H}_{EHMO} | \Phi(1, 2) \rangle &= \\ \langle \Psi_2(2) | \Psi_2(2) \rangle \langle \Psi_1(1) | \hat{h}(1) | \Psi_1(1) \rangle + \langle \Psi_1(1) | \Psi_1(1) \rangle \langle \Psi_2(2) | \hat{h}(2) | \Psi_2(2) \rangle &= (5.21) \end{aligned}$$

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

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

This leads to:

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

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

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

For this purpose, Ψ is inserted:

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

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:

$$\langle \Psi | \hat{h} | \Psi \rangle = \varepsilon(c_A, c_B) \langle \Psi | \Psi \rangle \quad (5.26)$$

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:

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

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

$$\langle \Psi | \hat{h} | \Psi \rangle = \langle (c_A\chi_A + c_B\chi_B) | \hat{h} | (c_A\chi_A + c_B\chi_B) \rangle \quad (5.28)$$

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

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

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

$$\langle \chi_A | \hat{h} | \chi_B \rangle = \langle \chi_B | \hat{h} | \chi_A \rangle \quad (5.29)$$

If the following abbreviations are applied,

$$h_{AA} = \langle \chi_A | \hat{h} | \chi_A \rangle \quad h_{AB} = \langle \chi_A | \hat{h} | \chi_B \rangle \quad (5.30)$$

$$h_{BB} = \langle \chi_B | \hat{h} | \chi_B \rangle \quad S = \langle \chi_A | \chi_B \rangle \quad (5.31)$$

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

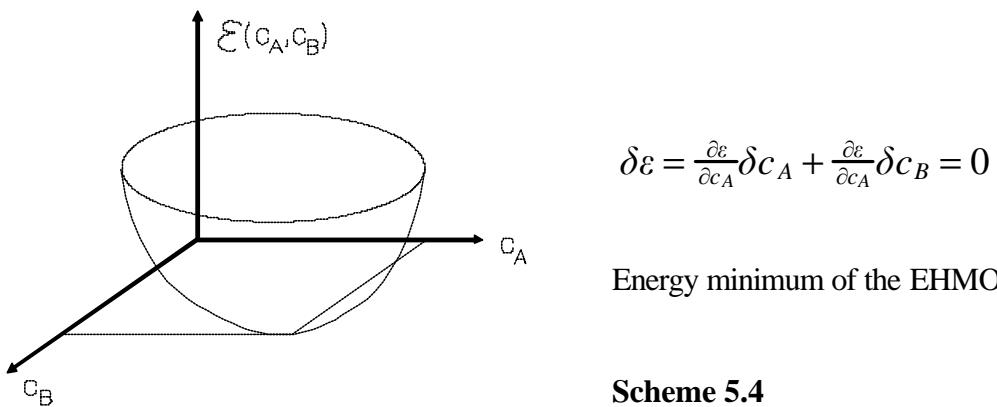
$$\langle \Psi | \hat{h} | \Psi \rangle = c_A^2 h_{AA} + c_B^2 h_{BB} + 2c_A c_B h_{AB} \quad (5.32)$$

$$\langle \Psi | \Psi \rangle = c_A^2 + c_B^2 + 2c_A c_B \cdot S \quad (5.33)$$

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

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

The coefficients c_A, c_B must be chosen in such a way that the energy values correspond to a physically acceptable situation. Because $\Psi^2 = c_A^2 \chi_A^2 + c_B^2 \chi_B^2 + 2c_A c_B \chi_A \chi_B$ 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.



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:

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

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 :

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

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

or:

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

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:

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

This leads to the following problem:

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

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

with the solutions:

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

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:

$$\langle \Psi^+ | \Psi^+ \rangle = 1 \quad \langle \Psi^- | \Psi^- \rangle = 1 \quad \langle \Psi^+ | \Psi^- \rangle = 0 \quad (5.41)$$

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

$$1 = c_A^2 + c_B^2 + 2c_A c_B S \quad c_A = -c_B \frac{h_{AB} - \epsilon S}{h_{AA} - \epsilon} \quad (5.42)$$

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:

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

and correspondingly

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

This leads to the following results:

$$\begin{vmatrix} h_{AA} - \epsilon & h_{AB} - \epsilon S \\ h_{BA} - \epsilon S & h_{AA} - \epsilon \end{vmatrix} = 0$$

$$\epsilon_-^+ = \frac{h_{AA} \pm h_{AB}}{1 \pm S} \quad \Psi_-^+ = \frac{1}{\sqrt{2 \pm 2S}} (\chi_A \pm \chi_B)$$

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 $\{\epsilon^+, \Psi^+\}$ which, compared with the initial state, is stabilized and in a destabilized orbital $\{\epsilon^-, \Psi^-\}$. The orbital stabilization energy $\Delta\epsilon^+$ and the orbital destabilization $\Delta\epsilon^-$ energy are expressed as:

$$\Delta\epsilon^+ = \frac{h_{AA} + h_{AB}}{1+S} - h_{AA} \Rightarrow \Delta\epsilon^+ = \frac{h_{AB} - Sh_{AA}}{1+S} \quad (5.43)$$

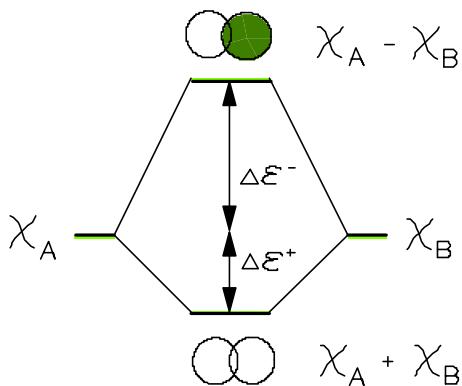
$$\Delta\epsilon^- = \frac{h_{AA} - h_{AB}}{1-S} - h_{AA} \Rightarrow \Delta\epsilon^- = \frac{h_{AB} - Sh_{AA}}{1-S} \quad (5.44)$$

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} :

$$\Delta E_{EHMO} = n^+ \Delta \varepsilon^+ + n^- \Delta \varepsilon^- \quad (5.45)$$

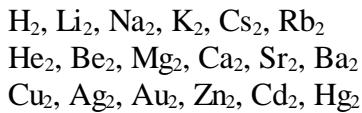
For a system to be stable within the EHMO theory, ΔE_{EHMO} must compensate the core-core repulsion, so that the following is true:

$$\Delta E_{EHMO} + E_{rep} < 0 \quad (5.46)$$



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



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.

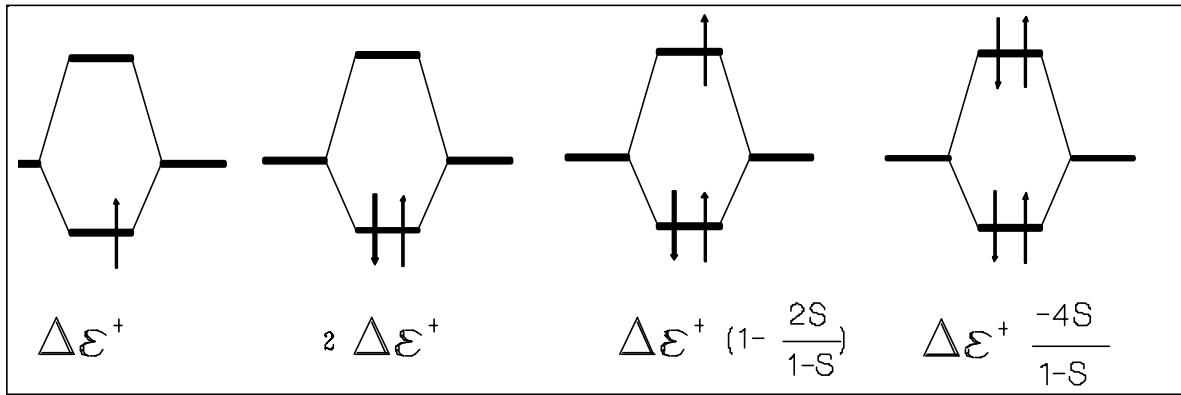


Figure 5.3: Orbital stabilization energies ΔE_{EHMO} in units of $\Delta\epsilon^+$ for the electron configurations $(\Psi_{\sigma_g})^1$, $(\Psi_{\sigma_g})^2$, $(\Psi_{\sigma_g})^2(\Psi_{\sigma_u})^1$, $(\Psi_{\sigma_g})^2(\Psi_{\sigma_u})^2$ with $(n^+, n^-) = (1,0), (2,0), (2,1), (2,2)$.

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.

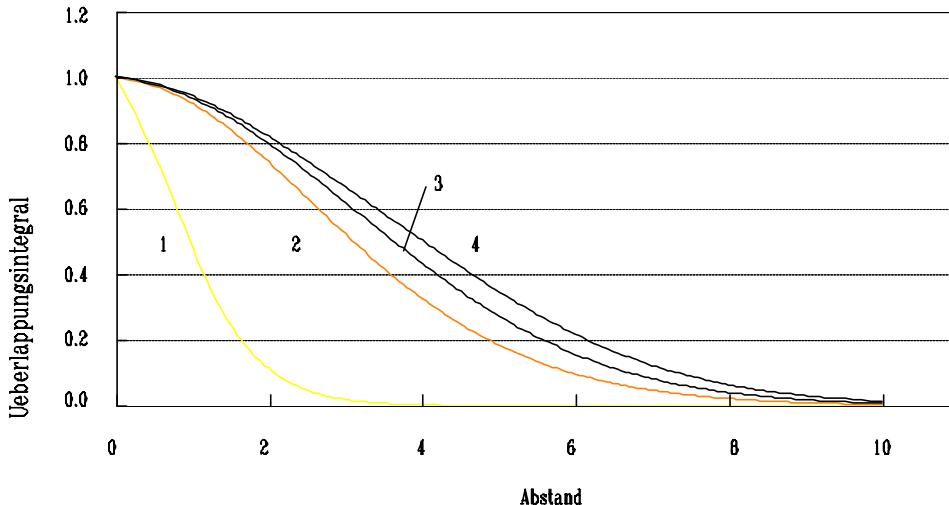


Figure 5.4: $\langle ns|ns \rangle$ overlap integrals of H_2 , Li_2 , Na_2 and K_2 as function of the distance (in Å). 1: $n=1$, $\zeta=1.3$; 2: $n=2$, $\zeta=0.64$; 3: $n=3$, $\zeta=0.733$; 4: $n=4$, $\zeta=0.816$.

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:

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

From this we can derive that the negative quantity h_{AB} is always smaller than $S h_{AA}$. Thus we obtain the certainty that $h_{AB} - S h_{AA}$ 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	$\Delta \varepsilon^+ \left(1 - \frac{2S}{1-S}\right)$	$S < 1/3$ 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	$1 - \Delta \varepsilon^+ \left(-\frac{4S}{1-S}\right)$	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:

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

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.

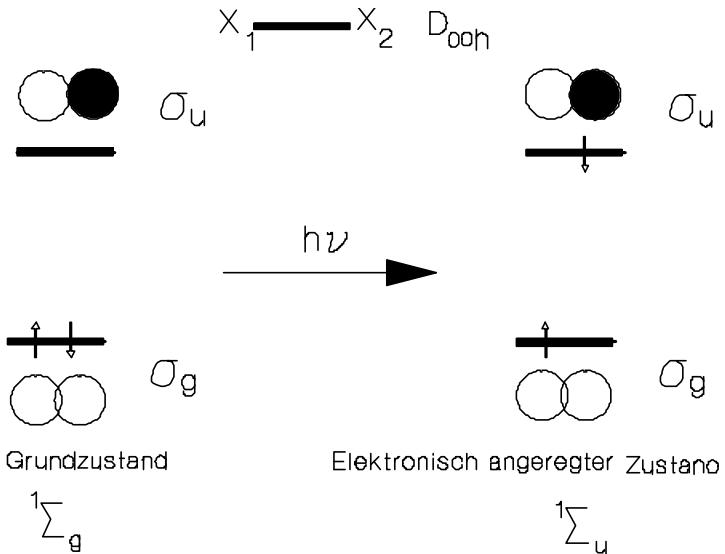


Figure 5.5: We illustrate the electronic ground state configuration σ_g^2 and the first excited state configuration $\sigma_g^1\sigma_u^1$. Indicated are also the symbols of the corresponding symmetry states.

In order to excite an electron from the σ_g to the σ_u orbital according to Figure 5.5, the excitation energy $\Delta E(\sigma_u \leftarrow \sigma_g) = h\nu$ (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:

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

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: $D_e = D_0 + \omega_e/2$. We remark that $\Delta E(B^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+)$ corresponds to $\Delta E(\sigma_u \leftarrow \sigma_g)$.

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 H₂ 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

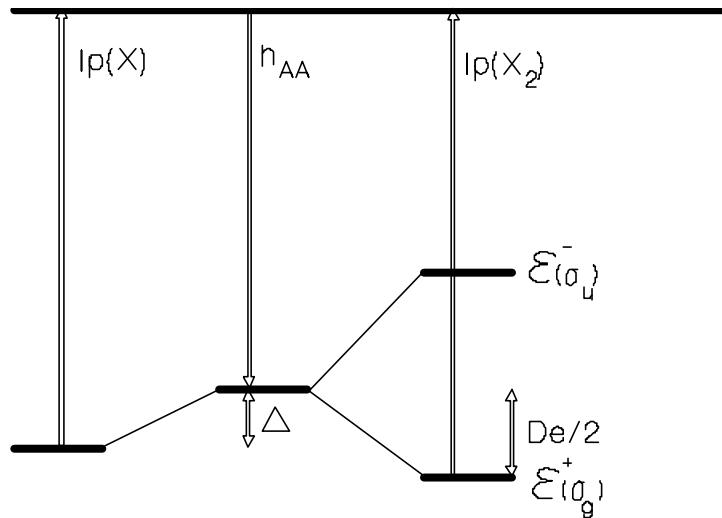


which takes place within about 10⁻¹⁵ s, it is expected that the first ionization energy of these molecules is approximately equal to the orbital energy $\varepsilon^+(\sigma_g)$:

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

$$\text{The use of } \frac{D_e}{2} = -\frac{h_{AA} + h_{AB}}{1+S} + h_{AA} \quad (5.53)$$

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



$$IP(X_2) = IP(X) - \Delta + De/2$$

Figure 5.6: 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:

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

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

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

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:

$$Ip(X_2) \approx b + m \cdot IP(X) \quad (5.57)$$

A comparison with (5.52) leads to:

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

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

$$h_{AB} = S \cdot k \cdot h_{AA} \quad (5.59)$$

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

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

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

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

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:

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

With $S = 0.6$ we obtain $k = 1.59$.

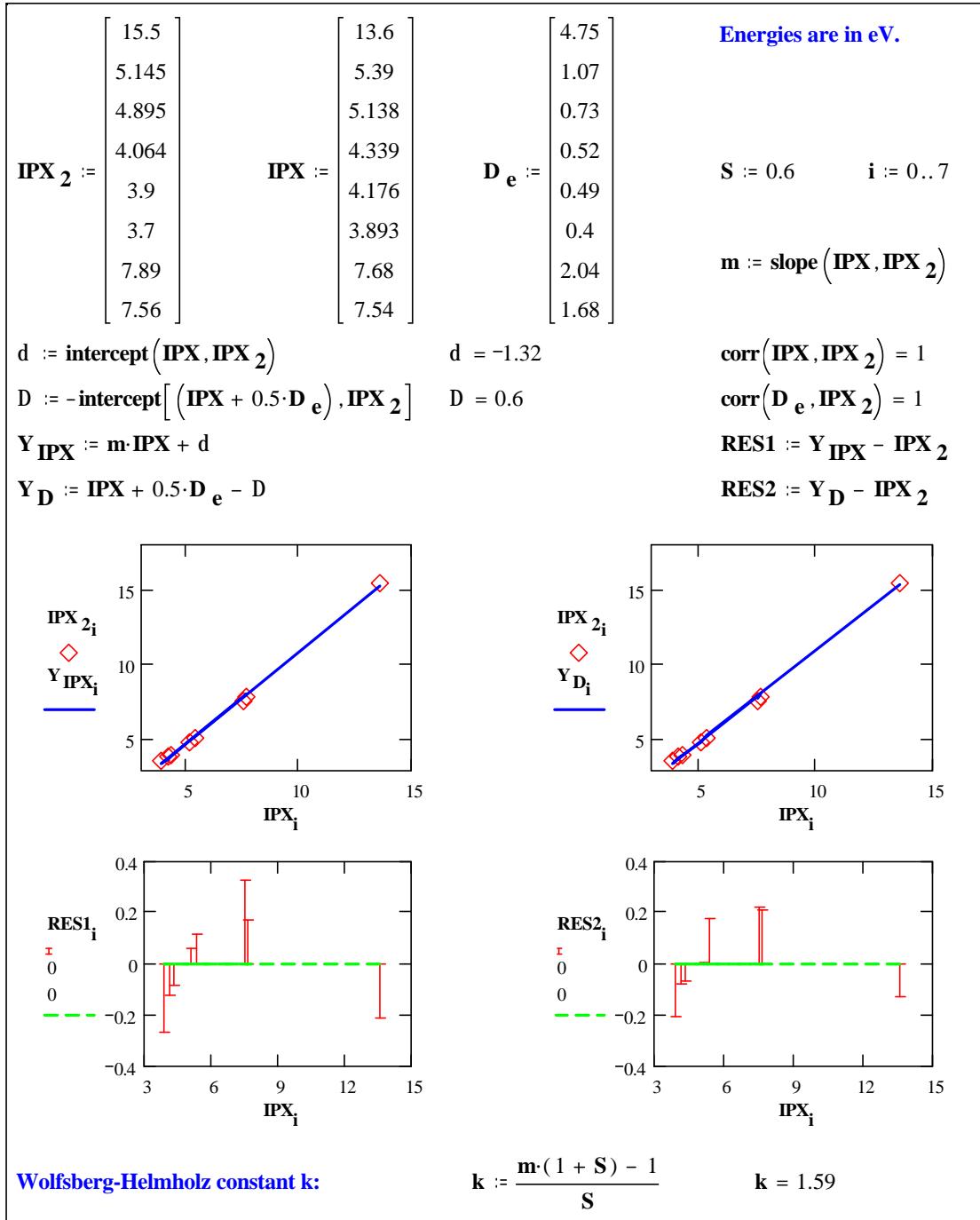


Figure 5.7: Correlation between the ionization potential of the atoms with the ionization potential and with the dissociation energy of the diatomic molecules.

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.)

```

HE2EN      Contains the input information in internal coordinate
           1   1   1   0
           1   0   1   0
HYDROGEN MOLECULE
  0 2 0 0 0 1FFFFFFFFF 1.58 .000 .000FFFFFFFFFFFFFFFFFF
           .410000
  1   2   -74140     .00000     .00000

```

* 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	N	EXP	S	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.

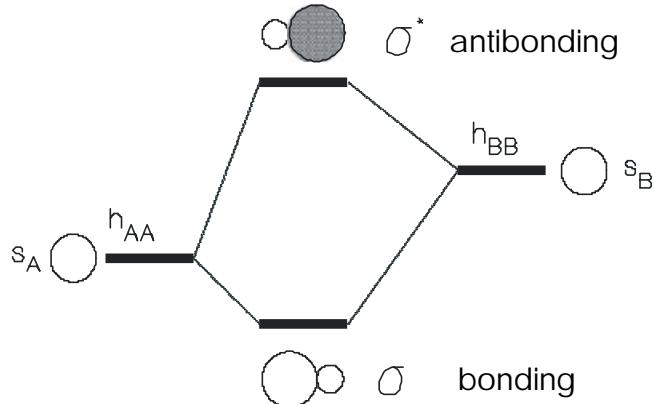


Figure 5.8: Molecular orbitals σ and σ^* , which result from the s_A and s_B atomic orbitals.

It will prove useful to introduce the following definitions:

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

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

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

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

$$\Psi = c_A \chi_A + c_B \chi_B \quad (5.65)$$

with the use of

$$\begin{pmatrix} a-\epsilon & \beta-\epsilon S \\ \beta-\epsilon S & -1-\epsilon \end{pmatrix} \cdot \begin{pmatrix} c_A \\ c_B \end{pmatrix} = 0 \quad (5.66)$$

The necessary equations are:

$$c_A^2 + c_B^2 + 2c_A c_B S = 1 \quad (5.67)$$

$$(a-\epsilon)c_A + (\beta-\epsilon S)c_B = 0$$

which, with

$$c_B = -\frac{a-\epsilon}{\beta-\epsilon S} c_A \quad q := -\frac{a-\epsilon}{\beta-\epsilon S} \quad c_A^2 + q^2 c_A^2 + 2c_A^2 q S = 1 \quad (5.68)$$

can be brought to the following form:

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

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_+ , $N_+ = 0, 1$ or 2 . The electron density distribution in this orbital is described by

$$N_+(\Psi_+)^2 = N_+(c_A^+)^2 \chi_A^2 + 2N_+ c_A^+ c_B^+ \chi_A \chi_B + N_+(c_B^+)^2 \chi_B^2 \quad (5.70)$$

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:

$$\begin{aligned} N_+ < \Psi_+ | \Psi_+ > &= N_+(c_A^+)^2 < \chi_A | \chi_A > + 2N_+ c_A^+ c_B^+ < \chi_A | \chi_B > + N_+(c_B^+)^2 < \chi_B | \chi_B > \\ \Rightarrow N_+ &= N_+(c_A^+)^2 + 2N_+ c_A^+ c_B^+ S + N_+(c_B^+)^2 \end{aligned} \quad (5.71)$$

$N_+(c_A^+)^2$	is called <i>net population</i> at the centre A.
$N_+(c_B^+)^2$	is called <i>net population</i> at the centre B.
$2N_+ c_A^+ c_B^+ S$	is called <i>overlap-population</i> $n(A,B)$ 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* $N(A)$.

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

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

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

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

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

$$\beta = \frac{k_S}{2}(a - 1) \quad (5.74)$$

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 .

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

$$i := 0..2 \cdot N$$

$$\alpha_i := -\frac{i}{N}$$

$$\beta_i := 0.5 \cdot k \cdot S \cdot (\alpha_i - 1)$$

abbreviations:

$$f_{1i} := \frac{\alpha_i - 1 - 2 \cdot \beta_i \cdot S}{2 \cdot (1 - S^2)}$$

$$f_{2i} := 4 \cdot (1 - S^2) \cdot \frac{\alpha_i + (\beta_i)^2}{(\alpha_i - 1 - 2 \cdot \beta_i \cdot S)^2}$$

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

$$\varepsilon_{bi} := f_{1i} \cdot \left(1 + \sqrt{1 + f_{2i}} \right) \quad \varepsilon_{ai} := f_{1i} \cdot \left(1 - \sqrt{1 + f_{2i}} \right)$$

abbreviations: -----

$$qb_i := \frac{\beta_i - \varepsilon_{bi} \cdot S}{\alpha_i - \varepsilon_{bi}}$$

$$qa_i := \frac{\beta_i - \varepsilon_{ai} \cdot S}{\alpha_i - \varepsilon_{ai}}$$

$$qcb_i := -\frac{1}{\text{if}(|qb_i| > 0, qb_i, qb_{i-1})}$$

$$qca_i := -\frac{1}{\text{if}(|qa_i| > 0, qa_i, qa_{i-1})}$$

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

$$cb_{Ai} := [1 + 2 \cdot S \cdot qcb_i + (qcb_i)^2]^{-0.5}$$

$$ca_{Ai} := [1 + 2 \cdot S \cdot qca_i + (qca_i)^2]^{-0.5}$$

$$cb_{Bi} := qcb_i \cdot cb_{Ai}$$

$$ca_{Bi} := -qca_i \cdot ca_{Ai}$$

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

$$opb_i := 2 \cdot cb_{Ai} \cdot cb_{Bi} \cdot S$$

$$nb_{Ai} := \frac{1}{2} \cdot opb_i + (cb_{Ai})^2$$

$$nb_{Bi} := \frac{1}{2} \cdot opb_i + (cb_{Bi})^2$$

$$opa_i := -2 \cdot ca_{Ai} \cdot ca_{Bi} \cdot S$$

$$na_{Ai} := \frac{1}{2} \cdot opa_i + (ca_{Ai})^2$$

$$na_{Bi} := \frac{1}{2} \cdot opa_i + (ca_{Bi})^2$$

Figure 5.9: Heteronuclear diatomics

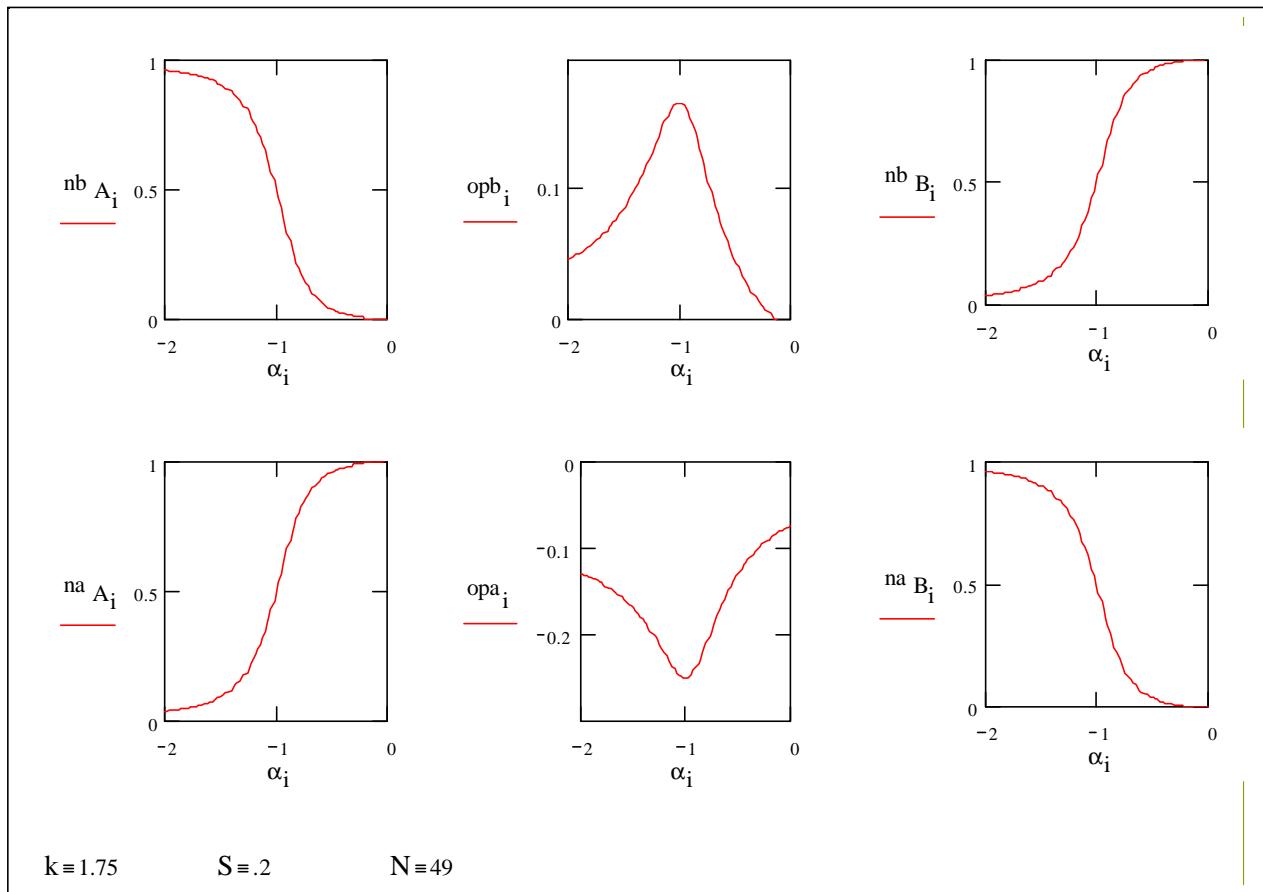
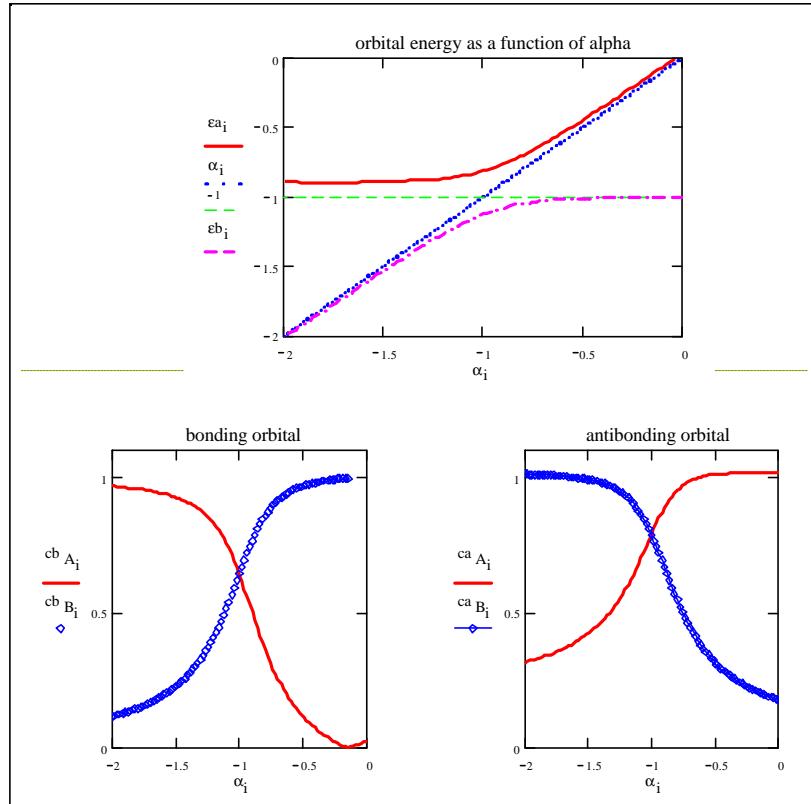


Figure 5.10: Heteronuclear diatomics

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:

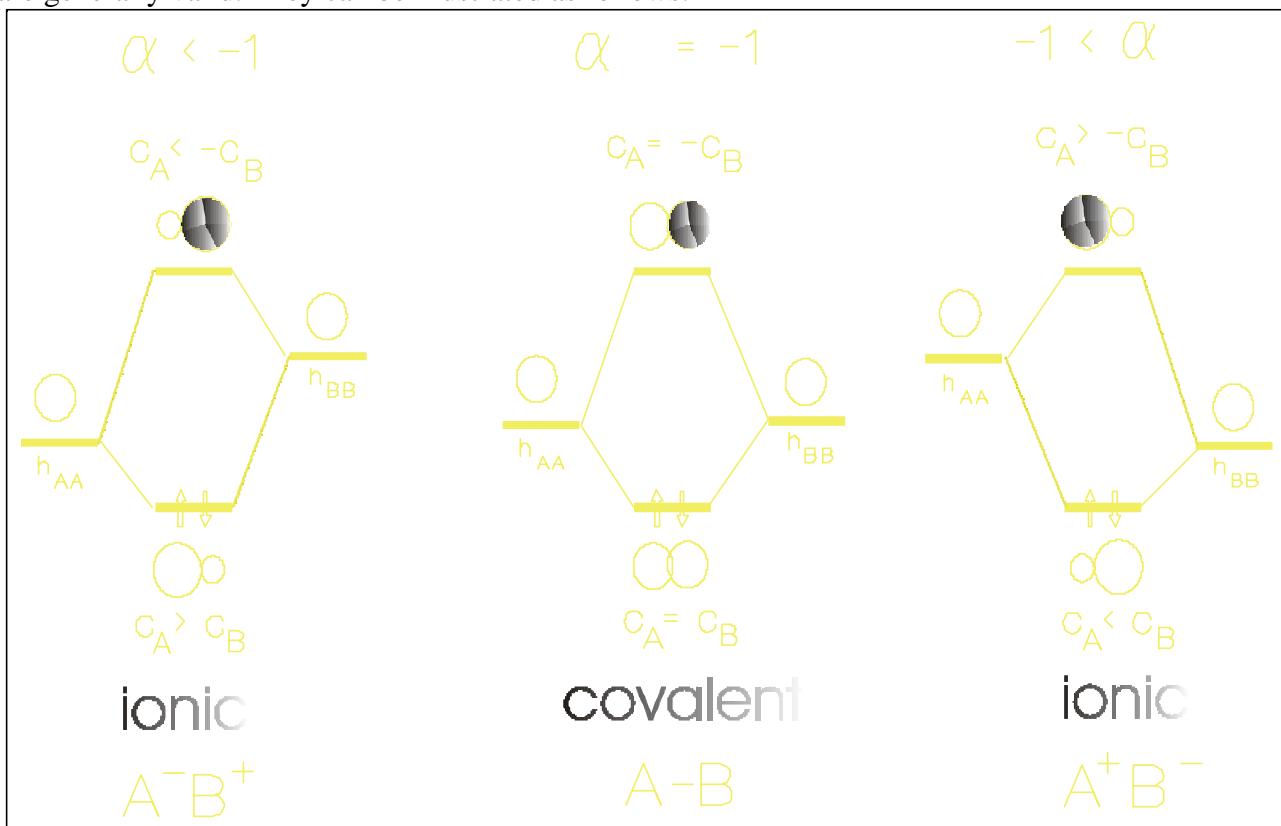


Figure 5.11: Qualitative comparison between covalent and ionic diatomics in the MO-picture.

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
$\alpha(HX)$	-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
$\bar{\lambda}_e[\text{cm}^{-1}]$	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, $h_{AA} = -Ip(H)$, $h_{XX} = -Ip(X)$, $\alpha = -Ip(X)/Ip(H)$. In the following diagram, the population analysis of the (s_A, s_B) σ orbital occupied by 2 electrons and the orbital stabilization energies $\Delta\epsilon_+$ and $\Delta\epsilon_-$ 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.

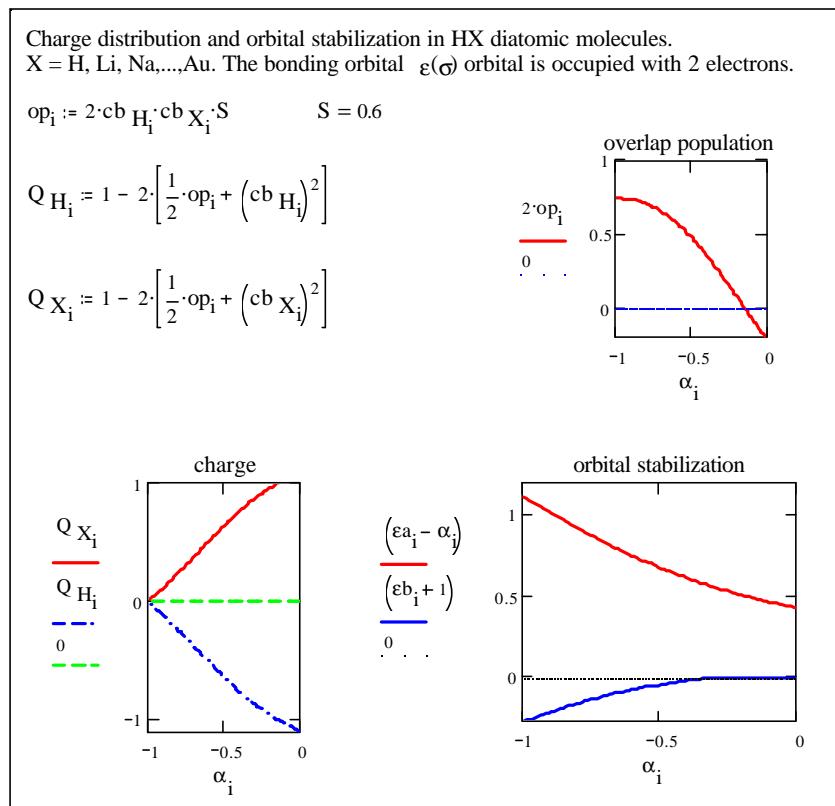


Figure 5.12: Illustration of the hydridic character of hydrogen bonded to a metal.

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, v, 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

$$\Psi_i = \sum_{r_k} c_{ir_k} \chi_{r_k} + \sum_{s_l} c_{is_l} \chi_{s_l} \quad (5.75)$$

and to the EHMO-Operator

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

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

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

(5.77)

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

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

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

$$\varepsilon = \varepsilon(c_1, c_2, \dots, c_n) = \frac{\left\langle \sum_{\mu=1}^n c_{\mu} \chi_{\mu} \mid \hat{h} \mid \sum_{v=1}^n c_v \chi_v \right\rangle}{\left\langle \sum_{\mu=1}^n c_{\mu} \chi_{\mu} \mid \sum_{v=1}^n c_v \chi_v \right\rangle} = \frac{Z}{N} \quad (5.79)$$

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:

$$d\varepsilon = \frac{\partial \varepsilon}{\partial c_1} dc_1 + \frac{\partial \varepsilon}{\partial c_2} dc_2 + \dots + \frac{\partial \varepsilon}{\partial c_n} dc_n = 0 \quad (5.80)$$

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

$$\frac{\partial \varepsilon}{\partial c_i} = 0 \quad \forall i \quad (5.81)$$

The calculation is carried out for c_n :

$$\frac{\partial \varepsilon}{\partial c_v} = \frac{\partial}{\partial c_v} \frac{Z}{N} = \frac{N \frac{\partial Z}{\partial c_v} - Z \frac{\partial N}{\partial c_v}}{N^2} = \frac{\left[\frac{\partial Z}{\partial c_v} - \frac{Z}{N} \cdot \frac{\partial N}{\partial c_v} \right]}{N} = 0 \quad (5.82)$$

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

$$\frac{\partial Z}{\partial c_v} - \frac{Z}{N} \cdot \frac{\partial N}{\partial c_v} = \frac{\partial Z}{\partial c_v} - \varepsilon \frac{\partial N}{\partial c_v} = 0; \quad v = 1, 2, \dots, n. \quad (5.83)$$

We introduce the following abbreviations:

$$h_{\mu\nu} := \langle \chi_\mu | \hat{h} | \chi_\nu \rangle \quad S_{\mu\nu} := \langle \chi_\mu | \chi_\nu \rangle \quad (5.84)$$

$$\frac{\partial Z}{\partial c_v} = \frac{\partial}{\partial c_v} \cdot \left\langle \sum_{\mu=1}^n c_\mu \chi_\mu | \hat{h} | \sum_{\rho=1}^n c_\rho \chi_\rho \right\rangle \quad (5.85)$$

$$\frac{\partial Z}{\partial c_v} = \frac{\partial}{\partial c_v} \cdot \sum_{\mu=1}^n \sum_{\rho=1}^n c_\mu c_\rho \langle \chi_\mu | \hat{h} | \chi_\rho \rangle \quad (5.86)$$

$$\frac{\partial Z}{\partial c_v} = \frac{\partial}{\partial c_v} \cdot \sum_{\mu=1}^n \sum_{\rho=1}^n c_\mu c_\rho h_{\mu\rho} \quad (5.87)$$

Calculation results in:

$$\frac{\partial Z}{\partial c_v} = 2 \sum_{\mu=1}^n c_\mu h_{v\mu} \quad (5.88)$$

In similar manner, the following can be found:

$$\frac{\partial N}{\partial c_v} = 2 \sum_{\mu=1}^n c_\mu S_{v\mu} \quad (5.89)$$

Insertion of these results in

$$\frac{\partial Z}{\partial c_v} - \varepsilon \frac{\partial N}{\partial c_v} = 0 \quad (5.90)$$

leads to the important result:

$$2 \sum_{\mu=1}^n c_\mu h_{v\mu} - 2\varepsilon \sum_{\mu=1}^n c_\mu S_{v\mu} = 0 \quad (5.91)$$

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

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

or written out in full:

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

$$c_1(h_{21} - \varepsilon S_{21}) + c_2(h_{22} - \varepsilon S_{22}) + \dots + c_n(h_{2n} - \varepsilon S_{2n}) = 0 \quad (5.94)$$

...

$$c_1(h_{n1} - \varepsilon S_{n1}) + c_2(h_{n2} - \varepsilon S_{n2}) + \dots + c_n(h_{nn} - \varepsilon S_{nn}) = 0 \quad (5.95)$$

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:

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

$$(H - \varepsilon S)C = 0 \quad (5.97)$$

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

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

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

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

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,

$$\varepsilon_i = \frac{\left\langle \sum_{\mu=1}^n c_{i\mu} \chi_\mu | \hat{h} | \sum_{v=1}^n c_{iv} \chi_v \right\rangle}{\left\langle \sum_{\mu=1}^n c_{i\mu} \chi_\mu | \sum_{\mu=1}^n c_{iv} \chi_v \right\rangle} \quad (5.100)$$

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

$$\varepsilon_i = \left\langle \sum_{\mu=1}^n c_{i\mu} \chi_\mu | \hat{h} | \sum_{v=1}^n c_{iv} \chi_v \right\rangle = \sum_{\mu=1}^n \sum_{v=1}^n c_{i\mu} c_{iv} h_{\mu v} \quad (5.101)$$

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

$$\varepsilon_i = \sum_{\mu=1}^n c_{i\mu}^2 h_{\mu\mu} + 2 \sum_{\mu<\nu} c_{i\mu} c_{i\nu} h_{\mu\nu} \quad (5.102)$$

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

$$E_{EHMO} = \sum_i b_i \varepsilon_i \quad (5.103)$$

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

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

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

$$\Delta E_{EHMO}(R) = E_{EHMO} - \sum_{\mu} b_{\mu} E_{\mu}^0 \quad (5.105)$$

$-\sum b_{\mu} E_{\mu}^0$ 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 $\rho(R_\alpha, r)$ for a diatomic molecule $\alpha - \beta$ is written as

$$\rho(R_\alpha, r) = \rho_a(R_\alpha - r) + \rho_{NPF}(R_\alpha, r) + \rho_\beta(r) \quad (5.106)$$

where the origin of the coordinate system is on nucleus \mathbf{b} . $\rho_\beta(r)$ and $\rho_a(R_\alpha - r)$ are atomic charge densities, centred on nucleus \mathbf{b} and nucleus \mathbf{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. $\rho_{NPF}(R_\alpha, r)$ 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 $E_{ab}(R)$ and the extended-Hückel binding energy $\Delta E_{EHMO}(R)$. $\rho_{NPF}(R_\alpha, r)$ can be estimated from the resulting wave functions.

$$E(R) = E_{ab}(R) + \Delta E_{EHMO}(R) \quad (5.107)$$

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

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

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:

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

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

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

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

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

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:

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

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:

$$\frac{\partial \hat{T}}{\partial R} = 0 \quad (5.113)$$

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

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

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

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

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:

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

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:

$$E = \left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle \quad (5.117)$$

and therefore:

$$\frac{\partial E}{\partial \lambda} = \left\langle \frac{\partial \Psi}{\partial \lambda} \left| \hat{H} \right| \Psi \right\rangle + \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \Psi \right\rangle + \left\langle \Psi \left| \hat{H} \right| \frac{\partial \Psi}{\partial \lambda} \right\rangle \quad (5.118)$$

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

$$\left\langle \Psi \left| \hat{H} \right| \frac{\partial \Psi}{\partial \lambda} \right\rangle = \left\langle \hat{H} \Psi \left| \frac{\partial \Psi}{\partial \lambda} \right\rangle \right\rangle = \left\langle \frac{\partial \Psi}{\partial \lambda} \left| \hat{H} \Psi \right\rangle \right\rangle = \text{real} \quad (5.119)$$

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

$$\frac{\partial E}{\partial \lambda} = \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \Psi \right\rangle + E \left\langle \frac{\partial \Psi}{\partial \lambda} \left| \Psi \right\rangle \right\rangle + E \left\langle \Psi \left| \frac{\partial \Psi}{\partial \lambda} \right\rangle \right\rangle \quad (5.120)$$

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

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

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

$$\frac{\partial \hat{H}}{\partial \lambda} = \frac{\partial \hat{T}}{\partial \lambda} + \frac{\partial \hat{V}}{\partial \lambda} = \frac{\partial \hat{V}}{\partial \lambda} \quad (5.123)$$

with which the Hellmann-Feynman theorem is proven:

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

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 :

$$F_R = -\frac{\partial V}{\partial R} \quad (5.125)$$

The quantum mechanical analog to this is:

$$F_R = \left\langle \frac{\partial V}{\partial R} \right\rangle \quad (5.126)$$

5.2.1 Application of the Hellmann-Feynman theorem

First we will examine the relation

$$F_R = \left\langle \frac{\partial V}{\partial R} \right\rangle \quad (5.127)$$

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

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

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:

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

$\mathbf{r}(x_i, y_i, z_i)$ is the probability density of electron i at x_i, y_i, z_i . We can write $\mathbf{r}(x_i, y_i, z_i)$ as $\mathbf{r}_i(x, y, z)$ and abbreviate it as \mathbf{r}_i . $e \mathbf{r}_i dt_i$ equals the charge contribution of electron i in the volume element dt_i .

Now we can write:

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

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:

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

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

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

results in the following equation

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

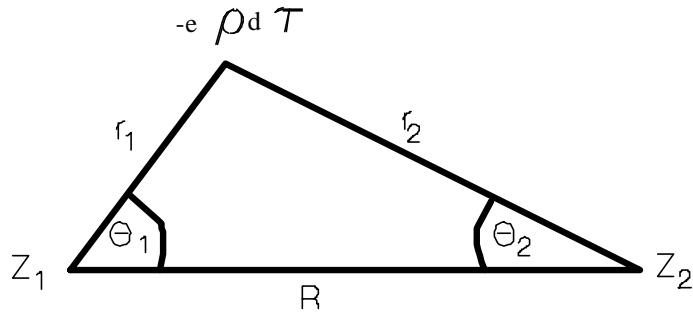


Figure 5.13

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

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

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

The derivative for $r_2 = \text{fix}$ is furnished by f_1 , and the one for $r_1 = \text{fix}$ is furnished by f_2 :

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

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

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

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

$e^2 f$ 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:

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

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 $d\tau$ are always positive, the sign of $f \rho d\tau$ 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:

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

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

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

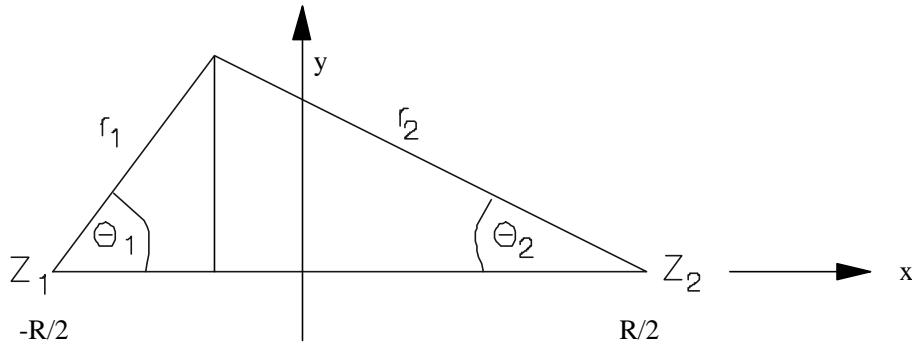


Figure 5.14

According to figure 5.14, we find:

$$r_1^2 = \left(\frac{1}{2}R + x\right)^2 + y^2 = \frac{1}{4}R^2[(1+\xi)^2 + \eta^2] \quad (5.142)$$

$$r_2^2 = \left(\frac{1}{2}R - x\right)^2 + y^2 = \frac{1}{4}R^2[(1-\xi)^2 + \eta^2] \quad (5.143)$$

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

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

Transformation of the *initial equations* leads to:

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

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

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

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 choosing 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.

Bonding and antibonding regions in diatomic molecules.

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

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

Starting value: $\eta := 0.01$

Given $\eta \geq 0$

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

$$f(\xi) := \text{Find}(\eta) \quad \eta_i := f(\xi_i)$$

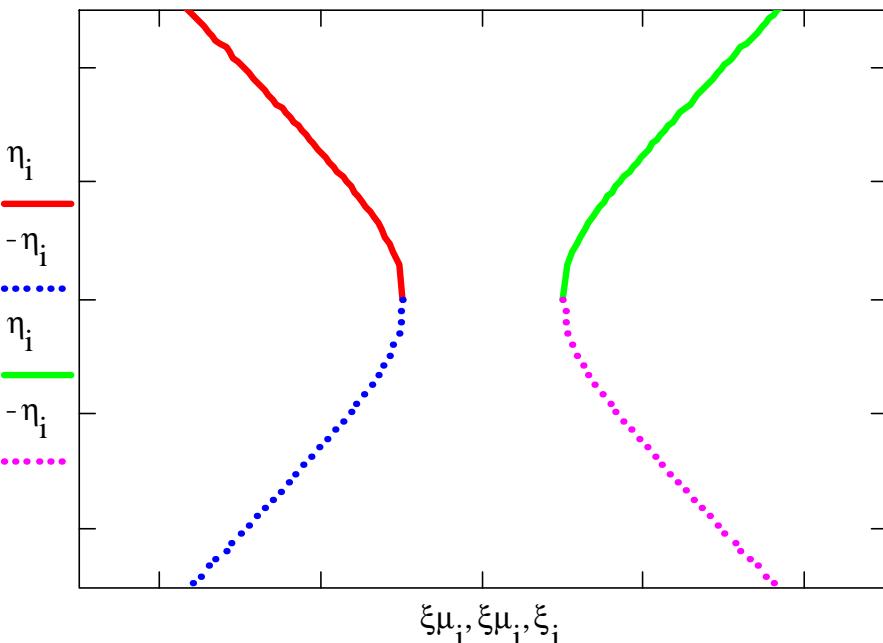


Figure 5.15: We observe that in the case of homonuclear molecules, the bonding region and the two antibonding regions are clearly separated. The bonding region mainly lies between the two nuclei, because with increasing $|\eta|$, the electron density decreases very rapidly.

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

First region:

$$\alpha := 0.5 \quad \eta := 0.01 \quad j := 0..100 \quad \xi_{1j} := 1.0 + j \cdot 0.01$$

Given

$$\left[\frac{(1 - \xi_1)}{(1 + \xi_1) \cdot \alpha} \right] = - \left[\frac{(1 - \xi_1)^2 + \eta^2}{(1 + \xi_1)^2 + \eta^2} \right]^{\frac{3}{2}} \quad \eta \geq 0 \quad f(\xi_1) := \text{Find}(\eta) \quad \eta_{1j} := f(\xi_{1j})$$

Second region:

$$\xi_{2j} := -1.0 - (j + 0.01) \cdot 0.0482 \quad \eta := -0.001$$

Given

$$\left[\frac{(1 - \xi_2)}{(1 + \xi_2) \cdot \alpha} \right] = - \left[\frac{(1 - \xi_2)^2 + \eta^2}{(1 + \xi_2)^2 + \eta^2} \right]^{\frac{3}{2}} \quad \eta \leq 0 \quad f(\xi_2) := \text{Find}(\eta) \quad \eta_{2j} := f(\xi_{2j})$$

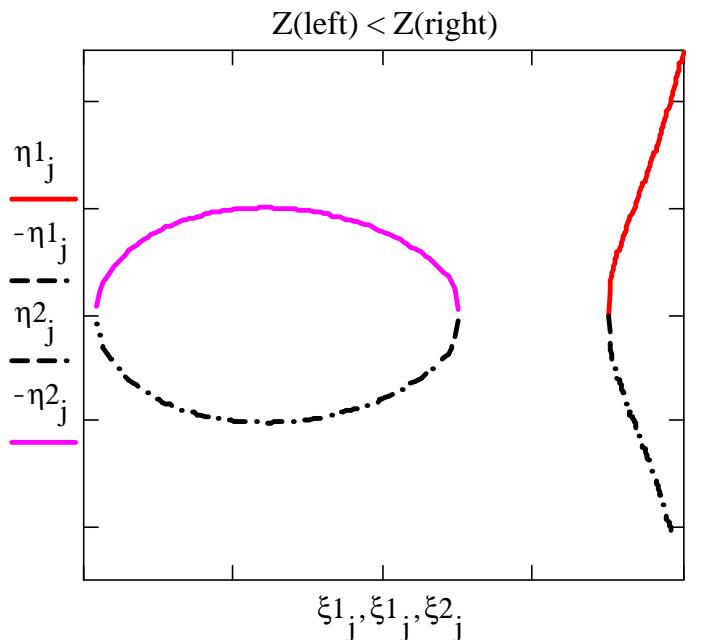


Figure 5.16: We observe that again the bonding region and the two antibonding regions are clearly separated. The antibonding region on the left side has an interesting shape.

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 \mathbf{r} in two parts: the part for the free atoms and the remaining part. The atomic components \mathbf{r}_a of \mathbf{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 \mathbf{r}_{npf} (not perfectly following). This leads to

$$\rho = \sum_a^{\text{atoms}} \rho_a + \rho_{npf} \quad (5.148)$$

This splitting is useful because in almost all cases, \mathbf{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 $\mathbf{a}-\mathbf{b}$, the following equation corresponds:

$$\rho = \rho_a + \rho_\beta + \rho_{npf} \quad (5.149)$$

If we put the origin of the coordinates in the nucleus α , the following is true because of the spherical symmetry of \mathbf{r}_a and \mathbf{r}_b :

$$\rho(r, R\beta) = \rho_a(r) + \rho_\beta(|R\beta - r|) + \rho_{npf}(r, R\beta) \quad (5.150)$$

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

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

Or, expressed according to (5.114):

$$\frac{\partial E}{\partial R} = -Z_\beta \left\{ \frac{Z_a}{R_\beta^3} + \int \rho_a(r) \frac{\partial}{\partial R_\beta} \cdot \frac{1}{|R_\beta - r|} dr \right\} + F(R\beta, \rho_{npf}) \quad (5.152)$$

The force $F_{R\alpha}$, 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:

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

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

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

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

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

Since the electron density distributions \mathbf{r}_a and \mathbf{r}_b of atoms are generally known well enough, the calculation of $E_{Rep}(R)$ is not difficult. The calculation of $\Delta E_{npf}(R)$ is much more difficult.

The EHMO-ASED procedure consists in the approximation of $\Delta E_{npf}(R)$ with $\Delta E_{EHMO}(R)$ 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.

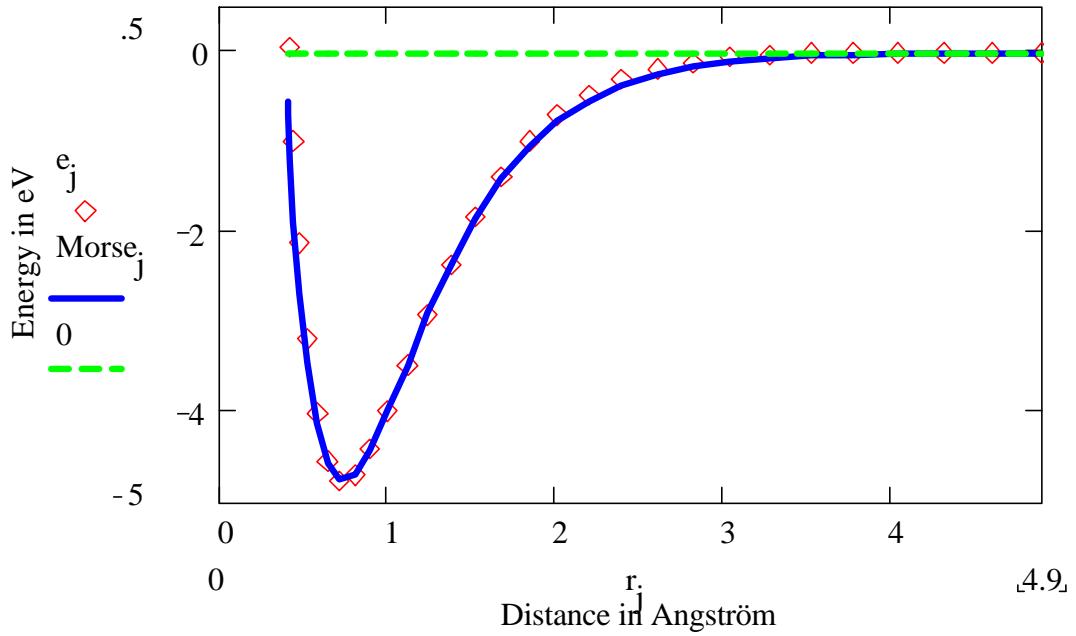


Figure 5.17:

Comparison of the result of an optimized EHMO-ASED calculation at the H_2 molecule (solid) with the Morse potential (diamonds).

The off-diagonal elements are calculated as

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

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 :

$$E_{Rep} = \sum_{\alpha < \beta} E_{Rep_{\alpha,\beta}} \quad (5.157)$$

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

$$E_{EHMO} = \sum_i b_i E_i \quad (5.158)$$

$$E_i = \sum_{\alpha_s} c_{i,\alpha_s}^2 H_{\alpha_s, \alpha_s} + 2 \sum_{\alpha_s < \beta_t} c_{i,\alpha_s} c_{i,\beta_t} H_{\alpha_s, \beta_t} \quad (5.159)$$

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

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

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.

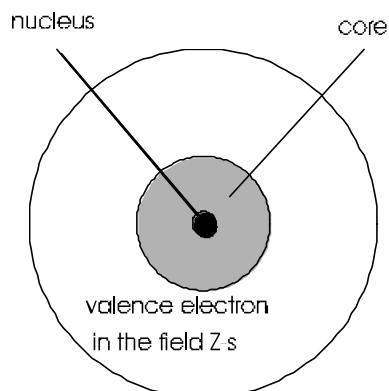
5.3.1 Valence state ionization energy VSIE

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 :

$$IP/eV = 13.6 \cdot \frac{Z^2}{n^2} \quad (5.161)1$$



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:

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

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

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

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^+	B^{2+}	C^{3+}	N^{4+}	O^{5+}	F^{6+}	Ne^{7+}
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:

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

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

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

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:

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

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

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.

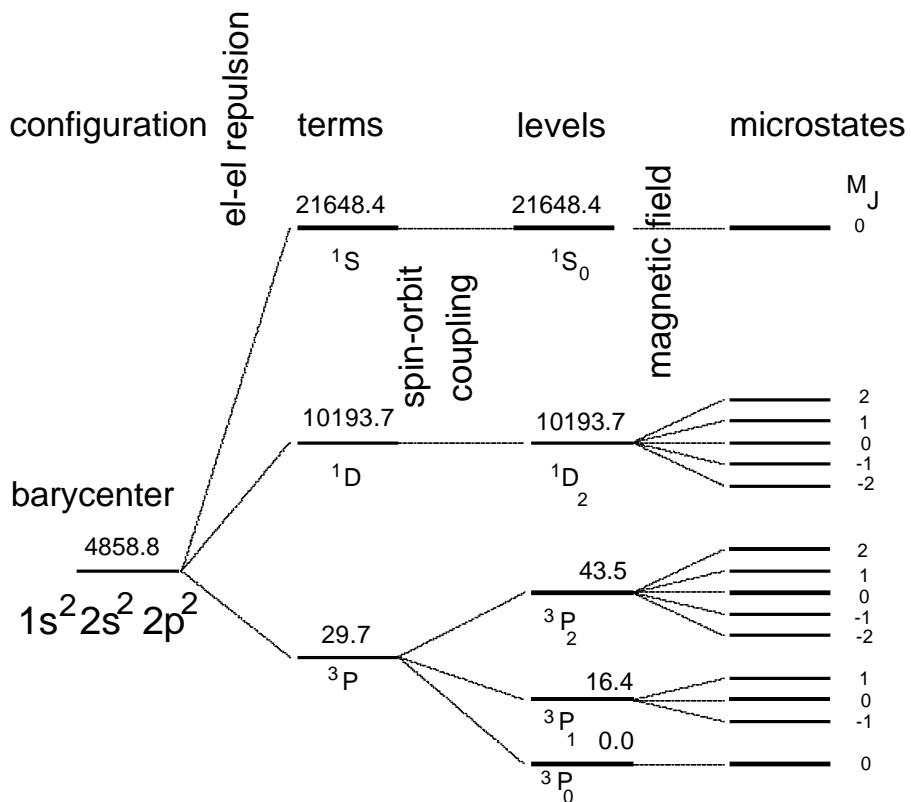


Figure 5.19: Definition of the barycenter of the electron configuration $1s^2 2s^2 2p^2$.

The barycenter is given by:

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

$$E(^3P) = \frac{1}{9} \{0 + 3 \cdot 16.4 + 5 \cdot 43.5\} = 29.633 \text{ cm}^{-1} \quad (5.168)$$

From this we find:

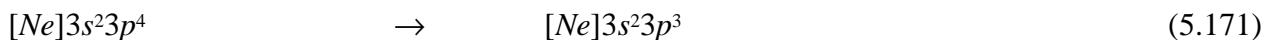
$$E(1s^2 2s^2 2p^2)_{av} = \frac{1}{1+5+9} \{ E(^1S) + 5E(^1D) + 9E(^3P) \} \quad (5.169)$$

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

We now explain by means of an example how it can be determined from experimental data. The 3pVSIE of the ...3s²3p⁴ configuration of S(I) is the energy of the ionization process



The states $^{2S+1}L_J$, belonging to these electron configurations are:



degeneracy: $5 + 9 + 1$

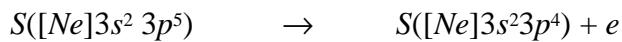
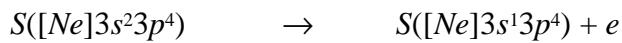
degeneracy: $10 + 6 + 4$

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

From this diagram follows:

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

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



v denotes the number of valence electrons.

$$S^+: n = 5, S^0: n = 6, S^{-1}: n = 7 \quad (5.174)$$

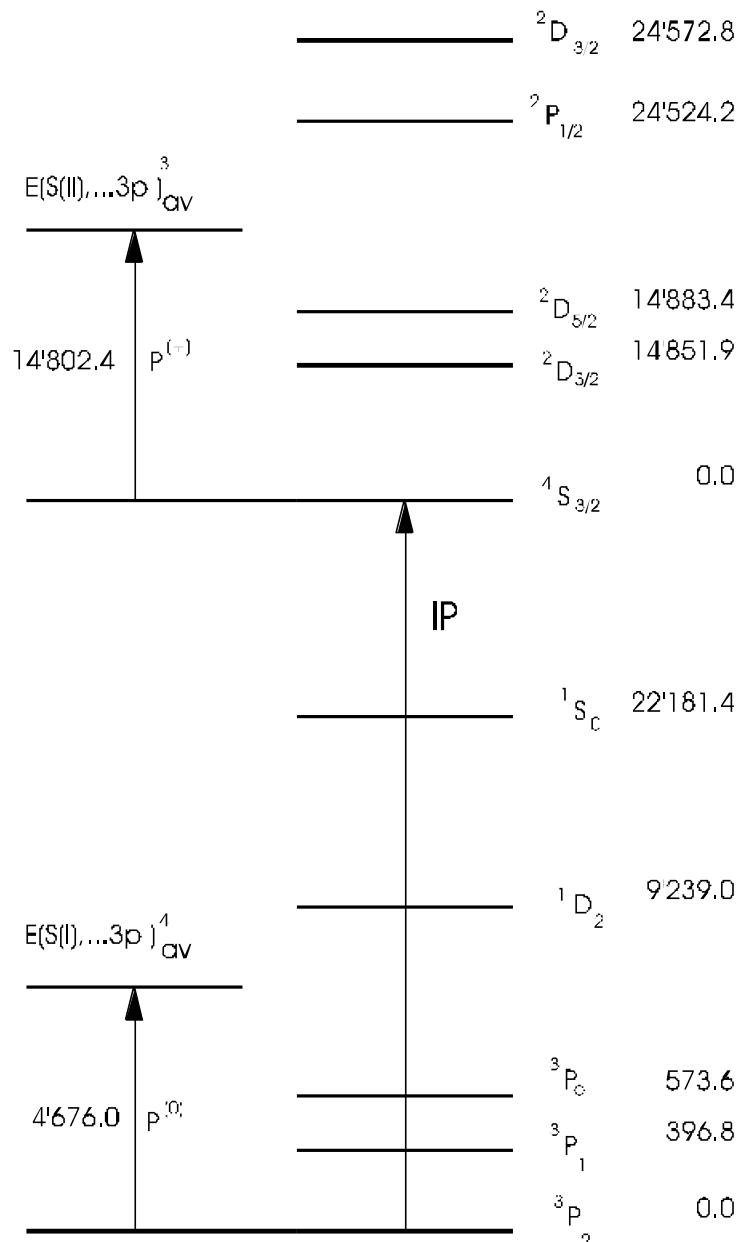


Figure 5.20: Levels, barycenters and promotion energies of sulfur S^0 and S^+ for the electron configurations $S[(I), \dots, 3p^4]$ and $S[(II), \dots, 3p^3]$.

The charge Q is then expressed as: $Q = (6 - n)$. 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} $Q = +1$
$3s$	$\dots 3s^2 3p^{v-2}$	11,04	20,7	33,4
$3p$	$\dots 3s^2 3p^{v-2}$	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^- :

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

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

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

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

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

$$\text{VSIE}(Q) = d_0 + d_1 \cdot Q + d_2 \cdot Q^2 \quad (5.177)$$

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 $(2s)^s(2p)^p$

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

and ask for the Coulomb integral:

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

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 $(2s)^1(2p)^{(n-1)}$:

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

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

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

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

The coefficients a and b can be calculated from

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

from which follows

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

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

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

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

$$= 0.6 \cdot 29.06 + 0.4 \cdot 30.82 = 29.76 \text{ eV}$$

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:

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

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

$$a + b + c = 1 \quad \rightarrow \quad b = s - 1 \quad (5.185)$$

$$a + 2b + c = s \quad \rightarrow \quad a = 2 - p - s$$

$$c = p$$

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

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

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

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

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

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

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:

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

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

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 $\delta = 0.35 \text{ \AA}^{-1}$. 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:

$$r_n = \frac{1}{\int_0^\infty \frac{1}{r} R_{nl}^2(r) r^2 dr} \quad (5.189)$$

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.

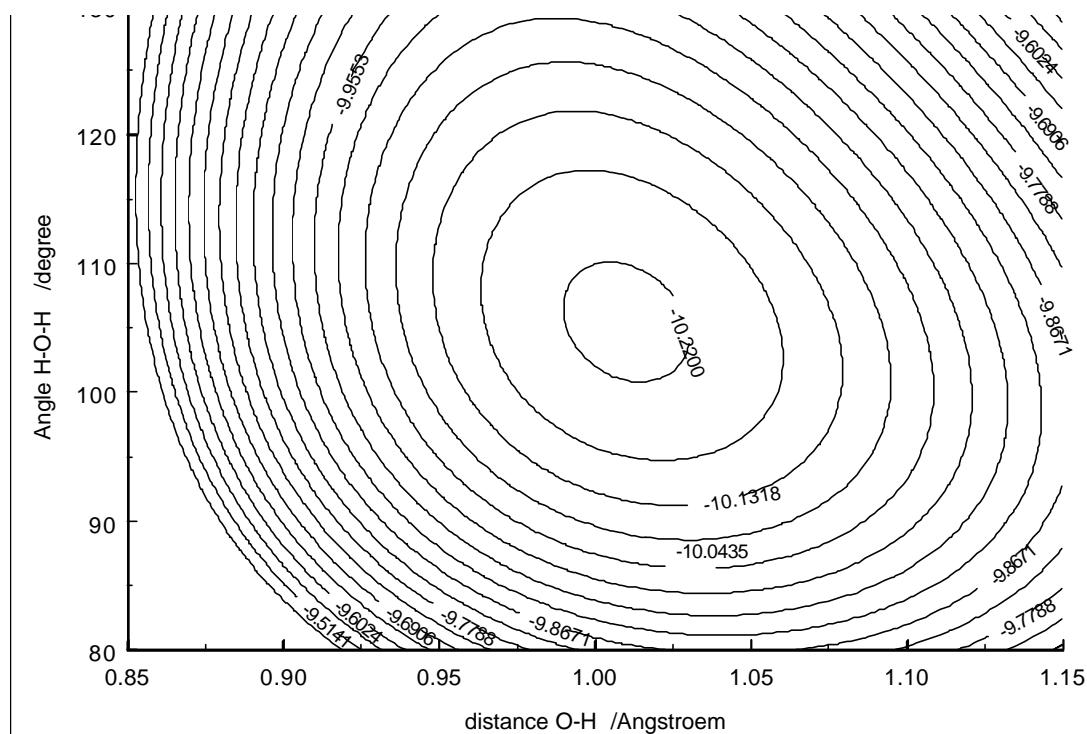


Figure 5.21 Energy hypersurface in [eV] for H₂O.

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_{ij} between orbitals i and j at different centres as a weighted average of the orbital densities f_{ii} and f_{jj} , i.e.

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

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

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

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

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

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 $\langle \phi_i | H | \phi_j \rangle$ would be given roughly by an expression of the form

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

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

$$\Delta = \frac{H_{ii} - H_{jj}}{H_{ii} + H_{jj}} \quad (5.194)$$

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

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

where, in general, K is a function of Δ which we choose so as to meet the following conditions

$$\Delta = 0 \quad H_{ij} = \frac{CON}{2} S_{ij} (H_{ii} + H_{jj}) \quad (5.196)$$

$$\Delta = 1 \quad H_{ij} = S_{ij} H_{ii}$$

$$\Delta = -1 \quad H_{ij} = S_{ij} H_{jj}$$

The $\Delta = 0$ condition is the normal Hückel formula.

This leads to the weighted H_{ij} formula

$$H_{ij} = [CON - (CON - 1)\Delta^2] \frac{S_{ij}}{2} [(1 + \Delta)H_{ii} + (1 - \Delta)H_{jj}] \quad (5.197)$$

which can be written in the more concise form

$$H_{ij} = k' \frac{S_{ij}}{2} (H_{ii} + H_{jj}) \quad \text{with } k' = CON + \Delta^2 + \Delta^4(1 - CON) \quad (5.198)$$

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.

Table 1: 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

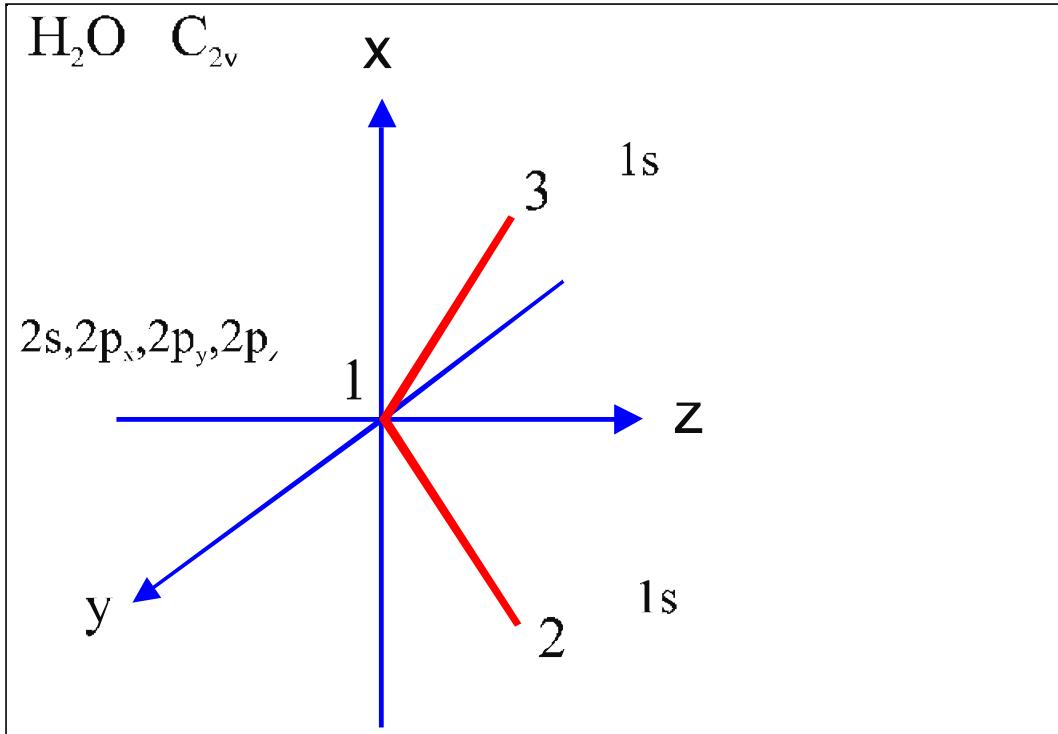


Figure 6.1: Coordinates and valence atomic orbitals.

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 :

$$\Psi_i = c_{i1}1s(H_1) + c_{i2}1s(H_2) + c_{i3}2s(O) + c_{i4}2p_x(O) + c_{i5}2p_y(O) + c_{i6}2p_z(O) \quad (6.1)$$

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 .000FFFFFFFFFFFFFFFFFF
      .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

$$\textbf{OVERLAP MATRIX} \quad S_{ii} = \langle \chi_i \mid \chi_i \rangle$$

	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 $h_{ij} = k(\kappa, \delta, R_{ij}) \cdot S_{ij} \cdot (h_{ii} + h_{jj})/2$

	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:

$$(h - e \cdot S) \cdot c = 0$$

$$\left(\begin{pmatrix} h_{11} & h_{12} & \dots & h_{16} \\ h_{21} & h_{22} & & h_{26} \\ \vdots & \vdots & & \vdots \\ h_{61} & h_{62} & \dots & h_{66} \end{pmatrix} - e \cdot \begin{pmatrix} S_{11} & S_{12} & \dots & S_{16} \\ S_{21} & S_{22} & & S_{26} \\ \vdots & \vdots & & \vdots \\ S_{61} & S_{62} & \dots & S_{66} \end{pmatrix} \right) \cdot c = 0$$

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
E(4) =	-13.39568	2.00	IP1(exp)=12.6
E(5) =	-16.25167	2.00	IP2(exp)=13.7
E(6) =	-30.83934	2.00	IP3(exp)=17.2

$$\begin{array}{lcl} \text{SUM OF ONE-ELECTRON ENERGIES} & = & -145.77337592 \text{ eV} \\ \text{ORBITAL STABILIZATION ENERGY} & = & -12.57337592 \text{ eV} \\ \text{CORE-CORE REPULSION ENERGY} & = & 3.63881174 \text{ eV} \\ \text{STABILIZATION + REPULSION} & = & -8.93456418 \text{ eV} \end{array} \quad \begin{array}{l} E_{EHMO} = \sum_i b_i E(i) \\ \Delta E = \sum_i b_i E(i) - \sum_s b_s^0 E_s^0 \\ E_{Rep} = \frac{1}{2} \sum_{\alpha, \beta} E_{Rep_{\alpha, \beta}} \\ E = \Delta E + E_{Rep} \end{array}$$

WAVE FUNCTIONS: MO'S IN COLUMNS, AO'S IN ROWS $\Psi_i = \sum_{r_k=1}^6 c_{ir_k} \chi_{r_k}$

	LUMO						HOMO					
	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6
O 1 (S)	-.8645	.0000	.0000	-.2507	.0000	.7898						
	.0000	-.9652	.0000	.0000	-.6328	.0000						
	.0000	.0000	1.0000	.0000	.0000	.0000						
	-.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.

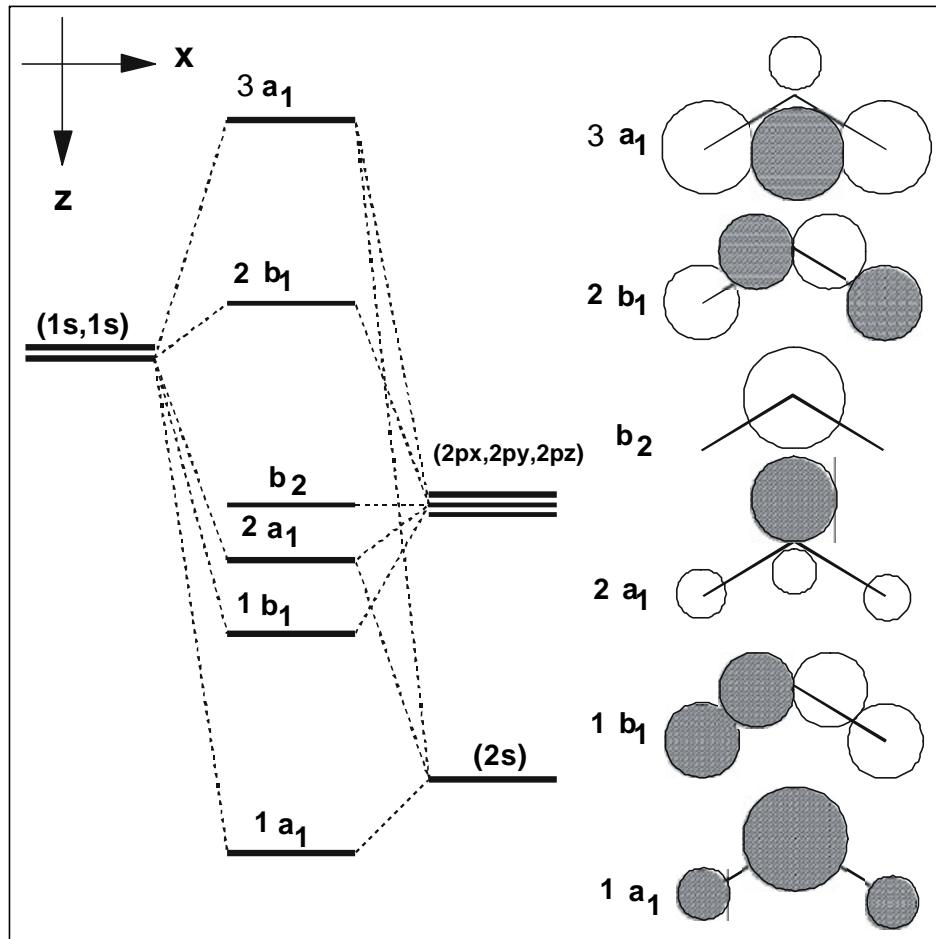


Figure 6.2: Correlation diagram of the water molecule.

DENSITY MATRIX		$D_{r_k s_l} = \sum_i b_i c_{ir_k} c_{is_l}$					
		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							$S_{r_k s_l} = 2 \sum_i b_i c_{ir_k} c_{is_l} S_{r_k s_l}$
		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			$P_{kl} = \sum_{r,s} P_{r_k s_l}$
O 1	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

						$Q_{ir_k} = 2c_{ir_k}(c_{ir_k} + \sum_{l \neq k} c_{is_l} S_{r_k s_l})$
	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

$$Q_{ri} = \sum_k Q_{ir_k}$$

	LUMO	HOMO				
	Ψ_1	Ψ_2	Ψ_3	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** **ATOMIC ORBITAL OCCUPATION FOR GIVEN MO OCCUPATION**

	$Q_r = N_0(r) - \sum_{occ} Q_{ri}$	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 $E_{r_k s_l} = a \sum_i b_i c_{ir_k} c_{is_l} h_{r_k s_l}$ $a = 1$ 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 $E_{kl} = \sum_{r,s} E_{r_k s_l}$

	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 .000FFFFFFFFFFFFFFFFFF
      .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=105.2°

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 $2sVSIE(2s^22p^2) = 3.46Q^2(2s) + 22.88Q(2s) + 32.33$
	3.46415	18.56678	$2pVSIE(2s^22p^2) = 3.46Q^2(2p) + 18.56Q(2p) + 15.79$
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

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
 $DENOM_k = \text{MAX}_r |Q_r^{\text{output}_k} - Q_r^{\text{input}_k}|$ stopping criterion: $\text{DENOM}_k < 0.005$

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

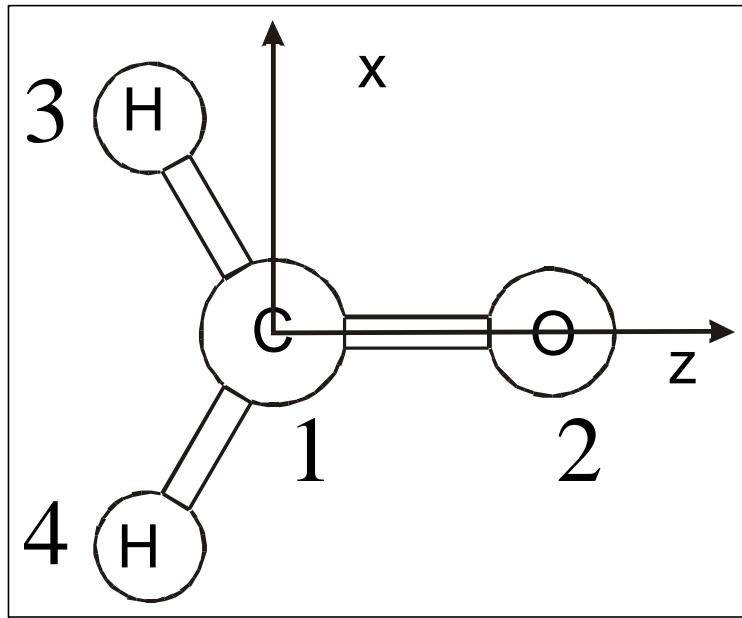
	1	2	3	4	5	6
1	.8099	1.0061	2.0000	1.7837	.9939	1.4064
2	.5950	.4970	.0000	.1081	.5030	.2968
3	.5950	.4970	.0000	.1081	.5030	.2968

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

6.2 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 .000FFFFFFFFFFFFFFFFFFFT
    .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   .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	.2146	.0000	.0000	.0364	-.0364
	(Y)	.0000	.0000	1.0000	.0000	.0000	.2146	.0000	.0000	.0000
	(Z)	.0000	.0000	.0000	1.0000	-.3125	.0000	.0000	-.3056	-.0685
C 2(S)	.3128	.0000	.0000	-.3125	1.0000	.0000	.0000	.0000	.4837	.4837
	(X)	.0000	.2146	.0000	.0000	1.0000	.0000	.0000	.4286	-.4286
	(Y)	.0000	.0000	.2146	.0000	.0000	1.0000	.0000	.0000	.0000
	(Z)	.4300	.0000	.0000	-.3056	.0000	.0000	.0000	1.0000	-.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
E(5) =	-12.09823	2.0000
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
	(Y)	.0000	.0000	.0000	.7315	.0000	.0000	.7164	.0000	.0000
	(Z)	.5739	-.5417	.0000	.0000	.0000	-.8454	.0000	.0000	-.1470
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

(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 CalculationInput File Formal.edi

TITLE Formaldehyde
KEYWRD MOFILE=Formal
KEYWRD GENFILE=Formal
KEYWRD POL=XYZ
KEYWRD MATRICE=ALL
KEYWRD CORRECT
KEYWRD TOLERANCE=0.00001
KEYWRD SPECOUT
KEYWRD TRANSOUT
[WAVERANGE]
START 4 6
END 7 7

OUTOUT File Formal.edo

FORMALDEHYDE

The following options have been selected:

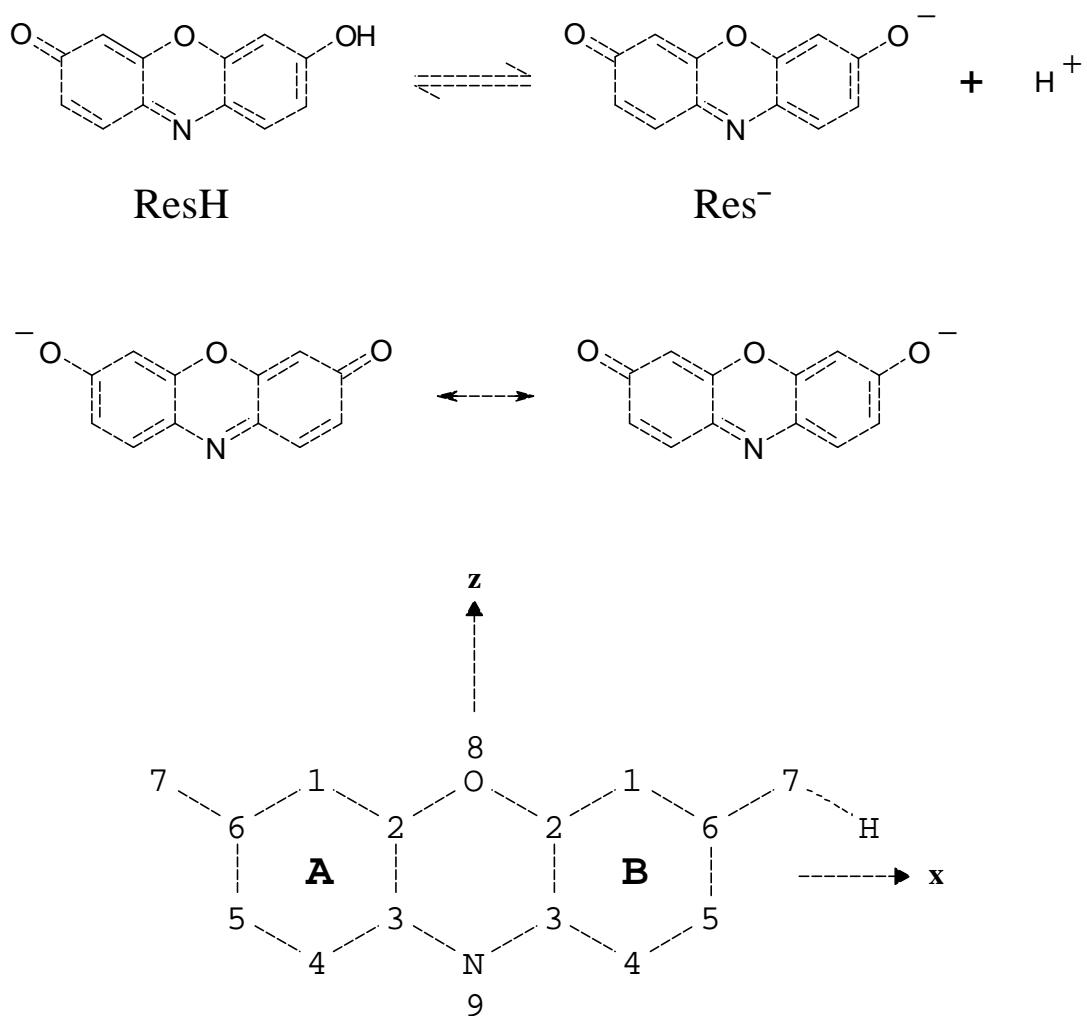
* MOFILE	- formal.mo
* GENFILE	- formal.gen
* SPECOUT	- formal.eds will contain the spectrum.
* POL	- X, Y, and Z transitions considered.
* MATRICE	- ALL transition elements are taken into account.
* CORRECT	- We correct for degeneracies (TOL = .00001)
* TRANSOUT	- We print the chosen transitions.

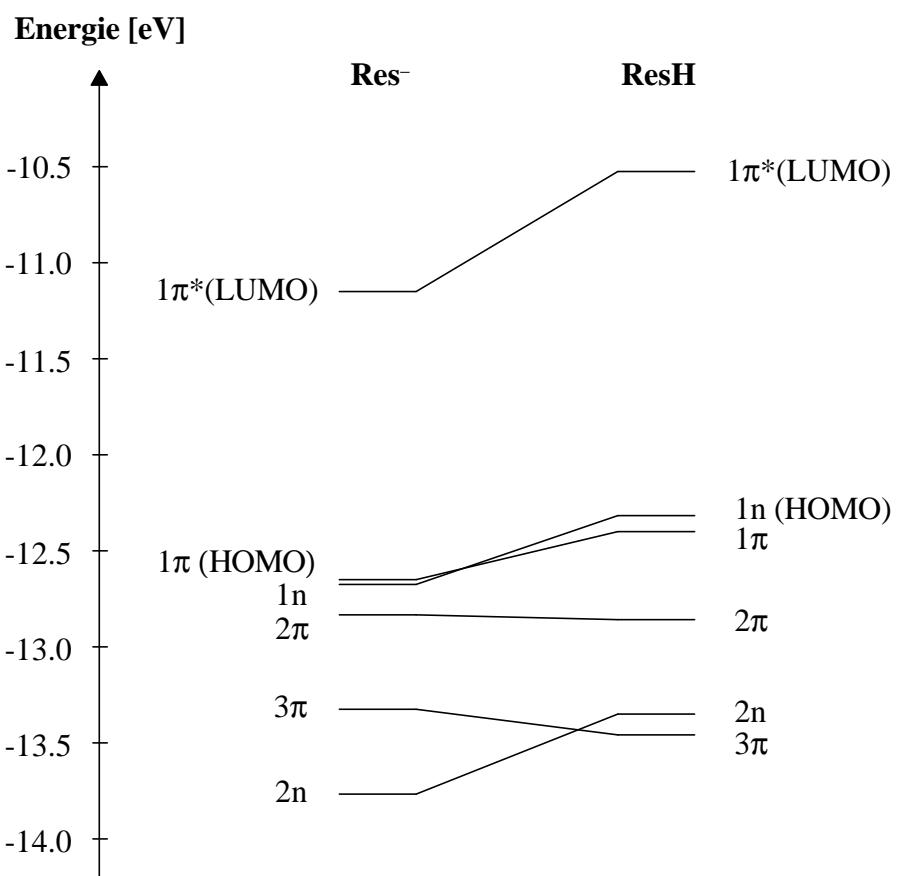
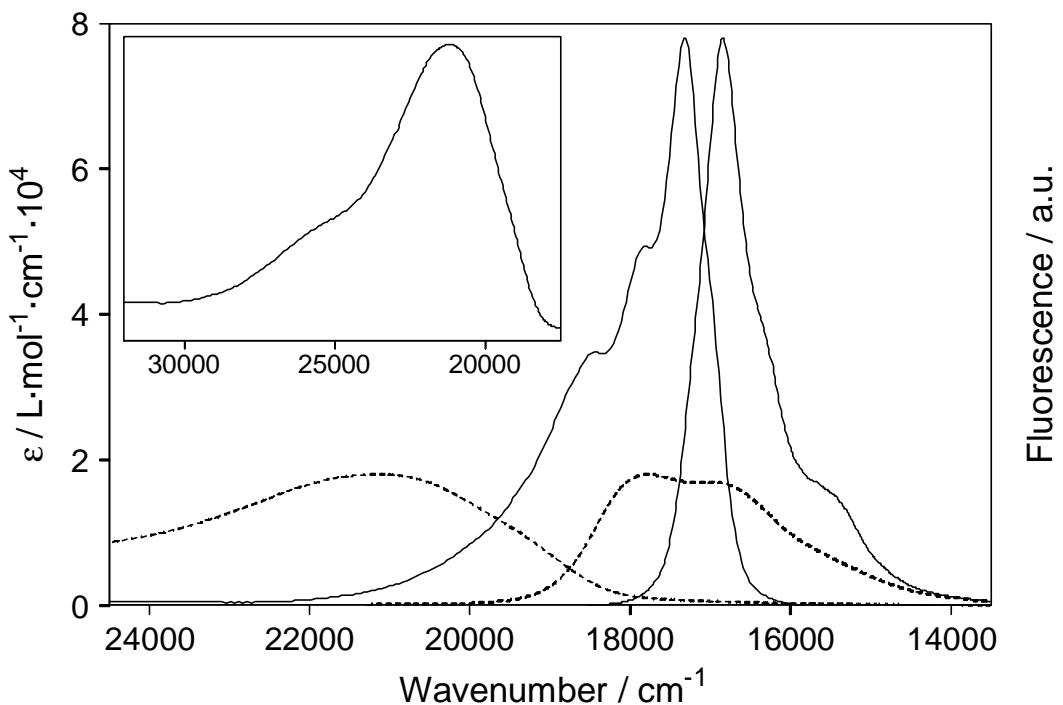
Initial wave function: 4
Final wave function: 7
Transition at: 42539.3 Wavenumbers (5.3 eV)
Oscillator strength along X: .00000
Oscillator strength along Y: .00000

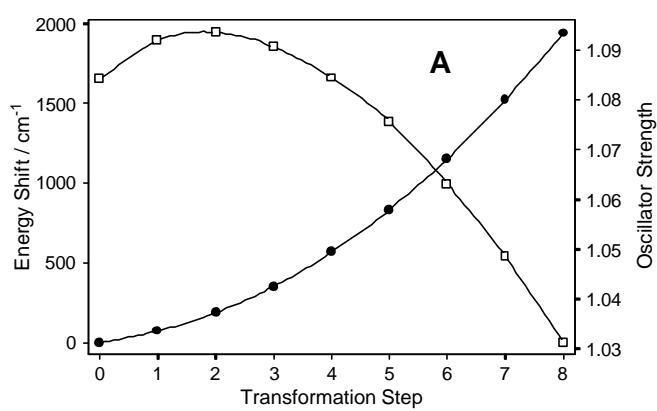
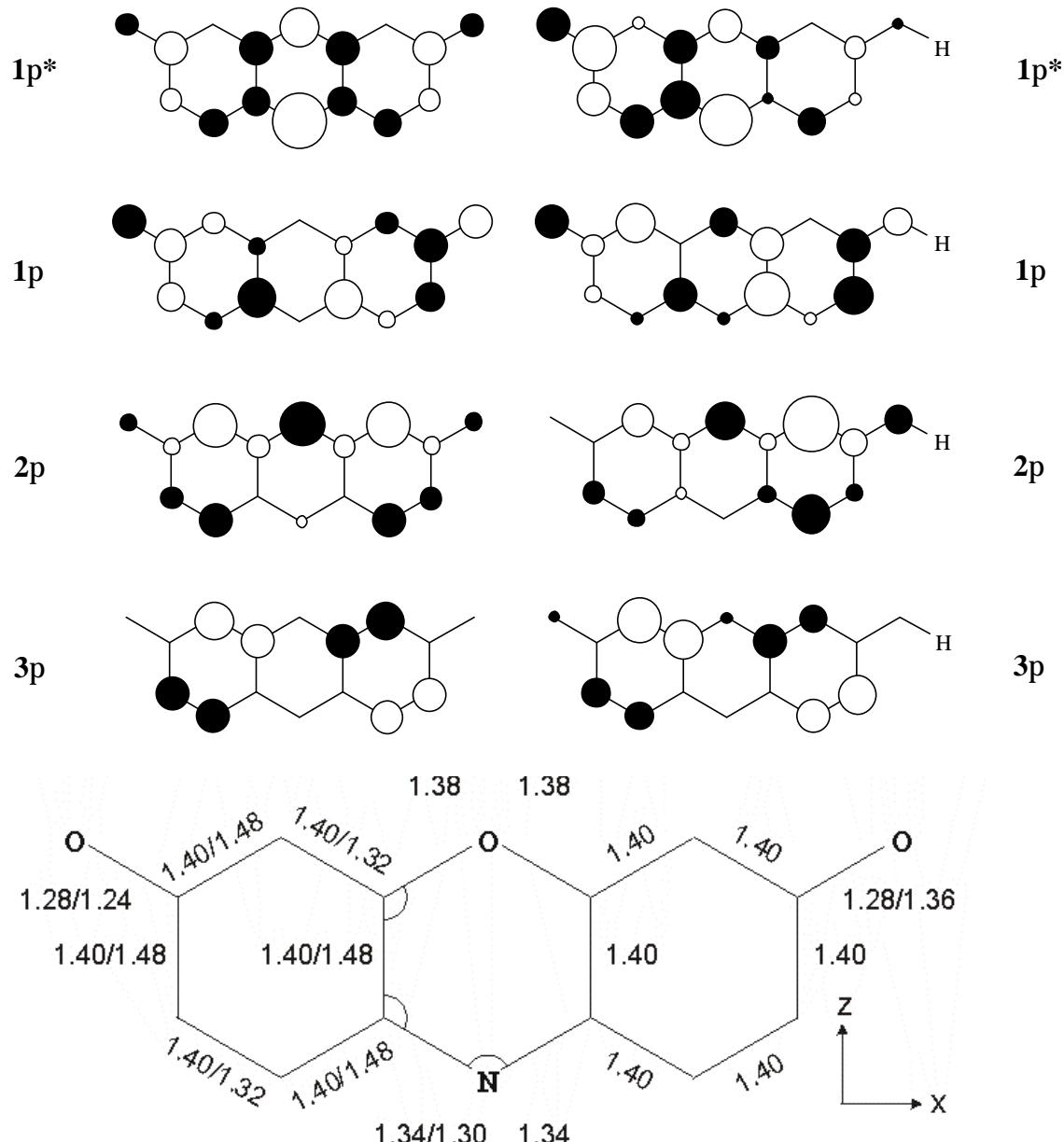
Oscillator strength along Z: .33983
Initial wave function: 5
Final wave function: 7
Transition at: 39780.5 Wavenumbers (4.9 eV)
Oscillator strength along X: .00000
Oscillator strength along Y: .00261
Oscillator strength along Z: .00000

Initial wave function: 6
Final wave function: 7
Transition at: 27347.1 Wavenumbers (3.4 eV)
Oscillator strength along X: .00000
Oscillator strength along Y: .00000
Oscillator strength along Z: .00000
Stop - Program terminated.

6.3 Resorufin







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  1FFFFFFF 2.00  .000  .00000000000000000000000000000000
                           .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 * 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 Resorufin Anion
KEYWRD MOFILE=res0
KEYWRD GENFILE=res0
KEYWRD POL=XYZ
KEYWRD MATRICE=ALL
KEYWRD CORRECT
KEYWRD TOLERANCE=0.00001
KEYWRD SPECOUT
KEYWRD TRANSOUT
[WAVERANGE]
START 30 39
END    40 40

```

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      IMPRINT = 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  4.1065  4.9253  4.7045  3.5499
  4  2.8248  2.4105  1.3400  .0000  1.3400  2.4105  3.6710  4.1386  3.6212  2.3339  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  2.4249  2.8000  2.4249  2.4249
  7  2.4076  1.4000  2.4249  .0000  4.1056  3.6710  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  5.1484  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  5.1484  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  3.4886  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	4.88882	.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	1.0472	2.1357	1.0074	-.0670	.0000
13	.0000	.0000	.0000	.0011	-.0771	-.0324	.0000	.0000	.0000	-.0901	1.0074	2.7693	1.1163	.0000
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	.0001	.0016	.0000	.0000	.0000	.0000						
3	.0017	.0001	.0024	-.0562	.0000	.0000	.0000	.0000						
4	.0000	.0000	.0000	-.0083	.0000	.0000	.0000	.0000						
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	-.0084	.6467	

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	.4153
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
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	.0401	.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	.0401	.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
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	.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	.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	.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	.0041	.0000	.0000	.0223	.0160	.0000	.0433	.0000	.0144	.0128	
18	.0000	.0000	.0000	.0118	.0000	.0000	.0155	.0144	.0000	.0002	.0000	.0564	.0335	
19	.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	.00													

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):

The following options have been selected:

- * MOFILE - res0.mo
 - * GENFILE - res0.gen
 - * SPECOUT - res0.eds will contain the spectrum.
 - * POL - X, Y, and Z transitions considered.
 - * MATRICE - ALL transition elements are taken into account.
 - * CORRECT - We correct for degeneracies (TOL = .00001)
 - * TRANSOUT - We print the chosen transitions.

Initial wave function: 30
Final wave function: 40
Transition at: 30889.2 Wavenumbers (3.8 eV)

Oscillator strength along X: .00000
 Oscillator strength along Y: .00000
 Oscillator strength along Z: .00000

 Initial wave function: 31
 Final wave function: 40
 Transition at: 30078.8 Wavenumbers (3.7 eV)
 Oscillator strength along X: .01193
 Oscillator strength along Y: .00000
 Oscillator strength along Z: .00000

 Initial wave function: 32
 Final wave function: 40
 Transition at: 26868.0 Wavenumbers (3.3 eV)
 Oscillator strength along X: .00000
 Oscillator strength along Y: .00000
 Oscillator strength along Z: .00000

 Initial wave function: 33
 Final wave function: 40
 Transition at: 22885.6 Wavenumbers (2.8 eV)
 Oscillator strength along X: .00000
 Oscillator strength along Y: .00000
 Oscillator strength along Z: .10821

 Initial wave function: 34
 Final wave function: 40
 Transition at: 21515.1 Wavenumbers (2.7 eV)
 Oscillator strength along X: .00000
 Oscillator strength along Y: .00001
 Oscillator strength along Z: .00000

 Initial wave function: 35
 Final wave function: 40
 Transition at: 20765.1 Wavenumbers (2.6 eV)
 Oscillator strength along X: .00000
 Oscillator strength along Y: .00000
 Oscillator strength along Z: .00000

 Initial wave function: 36
 Final wave function: 40
 Transition at: 18815.3 Wavenumbers (2.3 eV)
 Oscillator strength along X: .02212
 Oscillator strength along Y: .00000
 Oscillator strength along Z: .00000

 Initial wave function: 37
 Final wave function: 40
 Transition at: 14368.6 Wavenumbers (1.8 eV)
 Oscillator strength along X: .00000
 Oscillator strength along Y: .00000
 Oscillator strength along Z: .02458

 Initial wave function: 38
 Final wave function: 40
 Transition at: 13382.9 Wavenumbers (1.7 eV)
 Oscillator strength along X: .00000
 Oscillator strength along Y: .00009
 Oscillator strength along Z: .00000

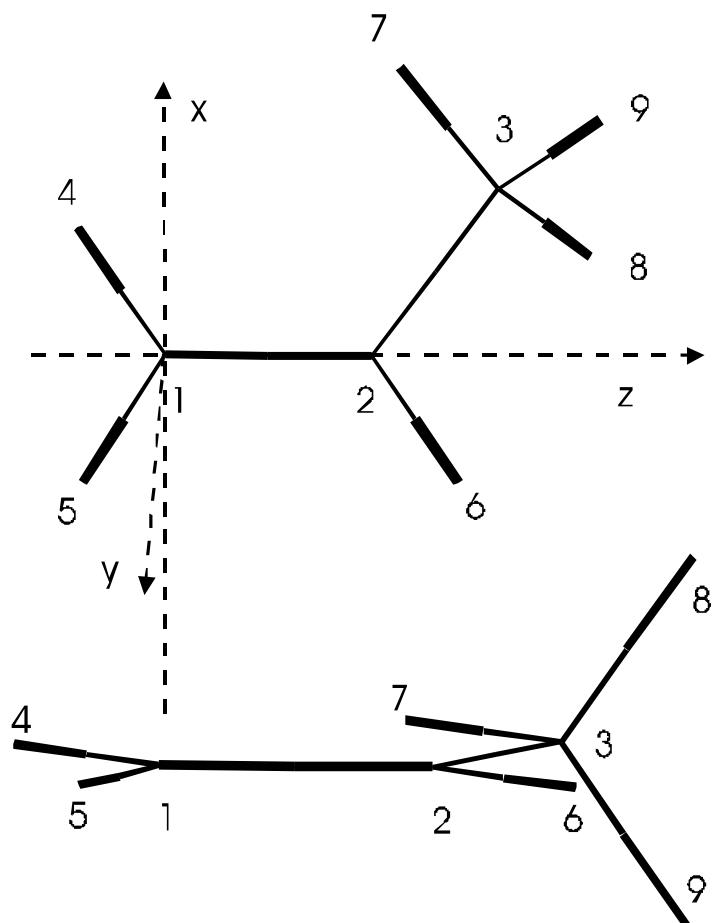
```
Initial wave function ....: 39
Final wave function .....: 40
Transition at .....: 12159.9 Wavenumbers ( 1.5 eV )
Oscillator strength along X: 1.08407
Oscillator strength along Y: .00000
Oscillator strength along Z: .00000
Stop - Program terminated.
```

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 1FFFFFFFFF 2.00 0.000 0.000FFFFFFFFFFFFFFFFFF
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)
FFFFFFFFFF          (Output options)

```



EXTENDED HUCKEL FMO CALCULATION, complete molecule

K IS CALCULATED WITH THE DISTANCE-DEPENDENT WEIGHTED FORMULA.
 delta = .3500, 1+kappa = 2.0000

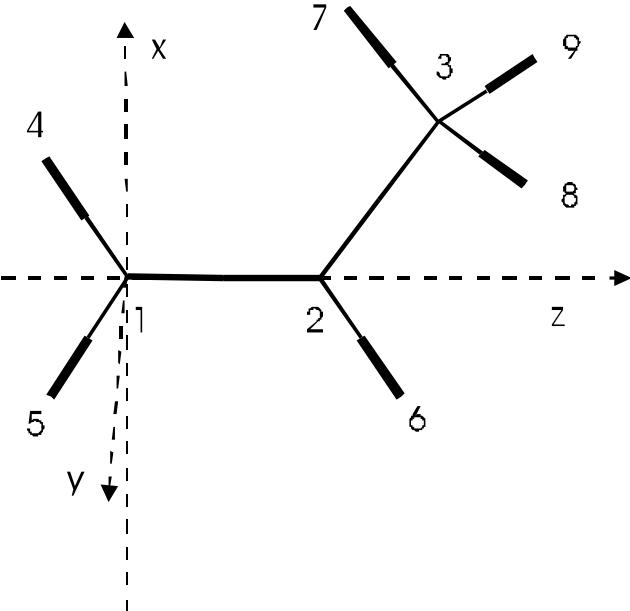
ATOM	X	Y	Z	S			P		
				N	EXP	COUL	N	EXP	COUL
C 1	.00000	.00000	.00000	2	1.7100	-21.4000	2	1.6250	-11.4000
C 2	.00000	.00000	1.33600	2	1.7100	-21.4000	2	1.6250	-11.4000
C 3	1.23997	.00000	2.18185	2	1.7100	-21.4000	2	1.6250	-11.4000
H 4	.94397	.00000	-.54500	1	1.3000	-13.6000			
H 5	-.94397	.00000	-.54500	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	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	-.0012	-.0077	-.0057	-.0070	-.0050	.4012	-.0020	-.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										



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

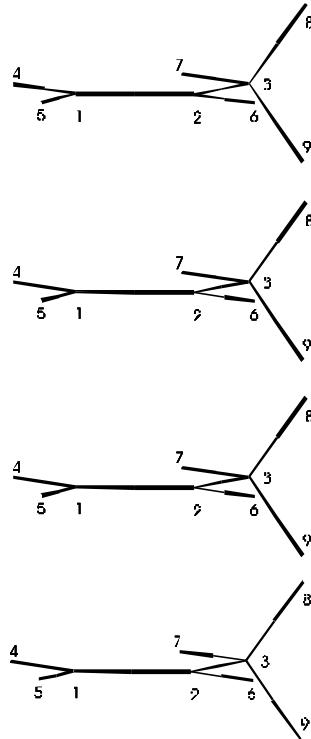
ORBITAL STABILIZATION ENERGY = -64.96181766 eV

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
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	^.0000	^.0000	^.0000	.0000
H 7(S)	.1533	.6029	.2911	.0404	.6829	.0000	-.6577	-.4402						.0000
H 8(S)	.0643	.6388	.1184	.3015	-.0778	-.8518	.5332	-.0663						-.4147
H 9(S)	.0643	.6388	.1184	.3015	-.0778	.8518	.5332	-.0663						.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										



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

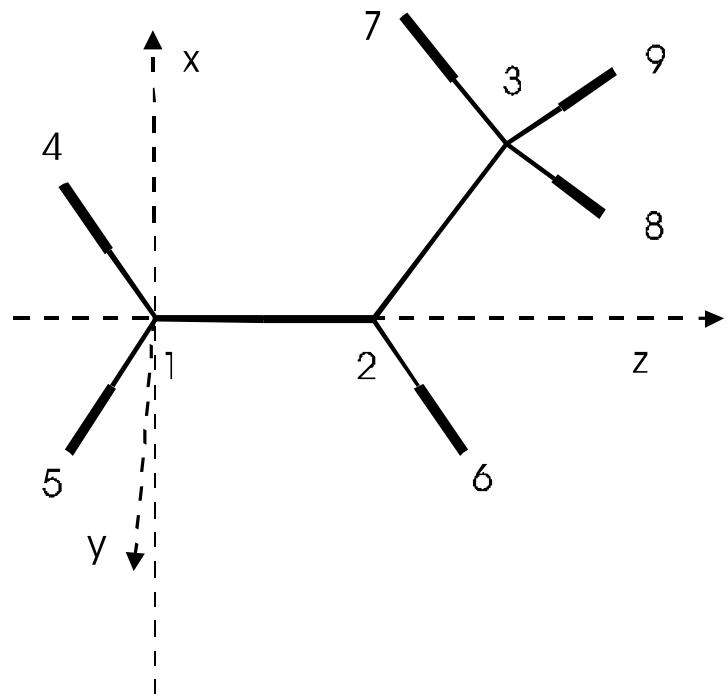
REDUCED CHARGE MATRIX, MO'S IN COLUMNS, ATOMS IN ROWS, NORMALIZED TO TWO ELECTRONS REGARDLESS OF OCCUPATION

	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	1.0041	.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										

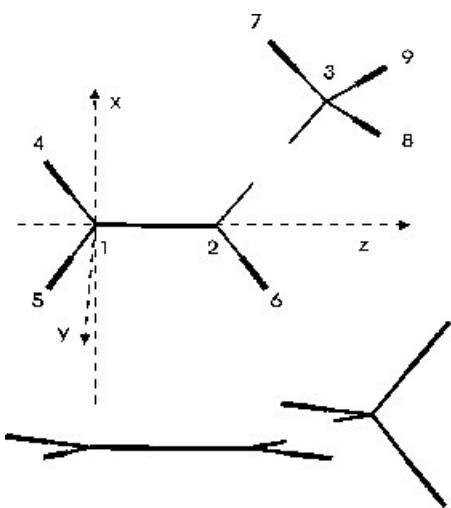
ATOM	NET CHG.	ATOMIC ORBITAL OCCUPATION FOR GIVEN MO OCCUPATION			
		S	X	Y	Z
C 1	-.12469	1.18577	.93042	1.06083	.94767
C 2	.02843	1.17887	.91732	.95544	.91995
C 3	-.03328	1.17337	.94467	.95476	.96048
H 4	.02948	.97052			
H 5	.02961	.97039			
H 6	.01751	.98249			
H 7	.01293	.98707			
H 8	.02001	.97999			
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

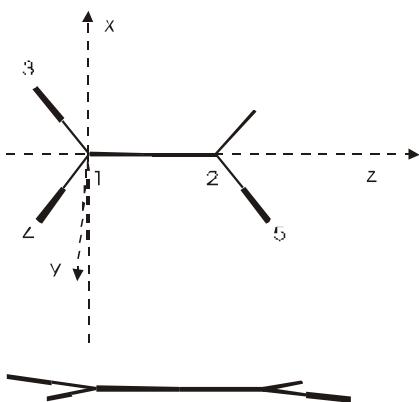
ATOM	X	Y	Z	S			P		
				N	EXP	COUL	N	EXP	COUL
C 1	.00000	.00000	.00000	2	1.7100	-21.4000	2	1.6250	-11.4000
C 2	.00000	.00000	1.33600	2	1.7100	-21.4000	2	1.6250	-11.4000
H 3	.94397	.00000	-.54500	1	1.3000	-13.6000			
H 4	-.94397	.00000	-.54500	1	1.3000	-13.6000			
H 5	-.94397	.00000	1.88100	1	1.3000	-13.6000			

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

the order 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	N EXP	COUL	N EXP	P	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

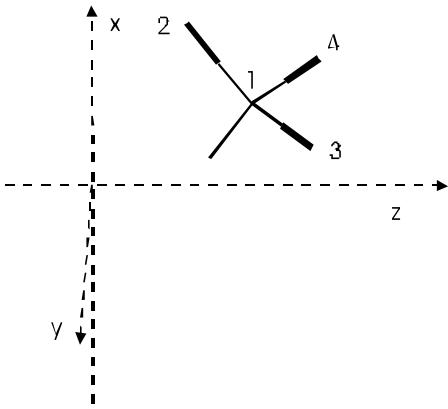
ENERGY LEVELS (eV)

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

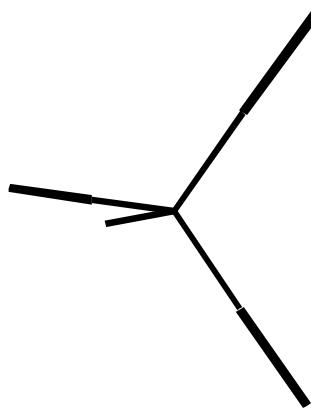
WAVE FUNCTIONS
MO'S IN COLUMNS, AO'S IN ROWS

	1	2	3	4	5	6	7
	$\pi^*(\text{CH}_3)$	LUMO	SOMO		$\pi(\text{CH}_3)$		
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

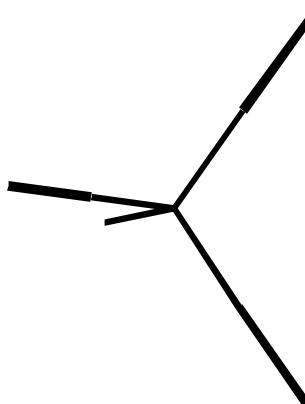


REDUCED OVERLAP POPULATION MATRIX, ATOM BY ATOM

	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

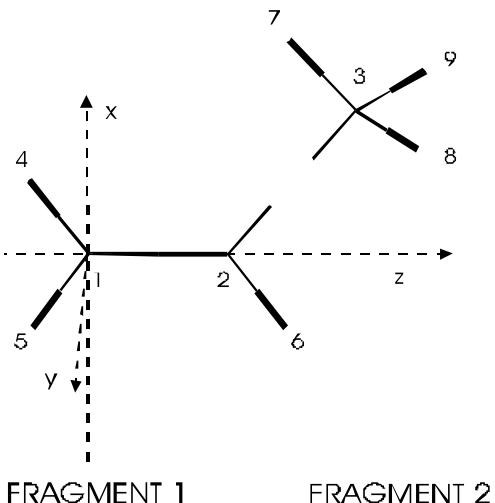
	1	2	3	4	5	6	7
1	.8252	1.0312	1.0283	1.9494	.9717	.9688	1.2254
2	.3947	.0000	.6434	.0167	.6869	.0000	.2583
3	.3900	.4844	.1642	.0169	.1707	.5156	.2582
4	.3900	.4844	.1642	.0169	.1707	.5156	.2582



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				

***** FMO *****

OVERLAP MATRIX (FOR FRAGMENT MOLECULAR ORBITALS)



WAVEFUNCTIONS

MOLECULE MOLECULAR ORBITALS IN COLUMNS, FRAGMENT MOLECULAR ORBITALS IN ROWS

(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

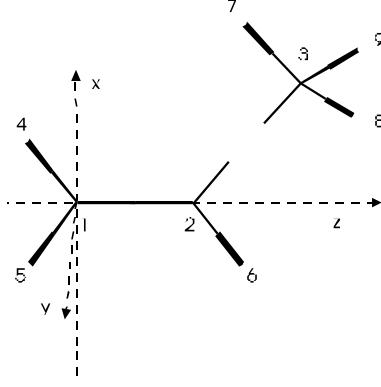
OVERLAP POPULATION MATRIX FOR 18 ELECTRONS

	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	.0001	.0000	.0000	.0000
	(3)	.0000	.0000	.0022	.0000	.0000	.0000	.0000	.0000	.0000	.0001	.0000	.0000	.0000
	(4)	.0000	.0000	.0000	.0024	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
	(5)	.0000	.0000	.0000	.0000	.0106	.0000	.0000	.0000	.0000	.0000	.0000	.0004	.0000
	(6)	.0000	.0000	.0000	.0000	.8328	.0000	.0000	.0000	.0000	.0106	.0000	.0000	.0000
	(7)	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0139	.0000	.0000	.0000
	(8)	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0002	.0000	.0079	.0000
	(9)	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.19879	.0000	.0000	.0002	.0000
	(10)	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.1.9240	.0000	.0020	.0000	.0004
	(11)	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.2.0093	.0005	.0000	.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	.0025	.0000	.0000
	(3)	.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
	(5)	.0001	.0016	.0015	.0043	.0000	-.0001	.0000	-.0270	-.0192	-.0140	-.0027	.0000	.0000
	(6)	.0000	.0000	.0000	.0000	.0329	.0000	-.0498	.0000	.0000	.0000	.0000	.0000	.0000
	(7)	-.0010	-.0018	.0018	.0019	.0000	-.0038	.0000	-.0012	-.0141	-.0316	-.0587	.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									

REDUCED OVERLAP POPULATION MATRIX,
FRAGMENT BY FRAGMENT1 2
FRAG 1 10.7908 .4577
FRAG 2 .4577 6.7515

FRAGMENT 1

FRAGMENT 2



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	.0010	.0009	.0000
	(3)	.0049	.0389	.0034	1.6033	.0429	.0000	.2327	.0687	.0000	.0000	.0023	.0000	.0005
	(4)	.0009	.0218	.0202	.0081	1.0083	.0000	.1416	.7921	.0000	.0000	.0018	.0013	.0019
	(5)	.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
	(7)	.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
	(9)	.0010	.0075	.0000	.0008	.0000	.0043	.0079	.0000	.0000	.0710	.0016	.2832	.0000
	(10)	.0030	.0284	.0008	.0021	.0075	.0000	.0076	.0303	.0000	.0000	.0543	.0058	.0029
	(11)	.0021	.0188	-.0003	-.0002	.0017	.0000	.0028	.0094	.0000	.0000	.0095	.0005	-.0001
FRAG 2(1)	.0353	1.4404	.1058	.1467	.0912	.0000	.0526	.1085	.0000	.0000	.0104	.0004	.0002	.0000
	(2)	.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	.0045	.0003	.0000
	(4)	.0569	.0938	.0716	.0817	.1080	.0000	.1414	.3738	.0000	.0000	.7821	.0280	.0083
	(5)	-.0001	.0001	.0013	.0008	.0016	.0000	.0005	.0005	.0000	.0126	.3734	1.3319	.0000
	(6)	.0000	.0000	.0000	.0000	.0000	.0007	.0000	.0248	.0876	.0000	.0000	.0000	1.8869
	(7)	.0115	.0153	.0107	.0114	.0114	.0000	.0117	.0246	.0000	.0000	.0268	.0015	.0005
	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									

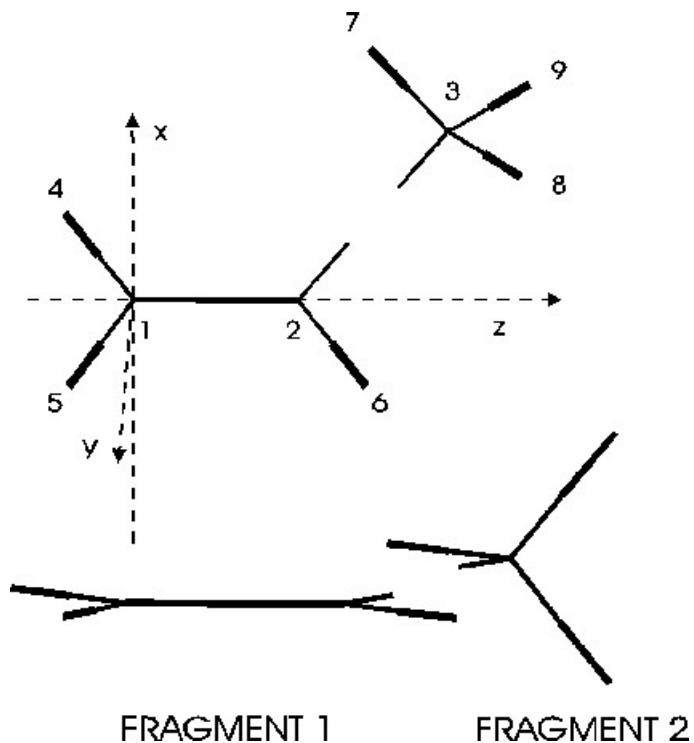
REDUCED CHARGE MATRIX, MO'S IN COLUMNS, FRAGMENTS IN ROWS

	1	2	3	4	5	6	7	8	9	LUMO	HOMO	10	11	12	13	14
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:



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)p₂* = 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)p * = 9.57776 .0000	
E(8) = 5.22319	.0000	E(4) = 9.55473	.0000	E(3) = 9.35041 .0000	
E(9)p₁* = -7.00648 .0000		E(5)p * = -7.19547 .0000			
E(10)p₁ = -13.59232 2.0000		E(6) = -11.70088	1.0000	E(4) = -11.82479	1.0000
E(11) = -14.93929	2.0000	E(7)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)p₂ = -16.85475 2.0000				E(6)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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