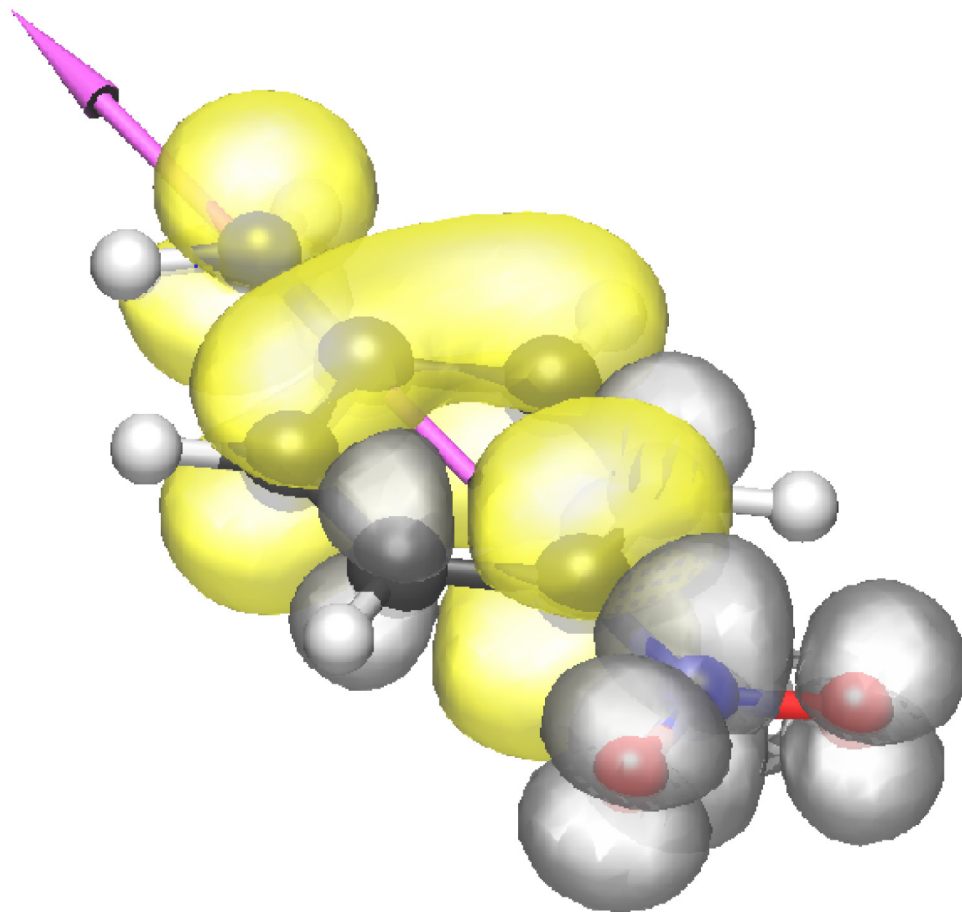



# Molecular Orbital Package MOS-F V4.2D

## User's Manual



  
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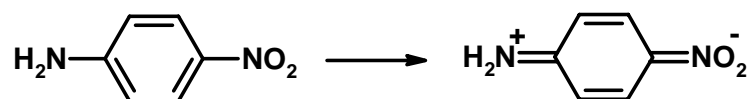
  
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## Front cover

Paranitroaniline is known as a fundamental molecule with nonlinear optical properties. The picture on the front cover shows the change in its electron density from the ground to excited state, calculated by MOS-F V4.2D<sup>a</sup> and visualized using WinMOPAC V3.

In the picture, increase of the density is shown by gray lobes and the decrease by yellow ones. The magenta arrow shows the difference in dipole moment between the ground and the excited state.

From these pictures, the electron density transfer from the amino group to the nitro group in Paranitroaniline can be observed.



One of the reasons for its large nonlinear optical character can be attributed to the charge transfer associated with photon absorption.

---

<sup>a</sup>Calculated by INDO/S for HOMO-LUMO transition.

# Dear Users

We would like to thank you very much for choosing MOS-F V4.2D. MOS-F V4.2D, based on semiempirical methods, runs on UNIX and Windows and it is designed to satisfy the requirements of calculating spectroscopic properties of many organic molecules. This manual explains how to use MOS-F V4.2D and illustrates the basic theories used in the program. For more theoretical details on the relevant molecular orbital theory, please see the references given.<sup>1-3</sup>

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**Note:** This manual has described in April 1998 and revised in February 1999 and July 2000. It may be changed without notice.

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# Chapter 1

## Introduction

### 1.1 Main Features

MOS-F (semiempirical Molecular Orbital package for Spectroscopy, FUJITSU) V4.2D has been modified extensively now with INDO/S, capability to calculate polarizability (e.g.  $\alpha$  and  $\gamma$ ) and other useful features as well as those from MOS-F V1<sup>4-6</sup>. Its main features are as follows:

- The semiempirical molecular orbital methods INDO/S (*s*, *p* and *d*-type functions),<sup>7-12</sup> CNDO/S,<sup>13-16</sup> CNDO/S2,<sup>17-22</sup> CNDO/S3,<sup>17-22</sup> and CNDO/2<sup>1,23</sup> are available.
- Spectroscopic calculations with configuration interaction singles (CIS).
- Electron density and dipole moment in excited states available from CIS wave function.
- Frequency-dependent polarizability,  $\alpha$ .<sup>24</sup>
- First hyperpolarizability  $\beta$  for Static, Electro-optic Pockels effect, Second harmonic generation and Optical-rectification  $\beta$ .<sup>25-29</sup>
- Second hyperpolarizability  $\gamma$  for Static, DC-electric field induced Kerr effect, DC-electric field induced second harmonics, Third harmonic generation, Degenerate four-wave mixing and DC-electric field induced optical rectification.<sup>26-29</sup>
- Prediction of the following molecular properties in the presence of a solvent using the SCRF calculation<sup>31-36</sup> by means of the Onsager model<sup>30</sup>:
  - Electronic spectrum.
  - Electron density and dipole moment in excited states.
  - Frequency-dependent polarizability,  $\alpha$ , first hyperpolarizability,  $\beta$ , and second hyperpolarizability,  $\gamma$ .
- Analytic,<sup>1,37</sup> Pariser-Parr,<sup>38</sup> Nishimoto-Mataga<sup>39</sup> (includes new formula<sup>40</sup>), Nishimoto-Mataga-Weiss,<sup>7</sup> Ohno,<sup>41</sup> Ohno-Klopman,<sup>42</sup> and DasGupta-Huzinaga<sup>43</sup> formulas for evaluation of the two-center electron repulsion integrals are available.
- Coordinate input format from the Gaussian<sup>45</sup> Symbolic Z-matrix and the MOPAC<sup>46</sup> Internal Coordinates.
- WinMOPAC IO interface (except WinMOPAC V1).
- Automatic calculation of the cavity radius for a solute.
- Automatic input system of dielectric constant and refractive index by specifying a solvent name.

- Output control of the difference density matrices between ground and excited states for WinMOPAC file.
- Displaying of the process of the MOS-F calculation on the standard error output (except the calculation on WinMOPAC).

Note: Molecular geometry for WinMOPAC V3 can be prepared only in the MOPAC compatible formats (`Coord=Inter` and `Coord=MCart`). The Z-matrix used in Gaussian (`Coord=Z`) and the standard Cartesian coordinates (`Coord=Cart`) are not available at present. These formats are available for running MOS-F V4.2D independently.

## 1.2 Program Limitations

### 1.2.1 Scale of Calculation

These values set the limit on calculation scale for MOS-F V4.2D.

- (1) Maximum number of atoms: 5,000.
- (2) Maximum number of basis functions: 10,000.
- (3) Maximum number of occupied orbitals for CI: 100.
- (4) Maximum number of virtual orbitals for CI: 100.

MOS-F V4.2D operates with dynamic memory allocation to meet the demand for large spaces to store orbital coefficients and CI vectors. The scale of performable calculation therefore depends on the hardware specification of each computer.

### 1.2.2 Available Methods

- (1) Ground state: Closed shell RHF only.
- (2) Excited state: CI singles for singlet and triplet state.

### 1.2.3 Available Atoms

MOS-F V4.2D has the following default settings.

INDO/S ... H, C, N, O, F<sup>†</sup>, S<sup>†</sup>, Cl, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu.<sup>‡</sup>

CNDO/2 ... H, Li, Be, B, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, Ge, As, Se, Br.

CNDO/S ... H, Li, Be, B, C, N, O, F, Na, Mg, Al, Si, P, S, Cl.

CNDO/S2 ... H, C, N, O, F, S, Cl, Br.

CNDO/S3 ... H, C, N, O, F, S, Cl, Br.

In MOS-F V4.2D, atoms up to Br can be used with user-defined atomic parameters, excluding the noble gases.

### 1.2.4 Using WinMOPAC

Molecular geometry for WinMOPAC V3 can be prepared only in the MOPAC compatible formats (Coord=Inter and Coord=MCart). The Z-matrix used in Gaussian (Coord=Z) and the standard Cartesian coordinates (Coord=Cart) are not available at present. These formats are available for running MOS-F V4.2D independently.

---

<sup>†</sup>When using the keyword UseCNDOParm

<sup>‡</sup>When using the keyword UseTripletParm, triplet parameters for H, C, N, O are available.



# Chapter 2

## Running MOS–F V4.2D

### 2.1 MOS–F-Related Files

#### 2.1.1 Input File Name

Users can use most file names as an input file which is available in the MOS–F-installed system.

The following are the file names that MOS–F V4.2D can not handle as an input file:

- File name with a length greater than 255 bytes.
- File name that begins with a dot “.” and includes only one dot.
- File name that is composed of dots only.
- File name that the system in which MOS–F V4.2D is installed can not handle.

MOS–F V4.2D regards a file with the `.mos` extension as an input file. When specifying the input file with `.mos`, users can omit the extension as shown in [Section 2.2](#). So, the file name with the `.mos` extension is recommended as an input file.

#### 2.1.2 Output File Name

MOS–F V4.2D produces the following three files with their extensions.

<code>&lt;filename&gt;.ims</code>	A copy of an input file such as <code>&lt;filename&gt;.mos</code> and <code>&lt;filename&gt;.dat</code> . This file is deleted with the termination of the program.
<code>&lt;filename&gt;.oms</code>	An output file of MOS–F V4.2D.
<code>&lt;filename&gt;.wms</code>	WinMOPAC file, a file for displaying the result by MOS–F V4.2D on WinMOPAC.

Note that MOS–F V4.2D does not output the WinMOPAC file by default. Please refer to [Appendix G.1.21](#) for the method of obtaining the WinMOPAC file.

### 2.2 Running MOS–F V4.2D on a Terminal

This section describes how to run MOS–F V4.2D on a terminal under the following conditions:

- MOS–F V4.2D is properly installed and the executable file is `mosf`.
- An input file for MOS–F V4.2D exists in the current directory.
- MOS–F V4.2D is executed in the current directory.

### 2.2.1 Input File Name is *filename.mos*

To run MOS-F V4.2D using the input file `testdata.mos`, type the following in the command line:

```
% mosf testdata.mos
```

In this case,

- Output file name is `testdata.oms`.
- WinMOPAC file name is `testdata.wms`.

Please refer to [Appendix G.1.21](#) for how to obtain the WinMOPAC file.

The user can omit the extension `.mos`.

```
% mosf testdata
```

In this case,

- MOS-F V4.2D first inquires whether the file `testdata` exists or not. If `testdata` exists, MOS-F V4.2D uses it as an input file. Otherwise MOS-F V4.2D inquires whether `testdata.mos` exists or not.
- Output file name is `testdata.oms`.
- WinMOPAC file name is `testdata.wms`.

Input redirection is also available to run MOS-F V4.2D as below.

```
% mosf < testdata.mos
```

In this case,

- User can not omit the extension `.mos`.
- Results are outputted to the standard output.
- WinMOPAC file name is fixed as `TestMOS.wms`.

### 2.2.2 Input File Name is *filename.xxx*

There are many extensions as input files such as `.dat`, `.data`, `.inp`, `.input`, and `.com`. The following is how to run MOS-F V4.2D with the input file `testdata.dat`:

```
% mosf testdata.dat
```

In this case,

- Output file name is `testdata.oms`.
- WinMOPAC file name is `testdata.wms`.

Input redirection is also available to run MOS-F V4.2D.



## Chapter 3

# Input Data

In order to calculate molecular properties with any molecular orbital theory software, the information of the molecule of interest must be supplied as an input data. This chapter explains how to prepare input data for this program.

Note: Molecular geometry for WinMOPAC V3 can be prepared only in the MOPAC compatible formats (`Coord=Inter` and `Coord=MCart`). The Z-matrix used in Gaussian (`Coord=Z`) and the standard Cartesian coordinates (`Coord=Cart`) are not available at present. These formats are available for running MOS-F V4.2D independently.

It should be noted that WinMOPAC saves the input data as `<filename>.mos`.

### 3.1 Summary

Figure 3.1 shows an example of typical input data. This example is based on Paranitroaniline and is aimed at calculating its singlet excitation energy with INDO/S-CI. Gaussian Symbolic Z-matrix format is used. Some of the atomic parameters are user-defined, and not the default. All the input is in free format.

Let us now go through this example.

The input data consist of the following five sections.

line 01-02 : Keywords to specify the method of calculation and output format.

line 03-05 : Title for calculation.

line 06-45 : Molecular specification.

line 46-51 : Atomic parameters (options available).

line 52-54 : Orbital specification for CI calculation (options available).

In order to run this program at least the keyword section, the title section and the molecular specification section must be supplied. The other two sections, namely the atomic parameters section and the CI orbitals section are needed only when specific keywords have been used in the keyword section and therefore unnecessary with default jobs.

Let us now go through these five sections in more detail.

Figure 3.1 A Typical Input Data

```

line 01 : INDO/S Coord=Z Plane=Z-Y Parm=Type CI=Read Alpha Beta Gamma WinMOPAC
line 02 :
line 03 : An example of input data ... INDO/S-CI with pi-pi* orbitals.
line 04 :           Paranitroaniline with C2v constraint obtained from MOPAC 97.
line 05 :
line 06 : X01Dummy
line 07 : X02Dummy X01Dummy Rcc1
line 08 : C01 X02Dummy RDmy X01Dummy F90
line 09 : N01Amino C01 Rcn1 X02Dummy F90 X01Dummy F180
line 10 : H01Amino N01Amino Rnh C01 hnc X02Dummy F90
line 11 : H02Amino N01Amino Rnh C01 hnc X02Dummy -F90
line 12 : C02 C01 Rcc2 N01Amino ccn1 H01Amino Zero
line 13 : C03 C02 Rcc3 C01 ccc1 N01Amino F180
line 14 : C04 X01Dummy RDmy X02Dummy F90 C01 Zero
line 15 : C06 C01 Rcc2 N01Amino ccn1 H01Amino F180
line 16 : C05 C06 Rcc3 C01 ccc1 N01Amino F180
line 17 : N02Nitro C04 Rcn2 X01Dummy F90 X02Dummy F180
line 18 : O01Nitro N02Nitro Ron C04 onc C03 Zero
line 19 : O02Nitro N02Nitro Ron C04 onc C05 Zero
line 20 : H03 C02 Rhc1 C01 hcc1 N01Amino Zero
line 21 : H04 C03 Rhc2 C02 hcc2 C01 F180
line 22 : H05 C05 Rhc2 C06 hcc2 C01 F180
line 23 : H06 C06 Rhc1 C01 hcc1 N01Amino Zero
line 24 :
line 25 : Rcc1 2.81151
line 26 : Rcc2 1.42238
line 27 : Rcc3 1.38296
line 28 : Rcn1 1.36974
line 29 : Rcn2 1.47693
line 30 : Rnh 0.98688
line 31 : Ron 1.20373
line 32 : Rhc1 1.10020
line 33 : Rhc2 1.10433
line 34 : hnc 120.21987
line 35 : ccn1 120.78988
line 36 : ccc1 120.69395
line 37 : onc 119.15834
line 38 : hcc1 120.09613
line 39 : hcc2 120.12039
line 40 :
line 41 : RDmy 5.0
line 42 : Zero 0.0
line 43 : F90 90.0
line 44 : F180 180.0
line 45 :
line 46 : C Es=19.42 Ep=10.7 G1sp=6.9 \
line 47 : F2pp=4.51 Zsp=1.6
line 48 : 7 Es=25.6 Zsp=1.9 Bsp=25.0 \
line 49 : Ep=13.3 G1sp=8.96 F2pp=6.46
line 50 : 0 Es=32.5 Ep=15.9
line 51 :
line 52 : 14 18 21 23 25 26
line 53 : 27 28 29 31
line 54 :

```

## 3.2 Keywords

Keywords need to be given to specify the desired method of calculation such as CNDO/S or INDO/S, the style of output for the orbital coefficients and so on.

The following rules apply to the keyword section.

- Free format (up to 80 columns).
- Maximum of nine lines.
- This section is terminated by a blank line.
- Keywords are separated with more than one blank space, or a comma.
- No distinction between upper and lower case.
- At least one keyword is required.
- No exponential notation for floating point.

```
SCFCrt=1.0e-5 ... bad!
```

```
SCFCrt=0.00001 ... good!
```

Please refer to [Appendix G](#) for the list of keywords used in MOS-F V4.2D.

## 3.3 Title

The user may wish to add some information about the calculation, such as the conditions, the molecule's name, and so on and this is where to add them.

The following restrictions apply to the title section.

- Free format (up to 80 columns).
- Maximum of nine lines.
- This section is terminated by a blank line.

## 3.4 Molecular Specification

Note: Molecular geometry for WinMOPAC V3 can be prepared only in the MOPAC compatible formats (`Coord=Inter` and `Coord=MCart`). The Z-matrix used in Gaussian (`Coord=Z`) and the standard Cartesian coordinates (`Coord=Cart`) are not available at present. These formats are available for running MOS-F V4.2D independently.

Molecular geometry can be prepared in the internal coordinate style used in MOPAC, the Z-matrix used in Gaussian and in standard Cartesian coordinates. It is specified with the appropriate keywords. The common restrictions regardless of the keyword used are as follows.

- One line per atom with its coordinate information.
- Free format (up to 80 columns).
- Strings must be separated with a space (or more) or a comma. The first string is then called the first field, the second string called the second field and so on. For example in [Figure 3.1](#), the ninth line is for the molecule's geometry, and `N01Amino` is the first field and `X02Dummy` is the fourth.

- Atom type is given by its standard symbol or atomic number. Extra characters may accompany the atomic symbols used for input. For example in [Figure 3.1](#), H01Amino and H02Nitro are being used to distinguish the hydrogen atoms, and up to eight characters may be used. Such string extension is called *atom identifier* in this manual.
- XX, X or 99 must be used for dummy atoms.
- No distinction between upper and lower case.
- Given coordinates are automatically translated to bring the nuclear charge to the origin of the corresponding electrons.
- MOPAC format, `Coord=Inter` is used as default.
- Coordinate system is right-handed.
- Default distance in Å and angle in degrees.
- For an interatomic distance  $R$ , bond angle  $\alpha$  and dihedral angle  $\beta$ , the limits are

- $0 < R$ ,
- $0^\circ < \alpha < 180^\circ$ ,
- $-360^\circ \leq \beta \leq 360^\circ$ .

### 3.4.1 Internal Coordinates and Z-matrix

User can specify either of them by giving `Coord=Inter` or `Coord=Z`.

#### Specifying `Coord=Inter`

An example is given in [Figure 3.2](#). When using `Coord=Inter`, the MOPAC convention will be followed. The MOPAC's symmetry feature is not supported. When using `Coord=Inter`, the following restrictions apply.

- The first field must have the atom type specified by its atomic number, standard symbol or atom identifier.
- The second field must have the atoms and interatomic distances given in the eighth field.
- The fourth field must include the bond angles given in the ninth and eighth field.
- The sixth field must include the dihedral-angles specified in the tenth, ninth and eighth field. The convention for specifying dihedral-angles is the same as in MOPAC or Gaussian, namely it is clockwise.
- The third, fifth and seventh fields should include suitable alphabetical or numerical characters. These fields include parameters for geometry optimization and reaction coordinates in MOPAC, but they are totally skipped in this program.
- Conversion from internal coordinate to Cartesian is based on MOPAC for atoms 1, 2, and 3, that is the atom 1 moves to the origin, the atom 2 to the positive x-axis and the atom 3 to the x-y plane. It can be modified with a keyword like `Plane=Z-X`, for example.
- This part is terminated by a blank line.

Figure 3.2 Example with Coord=Inter

```

line 01 : XX    0.00000000  0    0.00000000  0    0.00000000  0    0    0    0
line 02 : XX    2.81151000  0    0.00000000  0    0.00000000  0    1    0    0
line 03 : C     5.00000000  0    90.00000000  0    0.00000000  0    2    1    0
line 04 : N     1.36974000  0    90.00000000  0  180.00000000  0    3    2    1
line 05 : H     0.98688000  0  120.2198700  0    90.00000000  0    4    3    2
line 06 : H     0.98688000  0  120.2198700  0   -90.00000000  0    4    3    2
line 07 : C     1.42238000  0  120.7898800  0    0.00000000  0    3    4    5
line 08 : C     1.38296000  0  120.6939500  0  180.00000000  0    7    3    4
line 09 : C     5.00000000  0    90.00000000  0    0.00000000  0    1    2    3
line 10 : C     1.42238000  0  120.7898800  0  180.00000000  0    3    4    5
line 11 : C     1.38296000  0  120.6939500  0  180.00000000  0   10    3    4
line 12 : N     1.47693000  0    90.00000000  0  180.00000000  0    9    1    2
line 13 : O     1.20373000  0  119.1583400  0    0.00000000  0   12    9    8
line 14 : O     1.20373000  0  119.1583400  0    0.00000000  0   12    9   11
line 15 : H     1.10020000  0  120.0961300  0    0.00000000  0    7    3    4
line 16 : H     1.10433000  0  120.1203900  0  180.00000000  0    8    7    3
line 17 : H     1.10433000  0  120.1203900  0  180.00000000  0   11   10    3
line 18 : H     1.10020000  0  120.0961300  0    0.00000000  0   10    3    4
line 19 :

```

### Specifying Coord=Z

When Coord=Z is specified, the input format follows that of the Symbolic Z-Matrix used in Gaussian. In this case, the content of the eighth field, namely the  $j$ -value as in Gaussian, influences the content of the seventh field. There are two possible patterns as follows.

- Specify 0 or none at all
- Specify 1 or -1

The case where nothing is specified in the eighth field is illustrated in Figure 3.3 and with a methane molecule as an example, the case where 1 and -1 is specified is illustrated in Figures 3.4 and 3.5 respectively, where the data is equivalent.

First of all, let us go through the case where Coord=Z is specified for the common restrictions irrespective of the content in the eighth field with some illustration given in Figure 3.3.

- In the line 04 in Figure 3.3, we see Rcn1, F90 and F180 for the third, fifth and seventh field, which are not numbers. The program continues to read on despite the terminating blank line at the line 19 for the Z-matrix section and reads in the corresponding numerical data as appropriate. In this example, for Rcn1, the value 1.36974 Å will read in at the line 23. Rcn1 is called a *Z-matrix variable*.
- A sign may be used with strings, as illustrated in the line 06 where we can see -F90. For F90, the value 90.0 will be read in at the line 38 and -F90 then will be -90.0.
- Numerical input for strings will follow the following format (line 20-34, line 36-39).
 

```

string = a number
string (one space or more) a number

```
- A string must be no more than eight characters in length.

Figure 3.3 A Typical Example with Coord=Z where the Eighth Field Has No Entry Coord=Z

```

line 01 : X01Dummy
line 02 : X02Dummy  X01Dummy  Rcc1
line 03 : C01      X02Dummy  RDmy  X01Dummy  F90
line 04 : N01Amino C01      Rcn1  X02Dummy  F90  X01Dummy  F180
line 05 : H01Amino N01Amino Rnh   C01      hnc  X02Dummy  F90
line 06 : H02Amino N01Amino Rnh   C01      hnc  X02Dummy -F90
line 07 : C02      C01      Rcc2  N01Amino ccn1  H01Amino  Zero
line 08 : C03      C02      Rcc3  C01      ccc1  N01Amino  F180
line 09 : C04      X01Dummy RDmy  X02Dummy F90  C01      Zero
line 10 : C06      C01      Rcc2  N01Amino ccn1  H01Amino  F180
line 11 : C05      C06      Rcc3  C01      ccc1  N01Amino  F180
line 12 : N02Nitro C04      Rcn2  X01Dummy F90  X02Dummy  F180
line 13 : 001Nitro N02Nitro Ron   C04      onc  C03      Zero
line 14 : 002Nitro N02Nitro Ron   C04      onc  C05      Zero
line 15 : H03      C02      Rhc1  C01      hcc1  N01Amino  Zero
line 16 : H04      C03      Rhc2  C02      hcc2  C01      F180
line 17 : H05      C05      Rhc2  C06      hcc2  C01      F180
line 18 : H06      C06      Rhc1  C01      hcc1  N01Amino  Zero
line 19 :
line 20 : Rcc1    2.81151
line 21 : Rcc2    1.42238
line 22 : Rcc3    1.38296
line 23 : Rcn1    1.36974
line 24 : Rcn2    1.47693
line 25 : Rnh     0.98688
line 26 : Ron     1.20373
line 27 : Rhc1    1.10020
line 28 : Rhc2    1.10433
line 29 : hnc    120.21987
line 30 : ccn1   120.78988
line 31 : ccc1   120.69395
line 32 : onc    119.15834
line 33 : hcc1   120.09613
line 34 : hcc2   120.12039
line 35 :
line 36 : RDmy    5.0
line 37 : Zero    0.0
line 38 : F90     90.0
line 39 : F180   180.0
line 40 :

```

Figure 3.4 Another Example with Coord=Z where 1 or -1 is Specified in the Eighth Field (First Example with a Methane Molecule)

```
line 01 : H01
line 02 : C02 H01 Rch
line 03 : H03 C02 Rch H01 TetraHed
line 04 : H04 C02 Rch H01 TetraHed H03 TetraHed +1
line 05 : H05 C02 Rch H01 TetraHed H03 TetraHed -1
line 06 :
line 07 : Rch 1.10
line 08 : TetraHed 109.471220634
line 09 :
```

Figure 3.5 Yet Another Example with Coord=Z Where 1 or -1 is Specified in the Eighth Field (Second Example with a Methane Molecule)

```
line 01 : H
line 02 : C 1 Rch
line 03 : H 2 Rch 1 TetraHed
line 04 : H 2 Rch 1 TetraHed 3 TetraHed 1
line 05 : H 2 Rch 1 TetraHed 3 TetraHed -1
line 06 :
line 07 : Rch = 1.10
line 08 : TetraHed = 109.471220634
line 09 :
```

- The numerical data section (line 20–40) for the strings in the Z-matrix section must be terminated with two blank lines (line 35, line 40). If all the required data is read in before the first blank line, this first blank line will be regarded as the terminating blank line for the coordinate input.
- The line 20–34 have variables for geometry optimization and data in the line 36–39 will be treated as constants in the Gaussian format. In this program, however, the information given there is merely to specify molecular structure. Therefore, a blank line to separate variables and constants (line 35) is not necessary.
- By default, atom 1 will be placed at the origin, atom 2 on the positive x-axis and atom 3 on the x-y plane. This can be modified with a keyword such as `Plane=Z-X`.

Now let us go through the features dependent on the eighth field. Please note the difference from the previously mentioned case.

### 0 or None Specified in the Eighth Field

- In the first field, atom type must be specified (its atomic number or symbol with or without desired identifier).
- In the third field, the interatomic distance for the atoms specified in the second field needs to be given.
- In the fifth field, the bond angles for the atoms specified in the fourth and second field need to be given.
- In the seventh field, the dihedral angles for the atoms specified in the sixth, fourth and second field need to be given. The sign of a dihedral-angle is based on clockwise sense as in MOPAC and Gaussian.

### 1 or -1 Specified in the Eighth Field

- The first, third and fifth field are treated the same as in the case where “0 or none specified in the eighth field.”
- In the seventh field, the bond angles for the atoms specified in the second and sixth field need to be given. See [Figure 3.6](#).
- In the eighth field, the effect of  $\pm 1$  is the same as in Gaussian. As shown in [Figure 3.6](#), if the vector from the atom in the first field to the one in the second field is given by  $a$ , from the atom in the fourth field to the one in the second field  $b$ , from the atom in the sixth field to the one in the second field  $c$ . The Cartesian coordinates for the atom in the field is set up whilst satisfying the following.

$$- \quad \text{the eighth field} = +1 \quad \dots \quad a \cdot (b \times c) > 0$$

$$- \quad \text{the eighth field} = -1 \quad \dots \quad a \cdot (b \times c) < 0$$

If the atoms given in the first, second, fourth and sixth fields are not in the same plane, there are two different Cartesian coordinates satisfying the bond angles above. Therefore, one of the two is chosen with the vector triple products.

## 3.4.2 Cartesian Coordinates

There are two formats available, and the user can choose between them with the keywords `Coord=MCart` and `Coord=Cart`.



Figure 3.6 Specifying Bond Angles when the Eighth Field Has 1 or -1

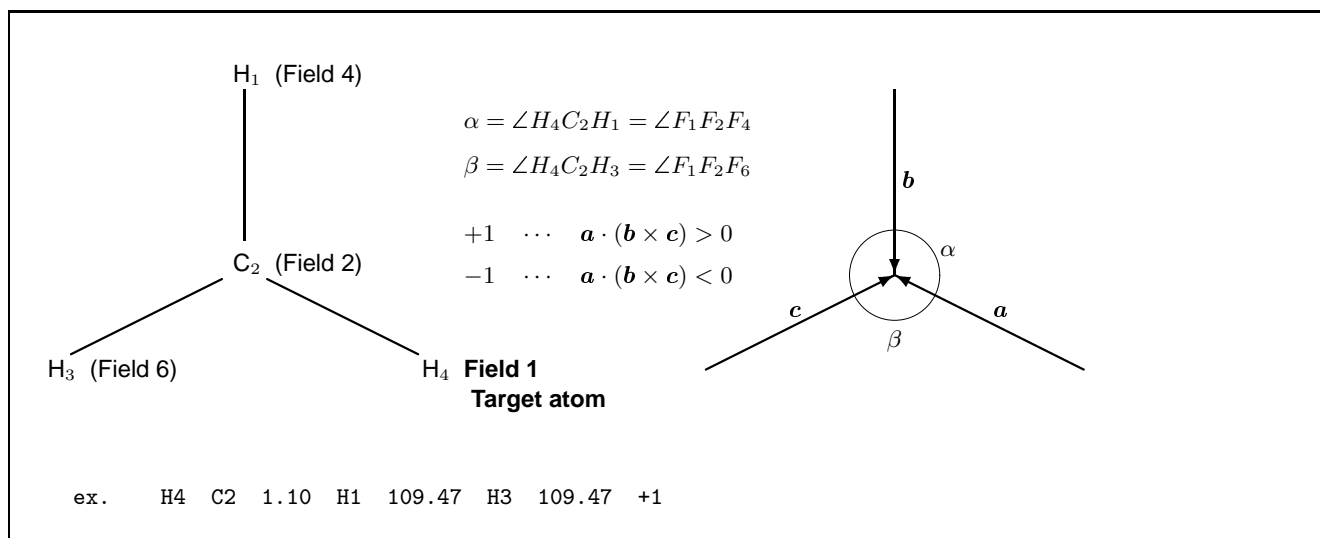


Figure 3.7 An Example with Coord=MCart

```

line 01 : C      0.00000000 0  5.00000000 0  2.81151000 0
line 02 : N      0.00000000 0  5.00000000 0  4.18125000 0
line 03 : H      0.852763308 0  5.00000000 0  4.677966090 0
line 04 : H     -0.852763308 0  5.00000000 0  4.677966090 0
line 05 : C      1.221896000 0  5.00000000 0  2.083406279 0
line 06 : C      1.219580519 0  5.00000000 0  0.700448217 0
line 07 : C      0.000000000 0  5.00000000 0  0.000000000 0
line 08 : C     -1.221896000 0  5.00000000 0  2.083406279 0
line 09 : C     -1.219580519 0  5.00000000 0  0.700448217 0
line 10 : N      0.000000000 0  5.00000000 0 -1.476930000 0
line 11 : O      1.051189207 0  5.00000000 0 -2.063417139 0
line 12 : O     -1.051189207 0  5.00000000 0 -2.063417139 0
line 13 : H      2.183089523 0  5.00000000 0  2.618707176 0
line 14 : H      2.173866845 0  5.00000000 0  0.144676360 0
line 15 : H     -2.173866845 0  5.00000000 0  0.144676360 0
line 16 : H     -2.183089523 0  5.00000000 0  2.618707176 0
line 17 :

```

Figure 3.8 An Example with Coord=Cart

line 01 :	C	0.000000000	5.000000000	2.811510000
line 02 :	N	0.000000000	5.000000000	4.181250000
line 03 :	H	0.852763308	5.000000000	4.677966090
line 04 :	H	-0.852763308	5.000000000	4.677966090
line 05 :	C	1.221896000	5.000000000	2.083406279
line 06 :	C	1.219580519	5.000000000	0.700448217
line 07 :	C	0.000000000	5.000000000	0.000000000
line 08 :	C	-1.221896000	5.000000000	2.083406279
line 09 :	C	-1.219580519	5.000000000	0.700448217
line 10 :	N	0.000000000	5.000000000	-1.476930000
line 11 :	O	1.051189207	5.000000000	-2.063417139
line 12 :	O	-1.051189207	5.000000000	-2.063417139
line 13 :	H	2.183089523	5.000000000	2.618707176
line 14 :	H	2.173866845	5.000000000	0.144676360
line 15 :	H	-2.173866845	5.000000000	0.144676360
line 16 :	H	-2.183089523	5.000000000	2.618707176
line 17 :				

**Using Coord=MCart**

An example is illustrated in [Figure 3.7](#).

When using Coord=MCart the following conditions apply.

- The MOPAC Cartesian format will be followed.
- Flags for optimization and reaction coordinate for MOPAC will be skipped.
- The first field should include the atom type (with the atomic number, standard symbol or atom identifier).
- The second, fourth and sixth fields should include the x, y and z component of the Cartesian coordinate.

**Using Coord=Cart**

An example is illustrated in [Figure 3.8](#).

When using Coord=Cart the following apply.

- The first field should include the atom type.
- The second to fourth fields should include the x, y and z components of the Cartesian coordinate.

## 3.5 Options

The input data that is explained here is not always necessary. Only when certain keywords are used, then extra data needs to be supplied.

### 3.5.1 Atomic Parameters

Users may supply their own values for the ionization potentials, resonance integrals, etc. instead of using the default values, or when the default values are unavailable. Please refer to [Appendix A](#) for these default values.

Figure 3.9 An Example with Parm=Type

```

line 01 : C  Es=19.42  Ep=10.7  G1sp=6.9 \
line 02 :      F2pp=4.51  Zsp=1.6
line 03 : 7  Es=25.6  Zsp=1.9  Bsp=25.0 \
line 04 :      Ep=13.3  G1sp=8.96  F2pp=6.46
line 05 : 0  Es=32.5  Ep=15.9
line 06 :

```

Either Parm=Type or Parm=Atom can be specified. The only difference to be noted is the data supplied for the first field. Let us first go through the common restrictions applicable to both cases.

- Free format (up to 80 columns).
- The atomic parameters part is terminated by a blank line.
- When the data supplied for an atom cannot fit into one line, it may continue to the next line with a back slash \ at the end of the first one. Please refer to [Figure 3.9](#) for an example.
- The syntax is as shown.

Keyword = *value*

- Parameters are always positive except the special case with respect to the resonance integral  $\beta$ .
- Slater exponent and Klondike parameter<sup>43</sup> are in Bohr<sup>-1</sup> whilst all the others are in eV.
- A space or comma is used to separate between the parameters and atom types.
- No distinction between upper and lower case.
- Please refer to [Appendix H](#) for the keywords for the atomic parameters.

### Using Parm=Type

Parm=Type is used when atomic parameters need to be specified for each type of atom. With Parm=Type, the first field should contain the atom type (given in its atomic number or symbol). An example is shown in [Figure 3.9](#) with INDO/S as the model Hamiltonian. Let us go through it.

- Carbon atom (line 01-02).
  - The ionization potential for *s* and *p*-orbitals are 19.42 and 10.7 eV respectively.
  - For the Slater-Condon parameters,  $G^1(sp)$  and  $F^2(pp)$  are set to 6.9 and 4.51 eV respectively.
  - The Slater exponent for *s* and *p*-orbitals are both set to 1.6 Bohr<sup>-1</sup>.
- Nitrogen atom (line 03-04).
  - The ionization potential for *s* and *p*-orbitals are 25.6 and 13.3 eV respectively.
  - *s* and *p*-orbital's resonance integral  $-\beta_s$  and  $-\beta_p$  are both set to 25.0 eV.
  - $G^1(sp)$  and  $F^2(pp)$  are both set to 8.96 and 6.46 eV respectively.

Figure 3.10 An Example with Parm=Atom

```

line 01 : N01Amino   Ep=26.70  G=17.44
line 02 : N02Nitro   Ep=20.40  G=14.89
line 03 : 13         Ep=20.80  G=16.50
line 04 : 002Nitro   Ep=20.80  G=16.50
line 05 :

```

- The Slater exponent for  $s$  and  $p$ -orbitals are both set to  $1.9 \text{ Bohr}^{-1}$ .
- Oxygen atom (line 05).
  - The ionization potential for  $s$  and  $p$ -orbitals are 32.5 and 15.9 eV respectively.

With Parm=Type, the following atomic parameters can be specified.

- Ionization potential.
- Resonance integral.
- Slater exponent.
- One-center electron repulsion integral,  $\gamma_{AA}$ .
- DasGupta-Huzinaga's Klondike parameter.
- Slater-Condon parameter.

### Using Parm=Atom

Parm=Atom is used when atomic parameters need to be specified for each type of atom, but unlike Parm=Type, different values can be given for the same type of atom. An example illustrated in Figure 3.10 uses Parm=Atom with the user supplied parameters for the nitrogen and oxygen, note that the parameter set for the Nitrogen atom in the amino group is not the same as that set for the one the nitro group. The first field should contain the serial number for the atoms or atomic symbols. **Dummy atoms are also counted.** When using the atomic symbols, they must be used in such a way as to allow distinction amongst them. For example, as with N01Amino in Figure 3.10, it must be unique in the first field (atomic symbol) in the molecular specification section shown in Figure 3.1.

For supplying the atomic parameters, note that,

- For the atom identifier N01Amino, namely the fourth nitrogen atom in series in Figure 3.1,
  - The ionization potential for the  $p$ -type orbital is set as 26.70 eV.
  - The one-center electron repulsion integral  $\gamma_{AA}$  is set to be 17.44 eV.
- The atom identifier N02Nitro, namely the twelfth atom, nitrogen, in Figure 3.1.
  - The ionization potential for the  $p$ -type orbital is set to be 20.40 eV.
  - The one-center electron repulsion integral  $\gamma_{AA}$  is set to be 14.89 eV.

- The thirteenth atom, oxygen with atom identifier of 001Nitro, in [Figure 3.1](#).
  - The ionization potential for the  $p$ -type orbital is set to be 20.80 eV.
  - The one-center electron repulsion integral  $\gamma_{AA}$  is set to be 16.50 eV.
- The atom identifier 002Nitro, namely the fourteenth atom in [Figure 3.1](#).
  - The ionization potential for the  $p$ -type orbital is set to be 20.80 eV.
  - The one-center electron repulsion integral  $\gamma_{AA}$  is set to be 16.50 eV.

With `Parm=Atom`, the following atomic parameters can be specified.

- Ionization potential.
- Resonance integral.
- Slater exponent.
- One-center electron repulsion integral,  $\gamma_{AA}$ .
- Klondike parameter in DasGupta-Huzinaga.

Unlike with `Parm=Type`, the Slater-Condon parameter cannot be changed.

### 3.5.2 Orbitals for CI Calculation

With `CI=Read`, the orbitals to be included for the CI calculation can be specified with a set of serial numbers which are not necessarily continuous. An example for a typical `CI=Read` case is illustrated in [Figure 3.11](#), where the following rules apply.

- Orbitals must be specified with their serial number.
- Free format (up to 80 columns).
- A blank line to terminate the data section.
- Each entry must be separated with a space or comma.

Figure 3.11 An Example for `CI=Read`

```
line 01 : 14 18 21 23 25 26
line 02 : 27 28 29 31
line 03 :
```



# Chapter 4

## Output

### 4.1 Example I

Note: Molecular geometry for WinMOPAC V3 can be prepared only in the MOPAC compatible formats (Coord=Inter and Coord=MCart). The Z-matrix used in Gaussian (Coord=Z) and the standard Cartesian coordinates (Coord=Cart) are not available at present. These formats are available for running MOS-F V4.2D independently.

The data shown in [Figure 3.1](#) will result an output shown below.

```
1
(1) MOS-F-related files
    Initialization for MOS-F I/O.
    Input file: testdata.mos
    Creating files ...
    Input:  testdata.ims
    OutPut: testdata.oms
1
MOS-F V4 ... A semiempirical MO package for spectroscopy.

    Copyright (c) 1994-2000 FUJITSU LABORATORIES LTD.
    All Rights Reserved.

Entering MOS-F system at Mon Jul 10 17:35:01 2000
*****
MOS-F version 4.2D ... Microsoft(R) Windows 95/98/NT/2000.
    By A. Matsuura. Fujitsu Labs Ltd.
*****
MOS-F> JCtrl entering.
(2) Keywords
-----
INDO/S Coord=Z Plane=Z-Y Parm=Type CI=Read Alpha Beta Gamma WinMOPAC
-----
INDO/S calculation
Silent mode on the stderr output specified.
(3) WinMOPAC file
    Creating WinMOPAC file ... testdata.wms
MOS-F> JCtrl done.  Elapsed time = 0.13 s. Total = 00h 00m 00s.
MOS-F> MInput entering.
(4) Title
-----
An example of input data ... INDO/S-CI with pi-pi* orbitals.
```

Paranitroaniline with C2v constraint obtained from MOPAC 97.

(5) **Symbolic Z-matrix**

Read Gaussian symbolic Z-matrix ...

```

X01Dummy
X02Dummy  X01Dummy  Rcc1
C01        X02Dummy  RDmy  X01Dummy  F90
N01Amino  C01        Rcn1  X02Dummy  F90  X01Dummy  F180  0
H01Amino  N01Amino  Rnh  C01        hnc  X02Dummy  F90  0
H02Amino  N01Amino  Rnh  C01        hnc  X02Dummy  -F90  0
C02        C01        Rcc2  N01Amino  ccn1  H01Amino  Zero  0
C03        C02        Rcc3  C01        ccc1  N01Amino  F180  0
C04        X01Dummy  RDmy  X02Dummy  F90  C01        Zero  0
C06        C01        Rcc2  N01Amino  ccn1  H01Amino  F180  0
C05        C06        Rcc3  C01        ccc1  N01Amino  F180  0
N02Nitro  C04        Rcn2  X01Dummy  F90  X02Dummy  F180  0
O01Nitro  N02Nitro  Ron  C04        onc  C03        Zero  0
O02Nitro  N02Nitro  Ron  C04        onc  C05        Zero  0
H03        C02        Rhc1  C01        hcc1  N01Amino  Zero  0
H04        C03        Rhc2  C02        hcc2  C01        F180  0
H05        C05        Rhc2  C06        hcc2  C01        F180  0
H06        C06        Rhc1  C01        hcc1  N01Amino  Zero  0

```

(6) **Values for the Z-matrix variables**

Variables ...

```

Rcc1  =  2.811510000000
Rcc2  =  1.422380000000
Rcc3  =  1.382960000000
Rcn1  =  1.369740000000
Rcn2  =  1.476930000000
Rnh   =  0.986880000000
Ron   =  1.203730000000
Rhc1  =  1.100200000000
Rhc2  =  1.104330000000
hnc   =  120.219870000000
ccn1  =  120.789880000000
ccc1  =  120.693950000000
onc   =  119.158340000000
hcc1  =  120.096130000000
hcc2  =  120.120390000000
RDmy  =  5.000000000000
Zero  =  0.000000000000
F90   =  90.000000000000
F180  =  180.000000000000

```

(7) **Z-matrix and the parameters**

Internal coordinates ...

```

-----
Center  Atomic          Internal coordinates (Ang and Deg)
number  symbol    na  Length    nb  Angle-1    nc  Angle-2    j
-----
  1      XX
  2      XX      1  2.811510
  3      C      2  5.000000    1  90.00000
  4      N      3  1.369740    2  90.00000    1  180.00000    0
  5      H      4  0.986880    3  120.21987    2  90.00000    0
  6      H      4  0.986880    3  120.21987    2 -90.00000    0
  7      C      3  1.422380    4  120.78988    5   0.00000    0
  8      C      7  1.382960    3  120.69395    4  180.00000    0
-----

```



9	C	1	5.000000	2	90.00000	3	0.00000	0
10	C	3	1.422380	4	120.78988	5	180.00000	0
11	C	10	1.382960	3	120.69395	4	180.00000	0
12	N	9	1.476930	1	90.00000	2	180.00000	0
13	O	12	1.203730	9	119.15834	8	0.00000	0
14	O	12	1.203730	9	119.15834	11	0.00000	0
15	H	7	1.100200	3	120.09613	4	0.00000	0
16	H	8	1.104330	7	120.12039	3	180.00000	0
17	H	11	1.104330	10	120.12039	3	180.00000	0
18	H	10	1.100200	3	120.09613	4	0.00000	0

-----  
 Atom 3 is placed on the Z-Y Plane.

(8) **Cartesian coordinate section**

Input geometry ...

Center number	Atomic symbol	Coordinates (Angstroms)		
		x	y	z
1	XX	0.00000000	0.00000000	0.00000000
2	XX	0.00000000	0.00000000	2.811510000
3	C	0.00000000	5.00000000	2.811510000
4	N	0.00000000	5.00000000	4.181250000
5	H	0.852763308	5.00000000	4.677966090
6	H	-0.852763308	5.00000000	4.677966090
7	C	1.221896000	5.00000000	2.083406279
8	C	1.219580519	5.00000000	0.700448217
9	C	0.00000000	5.00000000	0.00000000
10	C	-1.221896000	5.00000000	2.083406279
11	C	-1.219580519	5.00000000	0.700448217
12	N	0.00000000	5.00000000	-1.476930000
13	O	1.051189207	5.00000000	-2.063417139
14	O	-1.051189207	5.00000000	-2.063417139
15	H	2.183089523	5.00000000	2.618707176
16	H	2.173866845	5.00000000	0.144676360
17	H	-2.173866845	5.00000000	0.144676360
18	H	-2.183089523	5.00000000	2.618707176

-----  
 Reduced dummy atoms.

Translate molecule ... The origin is the center of nuclear charges.

(9) **Cartesian coordinates used by the calculation**

Standard geometry ...

Center number	Atomic symbol	Coordinates (Angstroms)		
		x	y	z
3	C	0.00000000	0.00000000	2.096891355
4	N	0.00000000	0.00000000	3.466631355
5	H	0.852763308	0.00000000	3.963347445
6	H	-0.852763308	0.00000000	3.963347445
7	C	1.221896000	0.00000000	1.368787633
8	C	1.219580519	0.00000000	-0.014170428
9	C	0.00000000	0.00000000	-0.714618645
10	C	-1.221896000	0.00000000	1.368787633
11	C	-1.219580519	0.00000000	-0.014170428
12	N	0.00000000	0.00000000	-2.191548645
13	O	1.051189207	0.00000000	-2.778035784
14	O	-1.051189207	0.00000000	-2.778035784

15	H	2.183089523	0.000000000	1.904088531
16	H	2.173866845	0.000000000	-0.569942285
17	H	-2.173866845	0.000000000	-0.569942285
18	H	-2.183089523	0.000000000	1.904088531

**(10) Molecule's chemical formula**

Chemical formula ... C6H6N2O2

**(11) Molecular weight**

Molecular mass ... 138.1259

MOS-F&gt; MInput done. Elapsed time = 0.02 s. Total = 00h 00m 00s.

MOS-F&gt; AtPrms entering.

Get the constituent atomic parameters.

**(12) User-defined atomic parameters**

Read user-defined atomic parameters ...

**(13) User-defined parameters for carbon**

Atomic number = 6

Es = 19.42000

Ep = 10.70000

G1sp = 6.90000

F2pp = 4.51000

Zsp = 1.60000

**(14) User-defined parameters for nitrogen**

Atomic number = 7

Es = 25.60000

Zsp = 1.90000

Bsp = 25.00000

Ep = 13.30000

G1sp = 8.96000

F2pp = 6.46000

**(15) User-defined parameters for oxygen**

Atomic number = 8

Es = 32.50000

Ep = 15.90000

**(16) Atomic parameters output**

=====

Atomic parameters

=====

Units ...

Energies ... eV

Slater exponent (Z[spd][ 12]) ... Bohr<sup>-1</sup>

Van der Waals radius (vdW) ... Angstrom

Others (CC[12], CSq[12]) ... Dimensionless

Abbreviations ...

Ionization potential : Es1, Ep1, Ed1, Es2, Ep2, Ed2, CSq1, CSq2

Resonance integral : Bs, Bp, Bd

Basis function : Zs, Zp, Zd1, Zd2, CC1, CC2

One-center ERI, Gamma : Gss, Gsd, Gdd

Slater-Condon parameter : G1sp, F2pp, G2sd, G1pd, F2pd, G3pd, F2dd, F4dd

-----

1. H : Es1 = 13.06000

Bs = 12.00000

Zs = 1.20000

Gss = 12.85000

vdW = 1.20000

6. C : Es1 = 19.42000 Ep1 = 10.70000  
 Bs = 17.00000 Bp = 17.00000  
 Zs = 1.60000 Zp = 1.60000  
 Gss = 11.11000  
 G1sp = 6.90000 F2pp = 4.51000  
 vdW = 1.70000

7. N : Es1 = 25.60000 Ep1 = 13.30000  
 Bs = 25.00000 Bp = 25.00000  
 Zs = 1.90000 Zp = 1.90000  
 Gss = 12.01000  
 G1sp = 8.96000 F2pp = 6.46000  
 vdW = 1.55000

8. O : Es1 = 32.50000 Ep1 = 15.90000  
 Bs = 34.00000 Bp = 34.00000  
 Zs = 2.27500 Zp = 2.27500  
 Gss = 13.00000  
 G1sp = 11.81545 F2pp = 6.90282  
 vdW = 1.52000

-----

**(17) Number of basis functions and electrons**

46 Basis functions.            52 Valence electrons.  
 26 Alpha electrons.           26 Beta electrons.

MOS-F> AtPrms done. Elapsed time = 0.02 s. Total = 00h 00m 00s.

MOS-F> CIInfo entering.

Window information

**(18) Orbitals used for the CI calculation**

Active MO range ...

Occupied : 6 MOs  
 14 18 21 23 25 26

Virtual : 4 MOs  
 27 28 29 31

MOS-F> CIInfo done. Elapsed time = 0.02 s. Total = 00h 00m 00s.

MOS-F> GetMem entering.

**(19) Dynamic memory allocation**

Perform the dynamic memory allocation

Routine-required memory space ...

SGInt	...	1625 double words:	13000 bytes:	0.01 MBytes.
Guess	...	6823 double words:	54584 bytes:	0.05 MBytes.
HFSCF	...	12182 double words:	97456 bytes:	0.09 MBytes.
GState	...	6685 double words:	53480 bytes:	0.05 MBytes.
TrnGab	...	1982 double words:	15856 bytes:	0.02 MBytes.
CIMat	...	1070 double words:	8560 bytes:	0.01 MBytes.
CIDiag	...	1826 double words:	14608 bytes:	0.01 MBytes.
TrnDip	...	1225 double words:	9800 bytes:	0.01 MBytes.
TMomG	...	1321 double words:	10568 bytes:	0.01 MBytes.
EState	...	2662 double words:	21296 bytes:	0.02 MBytes.
Polar	...	837 double words:	6696 bytes:	0.01 MBytes.
TMomE	...	1809 double words:	14472 bytes:	0.01 MBytes.
Hypol1	...	996 double words:	7968 bytes:	0.01 MBytes.
Hypol2	...	1572 double words:	12576 bytes:	0.01 MBytes.

Required memory ... 12182 double words: 97456 bytes: 0.09 MBytes.

Succeeded in the allocation!!

**(20) 12288\*8 bytes allocated**

Allocated memory ... 12288 double words: 98304 bytes: 0.09 MBytes.  
 Base address = 7186560 Mod(Base, 8) = 0  
 Allocated address = 8323136 Mod(Addr, 8) = 0  
 MOS-F> GetMem done. Elapsed time = 0.00 s. Total = 00h 00m 00s.  
 MOS-F> SGInt entering.  
 Overlap integrals for Slater-type orbitals.

**(21) Scaling factors for the overlap integrals**

Scaling factors for overlap integrals ...  
 p-sigma = 1.26700  
 p-pi = 0.58500  
 d-sigma = 1.00000  
 d-pi = 1.00000  
 d-delta = 1.00000

**(22) Indicating that Nishimoto-Mataga-Weiss formula is used**

Two-Center ERIs, Gamma ... Evaluated using Nishimoto-Mataga-Weiss formula.  
 f/(R+k\*f\*A) ... k = 1.0000 ; f = 1.2000  
 MOS-F> SGInt done. Elapsed time = 0.00 s. Total = 00h 00m 00s.

**(23) Initial orbital guess generated**

MOS-F> Guess entering.  
 Initial Huckel guess.  
 Matrix diagonalization ... Using rational QL and inverse iteration method.  
 MOS-F> Guess done. Elapsed time = 0.00 s. Total = 00h 00m 00s.

**(24) SCF calculation initiated**

MOS-F> HFSCF entering.  
 RHF closed shell SCF ... Maximum cycles = 100  
 SCF criterion ... Convergence on density matrix = 3.00D-05  
 Virtual MOs are shifted by 0.5000 Hartrees.

Iteration	Electronic energy (Hartree)	Convergence Energy	Density	Accelerator
1	-263.093806015			
2	-263.193174796	9.94D-02	1.56D-02	
3	-263.201880184	8.71D-03	4.23D-03	
4	-263.203217933	1.34D-03	1.88D-03	
5	-263.203471538	2.54D-04	7.72D-04	
6	-263.203525696	5.42D-05	3.80D-04	
7	-263.203538212	1.25D-05	1.69D-04	
8	-263.203541301	3.09D-06	9.13D-05	
9	-263.203542106	8.05D-07	4.22D-05	
10	-263.203542326	2.20D-07	2.46D-05	

**(25) SCF converged in 10 iterations**

Density converged to 2.46D-05 ... SCF criterion satisfied.  
 MOS-F> HFSCF done. Elapsed time = 0.06 s. Total = 00h 00m 00s.

**(26) Output state for the ground state**

MOS-F> GState entering.

**(27) Showing the energy values**

Energy table for ground state

	Hartree	Electron volt	kcal/mol
Total	-8.337900567	-226.88592	-5232.112
Electronic	-263.203542326	-7162.13585	-165162.737
Nuclear repulsion	254.865641759	6935.24994	159930.625

**(28) The index of HOMO**

```

Highest Occupied Molecular Orbital (HOMO) ... 26
(29) The index of LUMO
Lowest Unoccupied Molecular Orbital (LUMO) ... 27
(30) Showing orbital energies
Canonical orbital energies (Unit : eV)
Occupied MOs ...
  1 -50.7730   2 -45.5252   3 -40.6713   4 -40.3074   5 -33.8342
  6 -32.6186   7 -26.6834   8 -26.5831   9 -24.8314  10 -21.0168
 11 -20.8988  12 -19.2577  13 -18.2359  14 -17.4659  15 -16.7488
 16 -16.2025  17 -15.7676  18 -14.8413  19 -14.3525  20 -12.8066
 21 -12.0834  22 -11.1301  23 -10.7537  24 -10.7503  25  -9.8612
 26  -8.5612
Virtual MOs ...
 27 -1.2275  28  0.3097  29  0.5384  30  2.1652  31  2.5673
 32  2.8946  33  3.5248  34  4.2124  35  4.5077  36  5.2530
 37  6.1367  38  7.0604  39  7.9953  40  8.5238  41  9.0783
 42 10.9229  43 11.6995  44 11.8336  45 13.3374  46 14.2473
(31) Showing the atomic charges
Total atomic charges ...
  1 C  0.14887   2 N -0.25967   3 H  0.14354   4 H  0.14354
  5 C -0.05560   6 C  0.03004   7 C  0.04175   8 C -0.05560
  9 C  0.03004  10 N  0.64211  11 O -0.47233  12 O -0.47233
 13 H  0.02277  14 H  0.04505  15 H  0.04505  16 H  0.02277
(32) Showing the dipole moment
Dipole moment (Unit : Debye) ...
      x           y           z           Total
Total atomic charges      0.0000      0.0000      7.7777      7.7777
SP atomic polarization     0.0000      0.0000      0.5787      0.5787
PD atomic polarization     0.0000      0.0000      0.0000      0.0000
Total                      0.0000      0.0000      8.3563      8.3563
MOS-F> GState done. Elapsed time = 0.02 s. Total = 00h 00m 00s.
MOS-F> PreCI entering.
MOS-F> PreCI done. Elapsed time = 0.00 s. Total = 00h 00m 00s.
(33) Integral transformation being done
MOS-F> TrnGab entering.
Integral transformation for the INDO approximation
MOS-F> TrnGab done. Elapsed time = 0.02 s. Total = 00h 00m 00s.
(34) Generating CI matrix
MOS-F> CIMat entering.
CIS calculation for singlet state.
(35) CI matrix's dimension is 24
Number of spin-adapted CSFs = 24
MOS-F> CIMat done. Elapsed time = 0.00 s. Total = 00h 00m 00s.
(36) Diagonalizing the CI matrix
MOS-F> CIDiag entering.
MOS-F> CIDiag done. Elapsed time = 0.00 s. Total = 00h 00m 00s.
(37) Transforming the dipole moment matrices
MOS-F> TrnDip entering.
Evaluation of MO-based dipole matrices.
(38) Analytical evaluation of the one-center dipole integrals
One-center dipole integral ... Analytic computation.
MOS-F> TrnDip done. Elapsed time = 0.00 s. Total = 00h 00m 00s.
(39) Transition moment being computed
MOS-F> TMomG entering.
G->E transition moment.
MOS-F> TMomG done. Elapsed time = 0.00 s. Total = 00h 00m 00s.
(40) Output for the excited states

```

MOS-F> EState entering.

Electron transition spectra (G->E) for singlet state. NStates = 10

State	Transition energy			Oscillator strength	Main CSFs	
	eV	cm <sup>-1</sup>	nm		MO	CI coef.
1	3.92341	31644.40	316.012	0.542839	26-> 27	-0.97933 ( 96%)
2	4.35392	35116.74	284.764	0.005278	26-> 28	-0.73270 ( 54%)
					25-> 27	0.59048 ( 35%)
3	5.31901	42900.69	233.096	0.089628	25-> 27	-0.79376 ( 63%)
					26-> 28	-0.52823 ( 28%)
4	5.49832	44346.89	225.495	0.102518	26-> 29	-0.95596 ( 91%)
5	6.07852	49026.59	203.971	0.276163	23-> 27	-0.93496 ( 87%)
6	6.69405	53991.15	185.216	0.881096	25-> 29	0.84430 ( 71%)
					26-> 28	-0.42729 ( 18%)
7	6.76227	54541.38	183.347	0.652041	25-> 28	-0.83362 ( 69%)
					26-> 31	0.50531 ( 26%)
8	7.20237	58091.02	172.144	0.244177	26-> 31	0.84856 ( 72%)
					25-> 28	0.48187 ( 23%)
9	7.36618	59412.20	168.316	0.006642	21-> 27	0.94787 ( 90%)
10	7.47287	60272.78	165.912	0.080117	23-> 29	0.95312 ( 91%)

(41) Dipole moments for the excited states

Dipole moments (Unit: Debye)

State	Dipole				Delta D Total	Oscillator strength
	x	y	z	Total		
Ground	0.0000	0.0000	8.3563	8.3563		
1	0.0000	0.0000	19.9622	19.9622	11.6058	0.542839
2	0.0000	0.0000	10.4837	10.4837	2.1274	0.005278
3	0.0000	0.0000	18.4409	18.4409	10.0846	0.089628
4	0.0000	0.0000	12.8425	12.8425	4.4862	0.102518
5	0.0000	0.0000	5.7331	5.7331	2.6232	0.276163
6	0.0000	0.0000	10.9226	10.9226	2.5662	0.881096
7	0.0000	0.0000	9.1140	9.1140	0.7577	0.652041
8	0.0000	0.0000	11.7274	11.7274	3.3711	0.244177
9	0.0000	0.0000	19.6106	19.6106	11.2542	0.006642
10	0.0000	0.0000	-4.4831	4.4831	12.8395	0.080117

MOS-F> EState done. Elapsed time = 0.02 s. Total = 00h 00m 00s.

(42) Polarizability being computed

MOS-F> Polar entering.

Polarizability Alpha(i,j) by the SOS method.

Units ... 10<sup>(-24)</sup> cm<sup>3</sup>.

(43) Static polarizability shown

Static polarizability ... Alpha(0;0)

XX = 12.00406 XY = 0.00000 YY = 0.00000 XZ = 0.00000  
 YZ = 0.00000 ZZ = 19.22172 (XX+YY+ZZ)/3 = 10.40859

MOS-F> Polar done. Elapsed time = 0.00 s. Total = 00h 00m 00s.

(44) Transition moments between different excited states being computed

MOS-F> TMomE entering.

E->E' transition moment.

MOS-F> TMomE done. Elapsed time = 0.00 s. Total = 00h 00m 00s.

MOS-F> PreHyp entering.

MOS-F> PreHyp done. Elapsed time = 0.00 s. Total = 00h 00m 00s.

(45) **First hyperpolarizability being computed**

MOS-F> Hypol1 entering.

First hyperpolarizability Beta(i,j,k) by the SOS method.

Units ...  $10^{(-30)}$  cm<sup>5</sup>/esu.

(46) **The result of the static first hyperpolarizability**

-----  
 Static beta ... Beta(0;0,0)  
 -----

X =	0.000	Y =	0.000	Z =	10.122	Vec =	10.122	Tot =	10.122
XXX =	0.000	YYY =	0.000	ZZZ =	11.857	YYX =	0.000	YXY =	0.000
XXY =	0.000	ZZX =	0.000	ZXZ =	0.000	XZZ =	0.000	XXY =	0.000
XXY =	0.000	YXX =	0.000	ZZY =	0.000	ZYZ =	0.000	YZZ =	0.000
XXZ =	-1.735	XZX =	-1.735	ZXX =	-1.735	YYZ =	0.000	YZY =	0.000
ZYY =	0.000								

MOS-F> Hypol1 done. Elapsed time = 0.01 s. Total = 00h 00m 00s.

(47) **Second hyperpolarizability being computed**

MOS-F> Hypol2 entering.

Second hyperpolarizability Gamma(i,j,k,l) by the SOS method.

Units ...  $10^{(-36)}$  cm<sup>6</sup>/erg.

(48) **The result of the static second hyperpolarizability shown**

-----  
 Static gamma ... Gamma(0;0,0,0)  
 -----

Average =	0.0640342								
XXXX =	-2.225	YYYY =	0.000	ZZZZ =	7.619	XXYY =	0.000	YYXX =	0.000
XXYX =	0.000	XXZZ =	-2.537	XZXZ =	-2.537	XZZX =	-2.537	YYXX =	0.000
YXYX =	0.000	YXXY =	0.000	YYZZ =	0.000	YZYZ =	0.000	YZZY =	0.000
ZZXX =	-2.537	ZXZX =	-2.537	ZXXZ =	-2.537	ZZYY =	0.000	ZYZY =	0.000
ZYYZ =	0.000								

MOS-F> Hypol2 done. Elapsed time = 0.00 s. Total = 00h 00m 00s.

MOS-F> MInput entering.

MOS-F> MInput done. Elapsed time = 0.00 s. Total = 00h 00m 00s.

(49) **Calculation finished**

MOS-F> ExitMOS entering.

Leaving MOS-F system at Mon Jul 10 17:35:02 2000

(50) **The total time elapsed**

Elapsed time ... 00 Hr 00 Min 00 Sec.

(51) **Normal termination of the calculation**

Process terminated normally in ExitMOS.

Let us summarize the output shown in example I.

(1) **MOS-F-related files**

MOS-F-related files.

- `testdata.mos` Input file for MOS-F V4.2D.
- `testdata.ims` A copy of the input file `testdata.mos`. This file is deleted with the termination of the program.
- `testdata.oms` Output file for MOS-F V4.2D.

Please refer to [Section 2.1](#) for more details of MOS-F-related files.

(2) **Keywords**

This section shows all the keywords specified in the input.

(3) **WinMOPAC file**

WinMOPAC uses `testdata.wms` to display the result calculated by MOS-F V4.2D. By default, MOS-F V4.2D does not output the WinMOPAC file, when MOS-F V4.2D is not executed with WinMOPAC. Please refer to [Appendix G.1.21](#) for how to obtain the WinMOPAC file.

(4) **Title**

The title given is shown.

(5) **Symbolic Z-matrix**

Shows the symbolic Z-matrix read in.

(6) **Parameters of the Z-matrix**

Shows the parameters for the symbolic Z-matrix.

(7) **Z-matrix and the parameters**

The parameters for symbolic Z-matrix is shown in numbers.

(8) **Cartesian coordinate section**

The Cartesian coordinates are shown here. The message "Atom 3 is placed on the Z-Y Plane." indicates that the keyword `Plane=Z-Y` is used.

(9) **Cartesian coordinates used by the calculation**

As mentioned earlier, the Cartesian coordinates supplied are translated so as to position all the nuclei to the origin of the corresponding electrons. This translated coordinates are used in the actual calculation. Dummy atom's coordinates are not shown.

(10) **Molecule's chemical formula**

The chemical formula from the data supplied is shown here. The molecule specified in the input has a chemical formula  $C_6H_6N_2O_2$ .

(11) **Molecular weight**

The molecular weight from the data supplied is shown here. It is 138.1259.

(12) **User-defined atomic parameters**

User-defined atomic parameters are shown here.



**(13) User-defined atomic parameters**

Atomic number = 6 shows that the parameters are for carbon.

**(14) User-defined parameters for nitrogen**

Atomic number = 7 shows that the parameters are for nitrogen.

**(15) User-defined parameters for oxygen**

Atomic number = 8 shows that the parameters are for oxygen.

**(16) Atomic parameters output**

- If user-specified parameters are read in, the atomic parameters are shown automatically. In this example, `Parm=Type` is used and `ParmOut=Type` is followed for the parameter output.
- In the output list, the parameters such as ionization potentials are shown with the abbreviated notations like `Es1`, `Bs`, `G1sp` and so on. The style of abbreviation is identical to that for the keywords to specify the atomic parameters except for `CSq2`.<sup>†</sup> Please refer to [Appendix H](#) for more details.
- In this example, INDO/S is used as the model Hamiltonian and the ionization potentials are therefore shown in the output. For CNDO/2 and CNDO/S, instead of the ionization potentials, the average between the ionization potentials and electron affinities are shown. The applicable unit is eV.
- Resonance integrals are shown in eV with their signs reversed.
- In the basis set section, the Slater exponents, and for calculations with the transition metals the exponents and contraction coefficients of the primitive *d*-type orbitals, are shown. The applicable unit is Bohr<sup>-1</sup>.
- One-center electron repulsion integrals  $\gamma_{AA}$  are shown in eV. When CNDO/2 is specified as the model Hamiltonian,  $\gamma_{AA}$  are not shown.  
Slater-Condon parameter is shown only when INDO/S is used. The applicable unit is eV.

**(17) Number of basis functions and electrons**

It can be seen that the total number of basis functions is 46, there are 52 valence electrons, there are 26  $\alpha$  and  $\beta$  electrons, respectively.

**(18) Orbitals used for the CI calculation**

It can be seen that there are six occupied orbitals and four virtual orbitals for CI calculation. The orbital assignment for the occupied ones is 14 18 21 23 25 26 for the virtual ones it is 27 28 29 31.

**(19) Dynamic memory allocation**

Required amount of memory space is worked out for each principal subroutine and the value with some addition is actually allocated.

**(20) 12288\*8 bytes allocated**

The largest demanded amount is 12182\*8 byte for the subroutine HFSCF, but in this program memory space is allocated in the unit of 4096 bytes. Therefore, the actual allocated amount is then 12288\*8 bytes.

**(21) Scaling factors for the overlap integrals**

The scale factors of the overlap integrals in the local coordinate are shown here. In this calculation, the default values for INDO/S method, namely for *p* $\sigma$ -type, 1.267, and for *p* $\pi$ -type, 0.585, respectively, will be used.

---

<sup>†</sup>`CSq2` = 1 - `CSq1`.

**(22) Indicating that Nishimoto-Mataga-Weiss formula is used**

The output shows that Nishimoto-Mataga-Weiss formula is used to calculate two-center electron repulsion integrals, which is the default in INDO/S. The  $f_r$  and  $k$ -value for Nishimoto-Mataga-Weiss method are 1.2 and 1.0 respectively.

**(23) Initial orbital guess generated**

The subroutine `Guess` is used to estimate the initial orbital coefficients.

**(24) SCF calculation initiated**

The SCF calculation is carried out in the subroutine `HFSCF`. The maximum number of iterations is indicated to be 100 and the convergence criterion based on the density matrix is set to be  $3 \times 10^{-5}$  (3.00D-05). The criterion based on the density matrix is given by<sup>1,2</sup>

$$\Delta P \equiv \left( \left( \frac{n(n+1)}{2} \right)^{-2} \sum_{\mu \geq \nu}^n (P_{\mu\nu}^i - P_{\mu\nu}^{i-1})^2 \right)^{\frac{1}{2}},$$

and  $\Delta P$  must be less than  $3 \times 10^{-5}$  to achieve convergence in this example. The index  $i$  stands for the  $i$ -th iteration. If the Level-shift method or the density matrix extrapolation method is used, it will be shown as Level shift, Spiral (4-pt) or Aitken (3-pt) as appropriate.

**(25) SCF converged in 10 iterations**

This merely shows that after ten iteration SCF convergence of 2.46D-05 has been achieved, which meets the criterion of  $3 \times 10^{-5}$ .

**(26) Output for the ground state**

The ground state properties of a molecule is produced by the subroutine `GState`.

**(27) Showing the energy values**

The total, electronic and nuclear repulsion energies are given in Hartree, eV and kcal/mol.

**(28) The index of HOMO**

The index of the HOMO given as 26.

**(29) The index of LUMO**

The index of LUMO is given as 27, naturally.

**(30) Showing orbital energies**

The canonical orbital energies are listed for both occupied and virtual ones in eV.

**(31) Showing the atomic charges**

Atomic charges are listed here.

**(32) Showing the dipole moment**

The dipole moment is given in Debye. The contribution to the dipole moment by the atomic charges is given as well as the one by  $s$ - $p$  one-center dipole integrals and  $p$ - $d$  one-center dipole integrals.

**(33) Integral transformation being done**

The subroutine `TrnGab` transforms the electron repulsion integrals into the molecular-orbital based ones. In this example, INDO/S is used and therefore the transformation is based on the INDO type.

**(34) Generating CI matrix**

The elements of the CI matrix are generated.

**(35) CI matrix's dimension is 24**

There are 24 spin-adapted configuration state functions (CSF's), namely the CI matrix is 24 by 24.

**(36) Diagonalizing the CI matrix**

The subroutine `CIDiag` diagonalizes the CI matrix.

**(37) Transforming the dipole moment matrices**

The one-center dipole integrals needed for calculating the transition moment are transformed into the molecular-orbital based ones.

**(38) Analytical evaluation of the one-center dipole integrals**

The one-center dipole integrals required for the transition moment are calculated analytically. If the ZDO approximation is in used, it will be shown so.

**(39) Transition moment being computed**

The subroutine `TMomG` calculates the transition moment between the ground and excited state.

**(40) Output for the excited states**

The excited state properties are printed. Ten excited states are shown in the ascending order, as indicated by `NStates = 10`. The transition energy is shown in eV,  $\text{cm}^{-1}$  and nm. The oscillator strength is also given. `Main` CSFs are important configurations for the relevant excitations.

For example, the first transition energy is  $3.92341 \text{ eV} = 31644.40 \text{ cm}^{-1} = 316.012 \text{ nm}$  and its oscillator strength is given as 0.542839. For the first excitation, the electron promotion from the 26th to 27th orbital has CI coefficient  $-0.97933$  therefore it has 96 % dominance ( $\simeq (-0.97933)^2 \times 100$ ).

**(41) Dipole moments for the excited states**

Dipole moments are shown in Debye. `Delta D`, the difference between the dipole moment of the ground and excited state, is defined as follows.

$$\text{Delta D} \equiv \sqrt{(\mu_x^e - \mu_x^g)^2 + (\mu_y^e - \mu_y^g)^2 + (\mu_z^e - \mu_z^g)^2}.$$

**(42) Polarizability being computed**

Polarizability is calculated by the sum-over-states method and given in  $10^{-24} \text{ cm}^3$ .

**(43) Static polarizability shown**

Static polarizability is computed.  $(XX+YY+ZZ)/3$  represents  $\langle \alpha \rangle$  as given in [Section 5.5](#).

**(44) Transition moments between different excited states being computed**

The transition moments between the excited states are calculated by the subroutine `TMomE`.

**(45) First hyperpolarizability being computed**

The sum-over-states method is used to compute the first hyperpolarizability and it is given in  $10^{-30} \text{ cm}^5 \cdot \text{esu}^{-1}$ .

**(46) The result of the static first hyperpolarizability**

The value of the static first hyperpolarizability is printed. Note that `Vec` is the value of  $\beta_{\text{vec}}$  and `Tot` is the value  $\beta_{\text{total}}$  as in [Section 5.6](#).

**(47) Second hyperpolarizability being computed**

The value of the second hyperpolarizability is computed by the sum-over-states method and given in  $10^{-36} \text{ cm}^6 \text{ erg}^{-1}$ .

**(48) The result of the static second hyperpolarizability shown**

The result is shown for the calculation of the static second hyperpolarizability. Average is  $\langle \gamma \rangle$  as in [Section 5.7](#).

**(49) Calculation finished**

This is the message generated when the calculation comes to an end.

**(50) The total time elapsed**

The calculation took about 0 second.

**(51) Normal termination of the calculation**

The calculation was properly terminated in the subroutine `ExitMOS`.

# Chapter 5

## Theoretical Background

### 5.1 Calculation Structure

This section is intended to give a summary of the structure of this package.

- **Input**
  - Keywords
  - Molecular specification
  - Options
- **Computational Procedure**
  - Method used
  - Molecular coordinates
  - Atomic parameters
- **Dynamic Memory Allocation**
- **Overlap Integrals**
- **Electron Repulsion Integrals**
- **Initial MO Guess**
- **SCF Calculation**

⇒ **Result of SCF Calculation:**

- ◇ Total energy
- ◇ MO coefficients
- ◇ Charges
- ◇ Dipole moment
- ◇ MO electron density

- **Integral Transformation**
- **CIS Calculation**
- **Transition Moment**
  - ⇒ **Result of CI Calculation:**
    - ◇ Transition Energy
    - ◇ Oscillator Strength
    - ◇ Excited State Charges
    - ◇ Excited State Dipole Moment
  
- **Polarizability  $\alpha$** 
  - ⇒ **Output for  $\alpha$ :**
    - ◇ static
    - ◇ dynamic
  
- **Transition Moment between the Excited States**
- **First Hyperpolarizability  $\beta$** 
  - ⇒ **Output for  $\beta$ :**
    - ◇ Static
    - ◇ Second harmonic generation (SHG)
    - ◇ Electro-optic Pockels effect (EOPE)
    - ◇ Optical rectification (OR)
  
- **Second Hyperpolarizability  $\gamma$** 
  - ⇒ **Output for  $\gamma$ :**
    - ◇ Static
    - ◇ DC-electric field induced Kerr effect (EFIKE)
    - ◇ DC-electric field induced second harmonic (DC-SHG)
    - ◇ Third harmonic generation (THG)
    - ◇ Degenerate four-wave mixing (DFWM)
    - ◇ DC-electric field induced optical rectification (DC-OR)
  
- **Freeing Memory Space**

## 5.2 Summary of Semiempirical Molecular Orbital Theory

Before we go onto the practical aspects of some particular methods like CNDO/2, CNDO/S, CNDO/S2, CNDO/S3, and INDO/S, let us dwell briefly on the basic theory of these semiempirical methods.<sup>1-3</sup>

In the standard approach to the molecular orbital theory, an orbital  $\psi_i$  is approximated as a linear combination of atomic orbitals  $\chi_\mu$ .<sup>†</sup> Namely,

$$\psi_i = \sum_{\mu}^{\text{nbasis}} C_{\mu i} \chi_{\mu}.$$

$C_{\mu i}$  is called a molecular orbital (MO) coefficient. nbasis denotes the total number of such atomic orbitals. These atomic orbitals can be considered as a function set used to expand the molecular orbital, and for this reason, these functions are often called basis functions. From now on a set of the atomic orbitals will be called a *basis set*. Note that only real functions will be used in this documentation.

Generally, Slater-type orbitals (STO)<sup>53</sup> are used in the semiempirical methods and they are given as,

$$\chi = N r^{n-1} e^{-\zeta r} Y_l^m(\theta, \phi),$$

$$N = \frac{(2\zeta)^{n+\frac{1}{2}}}{\sqrt{(2n)!}},$$

$$Y_l^m(\theta, \phi) = (-1)^m \sqrt{\frac{2l+1}{4\pi} \cdot \frac{(l-m)!}{(l+m)!}} P_l^m(\cos\theta) e^{im\phi},$$

$$P_l^m(\cos\theta) = \frac{1}{2^l \cdot l!} (1 - \cos^2\theta)^{m/2} \frac{d^{l+m}}{d(\cos\theta)^{l+m}} (\cos^2\theta - 1)^l.$$

$\chi$ ,  $n$ ,  $l$ ,  $m$  and  $N$  are, a Slater-type orbital, the principal quantum number, the azimuthal quantum number, the magnetic quantum number and the normalization constant, respectively.  $r$ ,  $\theta$ , and  $\phi$  are the standard polar coordinates and  $\zeta$  denotes the Slater exponent.  $Y_l^m(\theta, \phi)$  is a spherical harmonic and  $P_l^m(\cos\theta)$  is the associated Legendre polynomial. The value of the Slater exponent is generally determined according to the Slater rule, but some methods have their own ways. For example, a  $2p_x$  orbital will have the following form according to the Slater rule,

$$\chi_{2p_x} = N e^{-1.625r} x.$$

Unlike the *ab initio* approach, only the basis representing the valence orbitals will be used in the semiempirical methods. This means, for hydrogen, only  $1s$  (naturally) will be used, and for carbon, only  $2s$ ,  $2p_x$ ,  $2p_y$  and  $2p_z$  types will be used for calculation.

The basic equation of the following form will result in a matrix equation when molecular orbitals are expanded with some basis set.

$$\mathbf{FC} = \mathbf{SCE}.$$

This is the famous Hartree-Fock-Roothaan equation, or HFR for short.  $F_{\mu\nu}$  is the Fock matrix element with  $\chi_\mu$  and  $\chi_\nu$ .  $C_{\mu i}$  is the MO coefficient for  $\psi_i$  which is in the expansion with  $\chi_\mu$ .  $S_{\mu\nu}$  is the overlap integral for  $\chi_\mu$  and  $\chi_\nu$  and  $E_{ii}$  is the energy of an orbital  $\psi_i$ .  $\mathbf{F}$  and  $\mathbf{S}$  are symmetric matrices and  $\mathbf{E}$  is a diagonal matrix.

<sup>†</sup>This is generally known as the LCAO approximation.

The *ab initio* methods go on to solve this equation explicitly. The semiempirical methods, on the other hand, solve this equation with the following approximation.<sup>1,3</sup> For a volume element  $d\tau$ , the differential overlap between the basis functions is given as,

$$\chi_\mu \chi_\nu d\tau.$$

But for a semiempirical method, it is written as,

$$\chi_\mu \chi_\nu d\tau = \delta_{\mu\nu} \chi_\mu^2 d\tau.$$

Where  $\delta_{\mu\nu}$  is Kronecker's delta. It is unity for the same indices, otherwise it is zero. This is called the Zero Differential Overlap (ZDO) approximation.

In semiempirical methods, the ZDO approximation is a normal approach and the overlap integral matrix becomes a mere unit matrix. HFR is correspondingly simplified as shown below.

$$FC = CE.$$

This version of the equation forms the starting point for the semiempirical methods. By simply solving this equation, the MO coefficients  $C$  and the orbital energies  $E$  can be obtained. It seems at first glance that  $C$  and  $E$  can be obtained by merely diagonalizing the Fock matrix  $F$ . This approach, in fact, is invalid. This is because  $F$  depends on  $C$  and the equation cannot yield the solution in one diagonalization. Instead, the following approach needs to be implemented to obtain  $C$  and  $E$ .

- (1) The initial values for  $C$  are computed by using a simpler method like the Hückel method.
- (2)  $F$  is obtained from this initial guess.
- (3)  $F$  is then diagonalized to compute  $C$  and  $E$ .
- (4) This new  $C$  matrix is used to calculate  $F$  for the next calculation for  $C$  and  $E$ .
- (5) The steps (2) to (4) are repeated until  $C$  has converged to meet the threshold.

The cycle from (2) to (4) is a repetitive calculation and is called a SCF (Self-Consistent Field) calculation.

The total electronic energy  $E_g^{\text{elec}}$  may be obtained by solving this HFR equation.  $E_g^{\text{elec}}$  is given by

$$E_g^{\text{elec}} = \frac{1}{2} \sum_{\mu,\nu}^{\text{nbasis}} P_{\mu\nu} (H_{\mu\nu} + F_{\mu\nu}),$$

where  $H_{\mu\nu}$  is a matrix element expressing the energy corresponding to the motion of electrons, nuclear attraction and repulsion.<sup>†</sup> nbasis is the number of basis functions.  $P_{\mu\nu}$  is a density matrix.

The most computationally intensive part of the Fock matrix are the electron repulsion integrals (given in atomic units).

$$(\mu\nu|\lambda\sigma) = \iint \chi_\mu(1)\chi_\nu(1)\frac{1}{r_{12}}\chi_\lambda(2)\chi_\sigma(2)d\tau_1d\tau_2.$$

$1/r_{12}$  is the distance between electron 1 and 2. It has been known in general that once these integrals begin to involve more than three atoms with Slater functions, the resulting multi-center integrals are very expensive.<sup>‡</sup> To do without this extra computational cost, some degree of approximation is applied to these integrals and all the integrals with equal to or greater than three centers are simply fixed at null. The degree of approximation

<sup>†</sup>This is called the core Hamiltonian and is independent of molecular orbital coefficients.

<sup>‡</sup>The use of Gaussian functions reduces four-center integrals to two-center integrals and this also reduces the computational cost. The *ab initio* methods take advantage of this feature in general.



is indicative in the title of a method. The names like CNDO (Complete Neglect of Differential Overlap), INDO (Intermediate Neglect of Differential Overlap), NDDO (Neglect of Diatomic Differential Overlap) all come from the level of approximation.<sup>1,3</sup>

In the CNDO/2 method,

$$(\mu\nu|\lambda\sigma) = \delta_{\mu\nu}\delta_{\lambda\sigma}(\mu\mu|\lambda\lambda),$$

and electron repulsion integrals including  $p$ -type basis functions are all replaced with the ones only of  $s$ -type. Namely,

$$\begin{aligned}\gamma_{AB} &\equiv (\mu_s^A \mu_s^A | \mu_s^B \mu_s^B) \\ &= (\mu_s^A \mu_s^A | \mu_p^B \mu_p^B) \\ &= (\mu_p^A \mu_p^A | \mu_p^B \mu_p^B),\end{aligned}$$

where  $\gamma_{AB}$  is a two-center electron repulsion integral between atoms A and B and  $\mu_s^A$  is an  $s$ -type basis function belonging to an atom A. The integrals purely of  $s$ -type are evaluated analytically.<sup>1,37</sup> The advantage of replacing the integrals including  $p$ -type basis functions with ones of  $s$ -type is not only to reduce the computational effort but also to eliminate the complication of coordinate-dependency of the calculated values.

One of the characteristics of the INDO approximation is that one-center integral,

$$\gamma_{AA} \equiv (\mu^A \nu^A | \lambda^A \sigma^A),$$

is not treated with the ZDO approximation. It does, however, apply to the two-center integrals,

$$\gamma_{AB} \equiv (\mu^A \nu^A | \lambda^B \sigma^B).$$

The one-center integrals ignored in the CNDO/2 approximation are evaluated with Slater-Condon parameters.<sup>47</sup>

In the NDDO approximation, the two-center integrals mentioned above are evaluated explicitly. MNDO,<sup>48</sup> AM1<sup>49</sup> and PM3<sup>50</sup> methods in MOPAC are all based on NDDO approximation.

The semiempirical methods like CNDO/S and INDO/S for the spectroscopic analysis in this program all use empirical formula of one form or another to evaluate electron repulsion integrals.<sup>†</sup> This is because the analytical approach does not reproduce experimentally obtained results for absorption spectra. The empirical formula used to evaluate electron repulsion integrals in this program are Pariser-Parr,<sup>38</sup> Nishimoto-Mataga<sup>39</sup> (including new formula<sup>40</sup>), Nishimoto-Mataga-Weiss,<sup>7</sup> Ohno,<sup>41</sup> Ohno-Klopman<sup>42</sup> and DasGupta-Huzinaga.<sup>43</sup>

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<sup>†</sup>S in CNDO/S and INDO/S stands for Spectroscopy.

## 5.3 Calculating Ground States

### 5.3.1 Overlap Integrals

#### Overlap Integrals in Local Coordinates

Because the ZDO approximation is employed in semiempirical methods as it has been mentioned, the overlap matrix in the RHF equations becomes a unit matrix. These overlap matrix,  $S_{\mu\nu}^{AB} = \int \chi_{\mu}^A \chi_{\nu}^B dv$ , however, are required for calculating non-diagonal matrix elements of the Fock matrix.

An overlap integral in a local coordinate  $S_{\mu\nu}^{AB}$  for Slater-type orbitals is given as,<sup>1,53</sup>

$$S_{\mu\nu}^{AB} = (-1)^{l_{\nu}+m} \sqrt{\frac{(\zeta_{\mu}R)^{2n_{\mu}+1}(\zeta_{\nu}R)^{2n_{\nu}+1}}{(2n_{\mu})!(2n_{\nu})!}}$$

$$\frac{1}{2} \sqrt{\frac{(2l_{\mu}+1)(2l_{\nu}+1)(l_{\mu}-m)!(l_{\nu}-m)!}{(l_{\mu}+m)!(l_{\nu}+m)!}} \sum_{j_{\mu}=0}^{(l_{\mu}-m)/2} \sum_{j_{\nu}=0}^{(l_{\nu}-m)/2} C'_{l_{\mu}m j_{\mu}} C'_{l_{\nu}m j_{\nu}} X_{j_{\mu}j_{\nu}}.$$

Note that,

$$C'_{lmj} \equiv \frac{(2(l-j))! \cdot (-1)^j}{2^l \cdot j! \cdot (l-j)! \cdot (l-m-2j)!},$$

$$X_{j_{\mu}j_{\nu}} \equiv \sum_{k_{\mu}=0}^m \sum_{k_{\nu}=0}^m \sum_{P_{\mu}=0}^{(n_{\mu}-l_{\mu}+2j_{\mu})} \sum_{P_{\nu}=0}^{(n_{\nu}-l_{\nu}+2j_{\nu})} \sum_{q_{\mu}=0}^{(l_{\mu}-m-2j_{\mu})} \sum_{q_{\nu}=0}^{(l_{\nu}-m-2j_{\nu})}$$

$$\frac{(m!)^2}{(m-k_{\mu})! k_{\mu}! (m-k_{\nu})! k_{\nu}!} \cdot \frac{(n_{\mu}-l_{\mu}+2j_{\mu})!}{(n_{\mu}-l_{\mu}+2j_{\mu}-P_{\mu})! P_{\mu}!} \cdot$$

$$\frac{(n_{\nu}-l_{\nu}+2j_{\nu})!}{(n_{\nu}-l_{\nu}+2j_{\nu}-P_{\nu})! P_{\nu}!} \cdot \frac{(l_{\mu}-m-2j_{\mu})!}{(l_{\mu}-m-2j_{\mu}-q_{\mu})! q_{\mu}!} \cdot$$

$$\frac{(l_{\nu}-m-2j_{\nu})!}{(l_{\nu}-m-2j_{\nu}-q_{\nu})! q_{\nu}!} \cdot (-1)^{k_{\mu}+k_{\nu}+m+P_{\mu}+q_{\nu}}$$

$$A_{2k_{\nu}+n_{\mu}-l_{\mu}+2j_{\mu}+n_{\nu}-l_{\nu}+2j_{\nu}-P_{\mu}-P_{\nu}+q_{\mu}+q_{\nu}} \left( \frac{R(\zeta_{\mu} + \zeta_{\nu})}{2} \right)$$

$$B_{2k_{\mu}+P_{\mu}+P_{\nu}+q_{\mu}+q_{\nu}} \left( \frac{R(\zeta_{\mu} - \zeta_{\nu})}{2} \right),$$

where  $(-1)^{l_{\nu}+m}$  is a phase factor to make  $p\sigma$ -overlap negative and  $p\pi$ -overlap positive.  $R$  is the distance between an atom A and B. Note further that,

$$A_n(x) \equiv n! x^{-(n+1)} e^{-x} \left( 1 + x + \frac{x^2}{2!} + \cdots + \frac{x^n}{n!} \right),$$

$$B_n(x) \equiv n! x^{-(n+1)} e^x \left( 1 - x + \frac{x^2}{2!} + \cdots + (-1)^n \frac{x^n}{n!} \right)$$

$$- n! x^{-(n+1)} e^{-x} \left( 1 + x + \frac{x^2}{2!} + \cdots + \frac{x^n}{n!} \right),$$

when  $x = 0$ ,

$$B_n(x) = \begin{cases} 0, & n, \text{ odd} \\ \frac{2}{n+1}, & n, \text{ even} \end{cases}$$

The auxiliary integral  $B_n(x)$  is likely to contain a large error for the following reason so a caution must be exercised. For the Taylor expansion for  $e^x$ ,

$$e^{\pm x} = 1 \pm x + \frac{x^2}{2!} \pm \frac{x^3}{3!} + \dots,$$

for small  $x$  or large  $n$ ,  $B_n(x)$  may be approximated as follows.

$$B_n(x) \equiv n! x^{-(n+1)} (e^x X - e^{-x} Y).$$

$$\begin{aligned} X &\equiv \left( 1 - x + \frac{x^2}{2!} + \dots + (-1)^n \frac{x^n}{n!} \right) \\ &\simeq e^{-x}. \end{aligned}$$

$$\begin{aligned} Y &\equiv \left( 1 + x + \frac{x^2}{2!} + \dots + \frac{x^n}{n!} \right) \\ &\simeq e^x. \end{aligned}$$

Since  $e^x X$  and  $e^{-x} Y$  will approximately be the same, the subtraction is likely to lead to a large error even when it is done with double precision. To remedy the situation, the expansion for  $e^{\pm}$  is used for above cases, that is,

$$\begin{aligned} B_{2n}(x) &= 2 \left\{ \frac{1}{(2n+1) \cdot 0!} + \frac{x^2}{(2n+3) \cdot 2!} + \frac{x^4}{(2n+5) \cdot 4!} + \frac{x^6}{(2n+7) \cdot 6!} + \dots \right\}, \\ B_{2n+1}(x) &= -2 \left\{ \frac{x}{(2n+3) \cdot 1!} + \frac{x^3}{(2n+5) \cdot 3!} + \frac{x^5}{(2n+7) \cdot 5!} + \frac{x^7}{(2n+9) \cdot 7!} + \dots \right\}. \end{aligned}$$

### Transformation from Local Coordinates to Molecular Coordinates

The overlap integrals obtained for the local coordinates need to be transformed into the ones for the molecular coordinates. The overlap matrix for the molecular coordinates  $S$  can be transformed into the one for the local coordinate  $S'$  through the following transformation.<sup>1</sup>

$$S = \tilde{T} S' T.$$

The transformation matrix  $T$  will have the following form.

$$T = \begin{pmatrix} 1 & & & & & & 0 \\ & \boxed{T_p} & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ 0 & & & & & \boxed{T_d} & \\ & & & & & & \end{pmatrix}.$$

$T_p$  and  $T_d$  are defined as follows for  $x, y$  and  $z$  as the local coordinate variables and  $X, Y$ , and  $Z$  as the molecular coordinate variables,

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = T_p \begin{pmatrix} x \\ y \\ z \end{pmatrix},$$

$$\begin{pmatrix} 2Z^2 - X^2 - Y^2 \\ ZX \\ YZ \\ X^2 - Y^2 \\ XY \end{pmatrix} = T_d \begin{pmatrix} 2z^2 - x^2 - y^2 \\ zx \\ yz \\ x^2 - y^2 \\ xy \end{pmatrix},$$

and note the relation that,

$$T_p = \begin{pmatrix} \cos \theta \cos \varphi & -\sin \varphi & \sin \theta \cos \varphi \\ \cos \theta \sin \varphi & \cos \varphi & \sin \theta \sin \varphi \\ -\sin \theta & 0 & \cos \theta \end{pmatrix},$$

$$T_d = \begin{pmatrix} \frac{1}{2}(3 \cos^2 \theta - 1) & -\frac{\sqrt{3}}{2} \sin 2\theta & 0 & \frac{\sqrt{3}}{2} \sin^2 \theta & 0 \\ \frac{\sqrt{3}}{2} \sin 2\theta \cos \varphi & \cos 2\theta \cos \varphi & -\cos \theta \sin \varphi & -\frac{1}{2} \sin 2\theta \cos \varphi & \sin \theta \sin \varphi \\ \frac{\sqrt{3}}{2} \sin 2\theta \sin \varphi & \cos 2\theta \sin \varphi & \cos \theta \cos \varphi & -\frac{1}{2} \sin 2\theta \sin \varphi & -\sin \theta \cos \varphi \\ \frac{\sqrt{3}}{2} \sin^2 \theta \cos 2\varphi & \frac{1}{2} \sin 2\theta \cos 2\varphi & -\sin \theta \sin 2\varphi & \frac{1}{2}(1 + \cos^2 \theta) \cos 2\varphi & -\cos \theta \sin 2\varphi \\ \frac{\sqrt{3}}{2} \sin^2 \theta \sin 2\varphi & \frac{1}{2} \sin 2\theta \sin 2\varphi & \sin \theta \cos 2\varphi & \frac{1}{2}(1 + \cos^2 \theta) \sin 2\varphi & \cos \theta \cos 2\varphi \end{pmatrix},$$

$\theta$  and  $\varphi$  are the relevant Euler angles.

### 5.3.2 Dipole Integrals

In the semiempirical molecular orbitals approach with Slater-type orbitals, two-center dipole integrals are ignored and only one-center dipole integrals are evaluated.<sup>1</sup>

Tables 5.1 to 5.3 show the values of some one-center dipole integrals, for their components  $x, y$  and  $z$ . A circle indicates that the value is finite and — indicates that the value is null. A dipole integral composed of the same orbitals is the nuclear coordinate about which the orbitals are centered. From Tables 5.1 to 5.3, it can be stated that,

$$\langle \chi_\mu^A | \mathbf{r} | \chi_\mu^A \rangle = \mathbf{R}_A,$$

namely, a dipole integral evaluated with the same orbitals gives the position vector of the nucleus to which the orbitals actually belong. Where  $\mathbf{r}$  is a position vector of an electron.

Table 5.1 One-Center Dipole Integrals, X-component

	$s$	$p_x$	$p_y$	$p_z$	$d_{z^2}$	$d_{xz}$	$d_{yz}$	$d_{x^2-y^2}$	$d_{xy}$
$s$	$X_A$								
$p_x$	○	$X_A$							
$p_y$	—	—	$X_A$						
$p_z$	—	—	—	$X_A$					
$d_{z^2}$	—	○	—	—	$X_A$				
$d_{xz}$	—	—	—	○	—	$X_A$			
$d_{yz}$	—	—	—	—	—	—	$X_A$		
$d_{x^2-y^2}$	—	○	—	—	—	—	—	$X_A$	
$d_{xy}$	—	—	○	—	—	—	—	—	$X_A$

$X_A$  is the x-component of the nuclear coordinate.

Table 5.2 One-Center Dipole Integrals, Y-component

	$s$	$p_x$	$p_y$	$p_z$	$d_{z^2}$	$d_{xz}$	$d_{yz}$	$d_{x^2-y^2}$	$d_{xy}$
$s$	$Y_A$								
$p_x$	—	$Y_A$							
$p_y$	○	—	$Y_A$						
$p_z$	—	—	—	$Y_A$					
$d_{z^2}$	—	—	○	—	$Y_A$				
$d_{xz}$	—	—	—	—	—	$Y_A$			
$d_{yz}$	—	—	—	○	—	—	$Y_A$		
$d_{x^2-y^2}$	—	—	○	—	—	—	—	$Y_A$	
$d_{xy}$	—	○	—	—	—	—	—	—	$Y_A$

$Y_A$  is the y-component of the nuclear coordinate.

### One-Center Integrals, S-P Type

All x, y and z-component of the one-center integrals have the same value. Namely,

$$\langle ns | r | np \rangle \equiv \langle \chi_s^A | x | \chi_{px}^A \rangle = \langle \chi_s^A | y | \chi_{py}^A \rangle = \langle \chi_s^A | z | \chi_{pz}^A \rangle.$$

where  $n$  is the principal quantum number,  $x$ ,  $y$  and  $z$  are the electron's coordinate components,  $\chi_s^A$ ,  $\chi_{px}^A$ ,  $\chi_{py}^A$  and  $\chi_{pz}^A$  an  $s$ -type STO on atom A,  $p_x$ -type STO on atom A,  $p_y$ -type STO on atom A and  $p_z$ -type STO on atom A, respectively.  $\langle ns | r | np \rangle$  is expressed as,

$$\langle ns | r | np \rangle = \frac{(2n+1) \cdot 2^{2n+1} \cdot (\zeta_s \zeta_p)^{n+\frac{1}{2}}}{\sqrt{3} (\zeta_s + \zeta_p)^{2n+2}}.$$

Table 5.3 One-Center Dipole Integrals, Z-component

	$s$	$p_x$	$p_y$	$p_z$	$d_{z^2}$	$d_{xz}$	$d_{yz}$	$d_{x^2-y^2}$	$d_{xy}$
$s$	$Z_A$								
$p_x$	—	$Z_A$							
$p_y$	—	—	$Z_A$						
$p_z$	○	—	—	$Z_A$					
$d_{z^2}$	—	—	—	○	$Z_A$				
$d_{xz}$	—	○	—	—	—	$Z_A$			
$d_{yz}$	—	—	○	—	—	—	$Z_A$		
$d_{x^2-y^2}$	—	—	—	—	—	—	—	$Z_A$	
$d_{xy}$	—	—	—	—	—	—	—	—	$Z_A$

$Z_A$  is the z-component of the nuclear coordinate.

where  $\zeta_s$  is the exponent of the  $s$ -type Slater orbital and  $\zeta_p$  is the exponent of the  $p$ -type Slater orbital. For a special case where  $\zeta_s = \zeta_p$ ,

$$\langle ns | r | np \rangle = \frac{(2n+1)}{2\sqrt{3}\zeta}.$$

### One-Center Dipole Integral, $P$ - $D$ Type

Unlike  $s$ - $p$  type, one-center dipole integrals of  $p$ - $d$  type depend on  $x$ ,  $y$  and  $z$ -components and the magnetic quantum number. The part independent of the magnetic quantum number,  $\langle n_p | r | n_d \rangle$ , can be written as,

$$\langle n_p | r | n_d \rangle = \frac{(n_p + n_d + 1)! \cdot 2^{n_p + n_d + 1} \cdot \zeta_p^{n_p + \frac{1}{2}} \cdot \zeta_d^{n_d + \frac{1}{2}}}{\sqrt{5} (\zeta_p + \zeta_d)^{n_p + n_d + 2} \cdot \sqrt{(2n_p)! (2n_d)!}}.$$

For special cases where  $n_p = n_d$ ,  $\zeta_p = \zeta_d$ ,

$$\langle n_p | r | n_d \rangle = \frac{(2n+1)}{2\sqrt{5}\zeta}.$$

The formula for calculating the  $p$ - $d$  type one-center dipole integrals for each component are as follows.

#### x-component

$$\begin{aligned} \langle p_x | x | d_{x^2-y^2} \rangle &= \langle n_p | r | n_d \rangle, \\ \langle p_x | x | d_{z^2} \rangle &= -\frac{1}{\sqrt{3}} \langle n_p | r | n_d \rangle, \\ \langle p_y | x | d_{xy} \rangle &= \langle n_p | r | n_d \rangle, \\ \langle p_z | x | d_{xz} \rangle &= \langle n_p | r | n_d \rangle. \end{aligned}$$

#### y-component

$$\begin{aligned} \langle p_x | y | d_{xy} \rangle &= \langle n_p | r | n_d \rangle, \\ \langle p_y | y | d_{x^2-y^2} \rangle &= -\langle n_p | r | n_d \rangle, \\ \langle p_y | y | d_{z^2} \rangle &= -\frac{1}{\sqrt{3}} \langle n_p | r | n_d \rangle, \\ \langle p_z | y | d_{yz} \rangle &= \langle n_p | r | n_d \rangle. \end{aligned}$$

z-component

$$\begin{aligned}\langle p_x | z | d_{xz} \rangle &= \langle n_p | r | n_d \rangle, \\ \langle p_y | z | d_{yz} \rangle &= \langle n_p | r | n_d \rangle, \\ \langle p_z | z | d_{z^2} \rangle &= \frac{2}{\sqrt{3}} \langle n_p | r | n_d \rangle.\end{aligned}$$

**5.3.3 Two-center Electron Repulsion Integrals  $\gamma_{AB}$** 

In the semiempirical methods for electronic spectroscopy like CNDO/S and INDO/S, the electron repulsion integrals  $\gamma_{AB}$  are evaluated with empirical formula of one form or another. The following formula represent such integrals where  $\gamma_{AA}$  is a one-center electron repulsion integral and is replaced by a numerical value.  $R_{AB}$  is the distance between atom A and B.  $\gamma_{AB}$  and  $R_{AB}$  are in eV and Å respectively for Pariser-Parr and for other formula the corresponding quantities are in Hartree and Bohr.

Note: **The Pariser-Parr and Roothaan's analytic formula are not applicable for the INDO/S method with first transition metals in MOS-F V4.2D.**

**Pariser-Parr**<sup>38</sup>

$$\gamma_{AB} = \begin{cases} \frac{7.1993}{R_{AB}} \left[ \left( 1 + \left( \frac{r_A - r_B}{2R_{AB}} \right)^2 \right)^{-\frac{1}{2}} + \left( 1 + \left( \frac{r_A + r_B}{2R_{AB}} \right)^2 \right)^{-\frac{1}{2}} \right], & 2.8\text{Å} \leq R_{AB} \\ \frac{1}{2}(\gamma_{AA} + \gamma_{BB}) - aR_{AB} - bR_{AB}^2, & R_{AB} \leq 2.8\text{Å} \end{cases}$$

where,

$$r_A = \frac{4.597}{Z_A}.$$

$Z_A$  is Slater's effective nuclear charge.  $a$  and  $b$  in the above expression are calculated as follows.

- Use the equation for  $2.8 \text{Å} \leq R_{AB}$  to work out  $\gamma_{AB}^{2.8}$  and  $\gamma_{AB}^{3.7}$  for  $R_{AB} = 2.8$  and  $3.7 \text{Å}$
- Substitute  $\gamma_{AB}^{2.8}$  and  $\gamma_{AB}^{3.7}$  into the equation for  $R_{AB} \leq 2.8 \text{Å}$  to establish a simultaneous equation for  $a$  and  $b$ .
- Solve the simultaneous equation for  $a$  and  $b$ .

The procedure above to determine the expression for  $R_{AB} \leq 2.8 \text{Å}$  gives rise to the fact that the Pariser-Parr formula is sometimes called "interpolation formula".

**Nishimoto-Mataga**<sup>39,40</sup>

$$\gamma_{AB} = \frac{1}{R_{AB} + \frac{2k}{\gamma_{AA} + \gamma_{BB}}}.$$

Where  $k = 1$  leads to the orthodox Nishimoto-Mataga formula and  $k \neq 1$  to its modified version.

**Nishimoto-Mataga-Weiss**<sup>7</sup>

$$\gamma_{AB} = \frac{f_r}{R_{AB} + \frac{2f_r k}{\gamma_{AA} + \gamma_{BB}}}.$$

This formula is used in Zerner's INDO/S. For INDO/S,  $f_r = 1.2$  and  $k = 1$ .

**Ohno**<sup>41</sup>

$$\gamma_{AB} = \frac{1}{\sqrt{R_{AB}^2 + \left(\frac{2}{\gamma_{AA} + \gamma_{BB}}\right)^2}}.$$

**Ohno-Klopman**<sup>42</sup>

$$\gamma_{AB} = \frac{1}{\sqrt{R_{AB}^2 + \left(\frac{1}{2\gamma_{AA}} + \frac{1}{2\gamma_{BB}}\right)^2}}.$$

**DasGupta-Huzinaga**<sup>43</sup>

$$\gamma_{AB} = \frac{1}{R_{AB} + \frac{1}{\frac{\gamma_{AA}}{2} e^{k_A R_{AB}} + \frac{\gamma_{BB}}{2} e^{k_B R_{AB}}}}.$$

Where  $k$  is called the Klondike parameter and is in a range  $0.4 \leq k \leq 0.8$ .

**5.3.4 Fock Matrix**

This section illustrates the features of CNDO/2, CNDO/S, CNDO/S2, CNDO/S3, and INDO/S by showing the elements of Fock matrix.

**The Elements of Fock Matrix for CNDO/2 and CNDO/S.**

Figure 5.1 shows the elements of Fock matrix for CNDO/2 and CNDO/S.<sup>1,13</sup> In Figure 5.1,

- $F_{\mu\mu}^A$  The diagonal element of the Fock matrix for an atomic orbital  $\mu$ .
- $F_{\mu\nu}^A$  The element of the Fock matrix between atomic orbitals  $\mu$  and  $\nu$  on atom A.
- $F_{\mu\nu}^{AB}$  The element of the Fock matrix with atomic orbitals on different atoms.
- $U_{\mu\mu}^A$  A core integral.<sup>†</sup>
- $I_\mu$  The ionization potential for an atomic orbital  $\mu$ .
- $A_\mu$  The electron affinity for an atomic orbital  $\mu$ .
- $Z_B$  The nuclear charge of an atom B (core excluded).
- $P_{\mu\nu}$  Density matrix.

<sup>†</sup>evaluated empirically from atomic spectra.



Figure 5.1 Fock Matrix Elements for CNDO/2 and CNDO/S

$$\begin{aligned}
 F_{\mu\mu}^A &= U_{\mu\mu}^A - \sum_{B \neq A} Z_B \gamma_{AB} - \frac{1}{2} P_{\mu\mu} \gamma_{AA} + \sum_B^{\text{All}} P_{BB} \gamma_{AB} \\
 F_{\mu\nu}^A &= -\frac{1}{2} P_{\mu\nu} \gamma_{AA} \\
 F_{\mu\nu}^{AB} &= \frac{1}{2} \bar{S}_{\mu\nu} (\beta_A + \beta_B) - \frac{1}{2} P_{\mu\nu} \gamma_{AB} \\
 U_{\mu\mu}^A &= -\frac{1}{2} (I_\mu + A_\mu) - (Z_A - \frac{1}{2}) \gamma_{AA}
 \end{aligned}$$

- $\bar{S}_{\mu\nu}$  The overlap integral between orbitals  $\mu, \nu$ .
- $\beta^A$  The resonance integral of an atom A (bonding parameter).

$\sum_B^{\text{All}}$  signifies that the sum is to be taken for all atoms in the molecule.  $P_{BB}$  is  $P_{\mu\mu}$ 's sum taken with respect to the atomic orbital  $\mu$ , namely,  $P_{BB} = \sum_{\mu \in B} P_{\mu\mu}$ .

The elements of the Fock matrix for CNDO/S is identical to the ones for CNDO/2, except that the electron repulsion and overlap integrals are evaluated differently. The features particular to CNDO/2 are as follows.

- The average of the ionization potential and electron affinity is used for the evaluation of the core Hamiltonian.
- The one-center electron repulsion integrals are replaced with the empirical values from the formula such as Pariser's.<sup>38</sup>
- Nishimoto-Mataga's formula is used for the two-electron repulsion integrals when calculating excited singlet state.
- Pariser-Parr's formula is used for the two-electron repulsion integrals when calculating excited triplet state.
- The overlap integrals in local coordinate are scaled then transformed into the ones based on the molecular coordinate. The overlap integrals of  $p\pi$ -type is multiplied by 0.585 in practice.

The reason for multiplying the overlap integrals of  $p\pi$ -type with 0.585 for scaling down is to reduce the splitting between  $\pi$  and  $\pi^*$  orbital. The relevant off-diagonal Fock matrix elements for the  $p\pi$ -type is made small by scaling down the overlap integrals of  $p\pi$ -type. Hence the splitting between  $\pi$  and  $\pi^*$  orbital is reduced.

### Fock Matrix Elements, CNDO/S2 and CNDO/S3

Figure 5.2 shows the elements of Fock matrix for CNDO/S2 and CNDO/S3.<sup>17</sup> In Figure 5.2,  $\beta^\mu$  is the resonance integral for an orbital  $\mu$ . The formalism is identical to that for CNDO/S. The features of CNDO/S2 and CNDO/S3 are as follows.

- Electron affinity is not used in the evaluation of the core Hamiltonian.

Figure 5.2 Fock Matrix Elements for CNDO/S2 and CNDO/S3

$$\begin{aligned}
 F_{\mu\mu}^A &= U_{\mu\mu} - \sum_{B \neq A} Z_B \gamma_{AB} - \frac{1}{2} P_{\mu\mu} \gamma_{AA} + \sum_B^{\text{All}} P_{BB} \gamma_{AB} \\
 F_{\mu\nu}^A &= -\frac{1}{2} P_{\mu\nu} \gamma_{AA} \\
 F_{\mu\nu}^{AB} &= \frac{1}{2} S_{\mu\nu} (\beta_\mu^A + \beta_\nu^B) - \frac{1}{2} P_{\mu\nu} \gamma_{AB} \\
 U_{\mu\mu}^A &= -I_\mu - (Z_A - 1) \gamma_{AA}
 \end{aligned}$$

- Formula used in MINDO/2,<sup>54</sup>  $\gamma_{AA} = (g_{ss} + 6g'_{sp} + 3g_{pp} + 6g'_{pp'})/16$ , is used for the one-center electron repulsion integrals.
- Nishimoto-Mataga formula is used for the two-center electron repulsion integrals.
- The value of resonance integral  $\beta$  is different for  $s$  and  $p$ -type orbital.
- Slater exponent for  $sp^3$ -hybrid orbital is not the same as that used for  $sp$  or  $sp^2$ -hybrid for carbon in CNDO/S3. CNDO/S2 on the other hand used the same values.

### Fock Matrix Elements, INDO/S

Figure 5.3 shows the elements of Fock matrix for the INDO/S method.<sup>7,10,11</sup> In Figure 5.3,  $U_{\mu\mu}^A$  and  $I$  are the one-center core integral for an electronic configuration  $s^l p^m d^n$  of the relevant atom and ionization potential, respectively.  $F$  and  $G$  are the Slater-Condon parameters. The values of the Slater-Condon parameters are specific to each type atom and they are evaluated experimentally.<sup>47</sup>  $C_1$  and  $C_2$  are the quantities used for evaluating the core Hamiltonians and represent the weight for the ionization process for the first series of transition metals shown below.

$$\begin{array}{ll}
 \text{Process I} & : \quad I_s \quad 3d^{n-1}4s \quad \longrightarrow \quad 3d^{n-1} \\
 & \quad I_p \quad 3d^{n-1}4p \quad \longrightarrow \quad 3d^{n-1} \\
 & \quad I_d \quad 3d^{n-1}4s \quad \longrightarrow \quad 3d^{n-2}4s \\
 \text{Process II} & : \quad I_s \quad 3d^{n-2}4s^2 \quad \longrightarrow \quad 3d^{n-2}4s \\
 & \quad I_p \quad 3d^{n-2}4s4p \quad \longrightarrow \quad 3d^{n-2}4s \\
 & \quad I_d \quad 3d^{n-2}4s^2 \quad \longrightarrow \quad 3d^{n-3}4s^2
 \end{array}$$

Note that the weight for Process I and II are  $C_2$  and  $C_1$ , respectively, and  $C_1 + C_2 = 1$ .

The INDO method<sup>1,3</sup> explicitly evaluates the repulsion energies for the electrons belonging to the orbitals on an atom and Zerner *et al* developed the parameterization scheme based on it which has lead to the INDO/S method.<sup>7-12,51</sup> The features of INDO/S are as follows.

Figure 5.3 Fock Matrix Elements for INDO/S

$$\begin{aligned}
F_{\mu\mu}^A &= C_1^A U_{1\mu\mu}^A - \sum_B C_1^B \left\{ (n_{1s}^B + n_{1p}^B) (\mu^A \mu^A | s^B s^B) + n_{1d}^B (\mu^A \mu^A | d^B d^B) \right\} \\
&+ C_2^A U_{2\mu\mu}^A - \sum_B C_2^B \left\{ (n_{2s}^B + n_{2p}^B) (\mu^A \mu^A | s^B s^B) + n_{2d}^B (\mu^A \mu^A | d^B d^B) \right\} \\
&+ \sum_{\sigma}^A \sum_{\lambda}^A P_{\sigma\lambda} \left\{ (\mu^A \mu^A | \sigma^A \lambda^A) - \frac{1}{2} (\mu^A \sigma^A | \mu^A \lambda^A) \right\} + \sum_{\sigma}^B P_{\sigma\sigma} (\mu^A \mu^A | \sigma^B \sigma^B) \\
F_{\mu\nu}^A &= \sum_{\sigma}^A \sum_{\lambda}^A P_{\sigma\lambda} \left\{ (\mu^A \nu^A | \sigma^A \lambda^A) - \frac{1}{2} (\mu^A \sigma^A | \nu^A \lambda^A) \right\} \\
F_{\mu\nu}^{AB} &= \frac{1}{2} \bar{S}_{\mu\nu} (\beta_{\mu}^A + \beta_{\nu}^B) - \frac{1}{2} P_{\mu\nu} (\mu^A \mu^A | \nu^B \nu^B) \\
U_{ss}^A &= -I_s - (l-1) F^0(ss) + m \left\{ F^0(sp) - \frac{1}{6} G^1(sp) \right\} - n \left\{ F^0(sd) - \frac{1}{10} G^2(sd) \right\} \\
U_{pp}^A &= -I_p - (m-1) \left\{ F^0(pp) - \frac{2}{25} F^2(pp) \right\} - l \left\{ F^0(sp) - \frac{1}{6} G^1(sp) \right\} \\
&- n \left\{ F^0(pd) - \frac{1}{15} G^1(pd) - \frac{3}{70} G^3(pd) \right\} \\
U_{dd}^A &= -I_d - (n-1) \left\{ F^0(dd) - \frac{2}{63} (F^2(dd) + F^4(dd)) \right\} - l \left\{ F^0(sd) - \frac{1}{10} G^2(sd) \right\} \\
&- m \left\{ F^0(pd) - \frac{1}{15} G^1(pd) - \frac{3}{70} G^3(pd) \right\}
\end{aligned}$$

- One-center electron repulsion integrals ignored in CNDO such as  $(sp|sp)$  and  $(pp'|pp')$  are evaluated by the Slater-Condon parameter.<sup>47</sup>
- Electron affinity is not used in the evaluation of the core Hamiltonian.
- The one-center electron repulsion integrals are replaced with the empirical values from the formula such as Pariser's.<sup>38</sup>
- Nishimoto-Mataga-Weiss formula<sup>7</sup> is used for the two-electron repulsion integrals when calculating excited singlet state.
- Pariser-Parr formula is used for the two-electron repulsion integrals when calculating excited triplet state.
- The calculation of excited states for molecules with the first series transition element is possible.
  - The values for the Process I and II mentioned above are used for the ionization potential for the transition element.
  - Contracted STO with two primitive STO is used to describe the  $d$ -type orbitals.
  - Electron repulsion integrals with  $d$ -type orbitals are evaluated in a manner different from the case only with  $sp$ -type.
- The scaling coefficient for  $p\pi$  and  $p\sigma$ -type overlap integrals in the local coordinate are 0.585 and 1.267 respectively for transforming them into the molecular coordinate when calculating singlet excited state. There are some cases in which the scaling coefficients for  $p\pi$ -type overlap integrals are set to 0.64 when calculating a molecule containing transition metals.
- The scaling coefficient for  $p\pi$  and  $p\sigma$ -type overlap integrals in the local coordinate are 0.680 and 1.267, respectively, for transforming them into the molecular coordinate when calculating triplet excited state.

The calculated value for  $\lambda_{\max}$  for molecules with lone pair electron such as those with OH and NH<sub>2</sub> species tends to be higher than the experimentally determined one for the CNDO/S method whereas INDO/S is known to give better agreement in general.<sup>52</sup> Please refer to [Appendix B.1](#) and [B.2](#) for the method of evaluating the one and two-center electron repulsion integrals in INDO/S.

### 5.3.5 Atomic Charges

The atomic charge for the ground state is determined in this program as follows. For closed-shell systems (RHF), the total number of electrons in the system  $N_{\text{elec}}$  is given by,

$$N_{\text{elec}} = \sum_j^{\text{occ}} \sum_{\mu,\nu}^{\text{nbasis}} 2C_{\mu j}C_{\nu j}S_{\mu\nu},$$

where  $C_{\mu j}$  and  $C_{\nu j}$  are the molecular orbital coefficients,  $S_{\mu\nu}$  is the overlap integral and  $\text{occ}$  is the number of occupied orbitals. Now,

$$P_{\mu\nu} \equiv \sum_j^{\text{occ}} 2C_{\mu j}C_{\nu j},$$

and upon introducing the ZDO approximation, the above expression becomes,

$$N_{\text{elec}} = \sum_{\mu,\nu}^{\text{nbasis}} P_{\mu\nu}S_{\mu\nu} = \sum_{\mu}^{\text{nbasis}} P_{\mu\mu} = \sum_A^{\text{All}} \sum_{\mu \in A} P_{\mu\mu} \equiv \sum_A^{\text{All}} P_{AA}.$$

$P_{AA}$  is the charge density of an atom A. If the nuclear charge is  $Z_A$ , the net charge on the atom A is given by  $Q_A^{\text{net}}$ ,

$$Q_A^{\text{net}} = Z_A - P_{AA},$$

where  $P_{\mu\nu}$  is the density matrix.

The electron density of a particular orbital such as the HOMO or LUMO may be calculated by specifying the keyword `MODENS` in this program. The electron density of a molecular orbital of an atom A  $\psi_i$ ,  $f_A^i$ , is given by

$$f_A^i = \sum_{\mu \in A} C_{\mu i} C_{\mu i},$$

in this program. Note that the sum of  $f_A^i$  for each atom is unity.

### 5.3.6 Dipole Moment

The dipole moment  $\mu$  in general may be calculated from the total wave function for the ground state  $|0\rangle$  as the expectation value of the dipole moment operator  $\hat{\mu}^{\text{mol}}$ .

$$\mu = \langle 0 | \hat{\mu}^{\text{mol}} | 0 \rangle.$$

$\hat{\mu}^{\text{mol}}$  is given by,

$$\begin{aligned} \hat{\mu}^{\text{mol}} &= \hat{\mu} + \hat{\mu}^{\text{nuc}}, \\ \hat{\mu} &= \sum_{i=1}^N (-e\mathbf{r}_i), \\ \hat{\mu}^{\text{nuc}} &= \sum_A eZ_A \mathbf{R}_A. \end{aligned}$$

$\hat{\mu}$  and  $\hat{\mu}^{\text{nuc}}$  are the electronic and nuclear dipole moment operator, respectively.  $e$ ,  $\mathbf{r}_i$ ,  $N$ ,  $Z_A$ ,  $\mathbf{R}_A$  are the electronic charge, the position vector of the  $i$ -th electron, the total number of electron, nuclear charge and the position vector of atom A, respectively. Rearranging the expressions above for the close-shell system,

$$\begin{aligned} \mu &= \langle 0 | \hat{\mu} | 0 \rangle + \langle 0 | \hat{\mu}^{\text{nuc}} | 0 \rangle \\ &= 2 \sum_i^{\text{occ}} \langle \psi_i | -e\mathbf{r} | \psi_i \rangle + \sum_A^{\text{all}} eZ_A \mathbf{R}_A \langle 0 | 0 \rangle \\ &= -2e \sum_i^{\text{occ}} \sum_{\mu, \nu}^{\text{nbasis}} C_{\mu i} C_{\nu i} \langle \chi_\mu | \mathbf{r} | \chi_\nu \rangle + e \sum_A^{\text{all}} Z_A \mathbf{R}_A \\ &= -e \sum_{\mu, \nu} P_{\mu\nu} \langle \chi_\mu | \mathbf{r} | \chi_\nu \rangle + e \sum_A^{\text{all}} Z_A \mathbf{R}_A \end{aligned}$$

$\mathbf{r}_i$  all have the same form and is therefore written as  $\mathbf{r}$ .

The expressions above are also used in *ab initio* calculations. In the semiempirical approach, the first term on the right hand side, a two-center dipole integral, is replaced with the Mulliken approximation. Namely,

$$\langle \chi_\mu^A | \mathbf{r} | \chi_\nu^B \rangle = \frac{1}{2} S_{\mu\nu} (\langle \chi_\mu^A | \mathbf{r} | \chi_\mu^A \rangle + \langle \chi_\nu^B | \mathbf{r} | \chi_\nu^B \rangle).$$

Within the ZDO approximation,  $S_{\mu\nu} = 0$  and the two-center dipole integrals can be ignored as a result. Then,

$$\mu = -e \sum_{\mu, \nu} P_{\mu\nu} \langle \chi_\mu | \mathbf{r} | \chi_\nu \rangle + e \sum_A^{\text{all}} Z_A \mathbf{R}_A$$

$$= -e \sum_A^{\text{all}} \sum_{\mu, \nu \in A} P_{\mu\nu} \langle \chi_\mu | \mathbf{r} | \chi_\nu \rangle + e \sum_A^{\text{all}} Z_A \mathbf{R}_A.$$

From Section 5.3.2

$$\langle \chi_\mu^A | \mathbf{r} | \chi_\mu^A \rangle = \mathbf{R}_A,$$

thus,

$$\begin{aligned} \boldsymbol{\mu} &= -e \sum_A^{\text{all}} P_{AA} \mathbf{R}_A - 2e \sum_A^{\text{all}} \sum_{\mu < \nu}^{\mu, \nu \in A} P_{\mu\nu} \langle \chi_\mu | \mathbf{r} | \chi_\nu \rangle + e \sum_A^{\text{all}} Z_A \mathbf{R}_A \\ &= e \sum_A^{\text{all}} (Z_A - P_{AA}) \mathbf{R}_A - 2e \sum_A^{\text{all}} \sum_{\mu < \nu}^{\mu, \nu \in A} P_{\mu\nu} \langle \chi_\mu | \mathbf{r} | \chi_\nu \rangle. \end{aligned}$$

From Section 5.3.5, the net charge on atom A  $Q_A^{\text{net}}$  is given by,

$$Q_A^{\text{net}} = Z_A - P_{AA}.$$

$$\boldsymbol{\mu} = e \sum_A^{\text{all}} Q_A^{\text{net}} \mathbf{R}_A - 2e \sum_A^{\text{all}} \sum_{\mu < \nu}^{\mu, \nu \in A} P_{\mu\nu} \langle \chi_\mu | \mathbf{r} | \chi_\nu \rangle.$$

The dipole moment is evaluated using the equation above in this program. The first term on the right represents the contribution of the net charge to the dipole moment. The second term on the right is often called the atomic dipole or the atomic polarization.

### 5.3.7 Level-Shift Method

The level-shift method is a very simple algorithm and it is a very effective supplement to achieve convergence despite its simplicity. MOS-F has adopted the algorithm in the original literature by Saunders *et al.*<sup>44</sup>

- (1) Use the equation below to obtain the Fock matrix with the molecular orbital basis.

$$\mathbf{F}_{\text{MO}} = \tilde{\mathbf{C}} \mathbf{F}_{\text{AO}} \mathbf{C}$$

- (2) Add the level-shift parameter  $\Delta S$  which is positive definite to the diagonal elements of  $\mathbf{F}_{\text{MO}}$  for the virtual orbitals.
- (3) Obtain the eigenvector  $\mathbf{C}^{\text{shift}}$  by diagonalizing  $\mathbf{F}_{\text{MO}}^{\text{shift}}$  shifted by  $\Delta S$ .
- (4) Obtain the new eigenvector  $\mathbf{C}^{\text{new}}$  renewed by the following.

$$\mathbf{C}^{\text{new}} = \mathbf{C} \mathbf{C}^{\text{shift}}$$

- (5) Generate  $\mathbf{F}_{\text{AO}}$  from  $\mathbf{C}^{\text{new}}$  and return to the beginning.
- (6) Once SCF has converged to the specified threshold, subtract  $\Delta S$  from the energies of the virtual orbitals and terminate the calculation.

The power of this level-shift approach is well illustrated by the following example with CO where the interatomic distance is fixed at 2 Å and  $\Delta S = 0.5$  Hartree is added from the virtual energies.<sup>†</sup> The run with and without the level-shift is compared and its effectiveness is immediately obvious.

- No level-shift . . . The total energy oscillates and convergence is not achieved even after 100 iteration.
- With level-shift . . . SCF converges after 25 iterations.

The effectiveness of the level-shift method is well exemplified.

<sup>†</sup>CNDO/2 is used for the model Hamiltonian.

## 5.4 Calculating Excited States

### 5.4.1 Configuration Interaction Singles Method

The semiempirical method generally employs the Configuration Interaction Singles Method (or CIS method for short) for calculation where the interest is directed at an excited state. In the CIS method, the wave function of the excited state  $\Psi_e$  is written as follows.

$$\Psi_e = \sum_{i,a} C_{i \rightarrow a} \Phi_{i \rightarrow a}.$$

$\Phi_{i \rightarrow a}$  and  $C_{i \rightarrow a}$  represents a spin-adapted configuration state function (CSF)<sup>†</sup> in which an electron in an occupied orbital  $\psi_i$  is promoted to a virtual orbital  $\psi_a$  and corresponding variational coefficient, respectively.  $C_{i \rightarrow a}$  is determined from the following matrix equation.

$$\mathbf{HC} = \mathbf{CE}.$$

Where  $H_{i \rightarrow a, j \rightarrow b}$  is the matrix element of the CIS matrix between the configuration  $\Phi_{i \rightarrow a}$  and  $\Phi_{j \rightarrow b}$ .  $C_{i \rightarrow a}^k$  is the coefficient of the configuration  $\Phi_{i \rightarrow a}$  in  $k$ -th excitation.  $E_{kk}$  is the transition energy from the ground to  $k$ -th excited state.  $\mathbf{H}$  is a symmetric matrix and  $\mathbf{E}$  is diagonal.

The CIS matrix elements are as follows.

Singlet

$$H_{i \rightarrow a, j \rightarrow b}^1 = \langle \Phi_{i \rightarrow a}^1 | \hat{H} | \Phi_{j \rightarrow b}^1 \rangle = 2(ia | jb) - (ij | ab) + \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i),$$

Triplet

$$H_{i \rightarrow a, j \rightarrow b}^3 = \langle \Phi_{i \rightarrow a}^3 | \hat{H} | \Phi_{j \rightarrow b}^3 \rangle = -(ij | ab) + \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i).$$

Where  $\varepsilon_a$  and  $\varepsilon_i$  are the orbital energies of  $\psi_a$  and  $\psi_i$  respectively.  $(ia | jb)$  and  $(ij | ab)$  are typically referred as molecular integrals and for example  $(ia | jb)$  is given as,

$$\begin{aligned} (ia | jb) &= \iint \psi_i(1) \psi_a(1) \frac{1}{r_{12}} \psi_j(2) \psi_b(2) d\tau_1 d\tau_2 \\ &= \sum_{\mu} \sum_{\nu} \sum_{\lambda} \sum_{\sigma} C_{\mu i} C_{\nu a} C_{\lambda j} C_{\sigma b} (\mu\nu | \lambda\sigma) \\ &= \sum_{\mu} \sum_{\nu} \sum_{\lambda} \sum_{\sigma} C_{\mu i} C_{\nu a} C_{\lambda j} C_{\sigma b} \iint \chi_{\mu}(1) \chi_{\nu}(1) \frac{1}{r_{12}} \chi_{\lambda}(2) \chi_{\sigma}(2) d\tau_1 d\tau_2. \end{aligned}$$

$(\mu\nu | \lambda\sigma)$  is the electron repulsion integral and  $C_{\mu i}$  is the orbital coefficient. This is often called an integral transformation and will be discussed in some more detail in [Section 5.4.2](#).

The CI matrix elements between the ground and excited configurations will be zero from the Brillouin's theorem in the CIS calculation and therefore by evaluating the diagonal elements in the CIS matrix with the ground state's energy being set to zero, the transition energy  $E_{kk}$  corresponding to a photo-absorption wavelength may be calculated.

<sup>†</sup> Configuration which is the eigenfunction of  $S^2$  where  $S$  is the total spin angular momentum operator.

## 5.4.2 Integral Transformation

In the *ab initio* MO approach, all the electron repulsion integrals are evaluated and the expression below gives molecular integrals.<sup>†</sup>

$$(ia | jb) = \sum_{\mu} \sum_{\nu} \sum_{\lambda} \sum_{\sigma} C_{\mu i} C_{\nu a} C_{\lambda j} C_{\sigma b} (\mu\nu | \lambda\sigma).$$

In the semiempirical MO approach, on the other hand, the molecular integrals are given by,

$$(ia | jb) = \sum_{A,B}^{\text{all}} \sum_{\mu,\nu \in A} \sum_{\lambda,\sigma \in B} C_{\mu i} C_{\nu a} C_{\lambda j} C_{\sigma b} (\mu\nu | \lambda\sigma),$$

as the integrals involving three-centers or more are all ignored. The CNDO approach goes a little further and uses the following approximation,

$$(\mu^A \nu^A | \lambda^B \sigma^B) = \delta_{\mu\nu} \delta_{\lambda\sigma} (\mu^A \mu^A | \lambda^B \lambda^B) \equiv \gamma_{AB},$$

and the integrals are thus given by

$$(ia | jb)_{\text{CNDO}} = \sum_{A,B}^{\text{all}} \gamma_{AB} \sum_{\mu \in A} \sum_{\lambda \in B} C_{\mu i} C_{\mu a} C_{\lambda j} C_{\lambda b},$$

which is much simpler.

In the INDO approach, the way one-center integrals are evaluated is somewhat different from the one used in the CNDO approach so it is a little more complicated.

## 5.4.3 Transition Moment

### Ground and Excited States

If the spin-adapted one electron excitation CSF corresponding to an excitation from an occupied orbital  $\psi_i$  to a virtual one  $\psi_a$  is  $\Phi_{i \rightarrow a}$ , the transition moment between the ground state  $|0\rangle$  and  $\Phi_{i \rightarrow a}$  is given by,

$$\langle 0 | \hat{\mu} | \Phi_{i \rightarrow a} \rangle = -\sqrt{2} e \langle \psi_i | \mathbf{r} | \psi_a \rangle.$$

$\hat{\mu}$  is the electric dipole moment operator and  $e$  is the electron charge.  $\mathbf{r}$  stands for the position vector of  $i$ -th electron  $r_i$  generalized.

The CIS wave function for the excited state  $\Psi_e$  is given as

$$\Psi_e = \sum_{i,a} C_{i \rightarrow a} \Phi_{i \rightarrow a},$$

and it then follows that,

$$\begin{aligned} \langle 0 | \hat{\mu} | e \rangle &= -\sqrt{2} e \sum_{i,a} C_{i \rightarrow a} \langle \psi_i | \mathbf{r} | \psi_a \rangle \\ &= -\sqrt{2} e \sum_{i,a} C_{i \rightarrow a} \sum_{\mu,\nu}^{\text{nbasis}} C_{\mu i} C_{\nu a} \langle \chi_{\mu} | \mathbf{r} | \chi_{\nu} \rangle \end{aligned}$$

<sup>†</sup>In the *ab initio* MO approach, however, integral transformation is carried out using the more effective algorithm such as a four-index transformation method since the computational cost of such transformation is proportional to  $O(n^8)$  for  $n$  basis functions.



where

$$T_{ia} \equiv \sum_{\mu,\nu}^{\text{nbasis}} C_{\mu i} C_{\nu a} \langle \chi_{\mu} | \mathbf{r} | \chi_{\nu} \rangle,$$

and then we obtain

$$\langle 0 | \hat{\boldsymbol{\mu}} | e \rangle = -\sqrt{2} e \sum_{i,a} C_{i \rightarrow a} T_{ia},$$

$T_{ia}$  is referred to as the MO-based dipole integral in this manual. The method with which the dipole integral is evaluated when calculating the transition moment is discussed later.

### Between Excited States

The transition moment between spin-adapted one-electron excitation CSF's  $\Phi_{i \rightarrow a}$  and  $\Phi_{j \rightarrow b}$  is given by,

$$\langle \Phi_{i \rightarrow a} | \hat{\boldsymbol{\mu}} | \Phi_{j \rightarrow b} \rangle = -e \left( \delta_{ij} \langle \psi_a | \mathbf{r} | \psi_b \rangle - \delta_{ab} \langle \psi_i | \mathbf{r} | \psi_j \rangle + 2\delta_{ij} \delta_{ab} \sum_p^{\text{occ}} \langle \psi_p | \mathbf{r} | \psi_p \rangle \right).$$

Therefore, the transition moment between excited states can be evaluated just like that between the ground and excited state.

$$\begin{aligned} \langle e | \hat{\boldsymbol{\mu}} | e' \rangle &= \sum_{i,a} \sum_{j,b} C_{i \rightarrow a} C'_{j \rightarrow b} \langle \Phi_{i \rightarrow a} | \hat{\boldsymbol{\mu}} | \Phi_{j \rightarrow b} \rangle \\ &= -e \sum_{i,a} \sum_{j,b} C_{i \rightarrow a} C'_{j \rightarrow b} \left( \delta_{ij} \langle \psi_a | \mathbf{r} | \psi_b \rangle - \delta_{ab} \langle \psi_i | \mathbf{r} | \psi_j \rangle + 2\delta_{ij} \delta_{ab} \sum_p^{\text{occ}} \langle \psi_p | \mathbf{r} | \psi_p \rangle \right) \\ &= -e \sum_{i,a} \sum_{j,b} C_{i \rightarrow a} C'_{j \rightarrow b} \left( \delta_{ij} \sum_{\mu,\nu}^{\text{nbasis}} C_{\mu a} C_{\nu b} \langle \chi_{\mu} | \mathbf{r} | \chi_{\nu} \rangle - \delta_{ab} \sum_{\mu,\nu}^{\text{nbasis}} C_{\mu i} C_{\nu j} \langle \chi_{\mu} | \mathbf{r} | \chi_{\nu} \rangle \right. \\ &\quad \left. + 2\delta_{ij} \delta_{ab} \sum_p^{\text{occ}} \sum_{\mu,\nu}^{\text{nbasis}} C_{\mu p} C_{\nu p} \langle \chi_{\mu} | \mathbf{r} | \chi_{\nu} \rangle \right), \end{aligned}$$

If the MO-based dipole integral  $T$  is introduced,

$$\begin{aligned} \langle e | \hat{\boldsymbol{\mu}} | e' \rangle &= -e \sum_{i,a} \sum_{j,b} C_{i \rightarrow a} C'_{j \rightarrow b} \left( \delta_{ij} T_{ab} - \delta_{ab} T_{ij} + 2\delta_{ij} \delta_{ab} \sum_p^{\text{occ}} T_{pp} \right) \\ &= -e \left( \sum_{a,b} T_{ab} \sum_i C_{i \rightarrow a} C'_{i \rightarrow b} - \sum_{i,j} T_{ij} \sum_a C_{i \rightarrow a} C'_{j \rightarrow a} + 2 \sum_p^{\text{occ}} T_{pp} \cdot \sum_{i,a} C_{i \rightarrow a} C'_{i \rightarrow a} \right) \\ &= -e \left( \sum_{a,b} T_{ab} \sum_i C_{i \rightarrow a} C'_{i \rightarrow b} - \sum_{i,j} T_{ij} \sum_a C_{i \rightarrow a} C'_{j \rightarrow a} + 2\delta_{ee'} \sum_p^{\text{occ}} T_{pp} \right). \end{aligned}$$

where

$$\langle e | e' \rangle = \sum_{i,a} \sum_{j,b} C_{i \rightarrow a} C'_{j \rightarrow b} \langle \Phi_{j \rightarrow b} | \Phi_{i \rightarrow a} \rangle = \sum_{i,a} C_{i \rightarrow a} C'_{i \rightarrow a} = \delta_{ee'},$$

for the above derivation.

$\langle e | \tilde{\boldsymbol{\mu}} | e' \rangle$  used for calculating the hyperpolarizability tensor is calculated with

$$\begin{aligned} \langle e | \tilde{\boldsymbol{\mu}} | e' \rangle &= \langle e | \hat{\boldsymbol{\mu}} - \langle 0 | \hat{\boldsymbol{\mu}} | 0 \rangle | e' \rangle \\ &= \langle e | \hat{\boldsymbol{\mu}} | e' \rangle - \langle 0 | \hat{\boldsymbol{\mu}} | 0 \rangle \langle e | e' \rangle \\ &= \langle e | \hat{\boldsymbol{\mu}} | e' \rangle - \delta_{ee'} \langle 0 | \hat{\boldsymbol{\mu}} | 0 \rangle \\ &= -e \left( \sum_{a,b} T_{ab} \sum_i C_{i \rightarrow a} C'_{i \rightarrow b} - \sum_{i,j} T_{ij} \sum_a C_{i \rightarrow a} C'_{j \rightarrow a} \right). \end{aligned}$$

For more details about the method of calculating hyperpolarizability, please refer to [Sections 5.6](#) and [5.7](#).

### Evaluating Dipole Integrals

The Mulliken approximation is used for the two-center dipole integral when calculating the ground state dipole integral (see [Section 5.3.6](#)). For evaluating the transition moment, the same Mulliken approximation may be used for one-center dipole integrals. Namely,

$$\langle \chi_\mu^A | \mathbf{r} | \chi_\nu^A \rangle = \frac{1}{2} S_{\mu\nu} (\langle \chi_\mu^A | \mathbf{r} | \chi_\mu^A \rangle + \langle \chi_\nu^A | \mathbf{r} | \chi_\nu^A \rangle).$$

If the ZDO approximation is used,  $S_{\mu\nu} = 0$  and all the integrals except the ones between the same orbitals in the one-center integrals are ignored.<sup>14</sup> In this program, the Mulliken approximation is applied to the evaluation of one-center dipole integrals only when the keyword `Dipole=ZDO` is specified.

### 5.4.4 Oscillator Strength

The oscillator strength for the excitation from the ground to  $k$ -th excited state,  $f_{0 \rightarrow k}$ , is given by,

$$\begin{aligned} f_{0 \rightarrow k} &= \frac{2m \cdot 2\pi\nu}{3\hbar e^2} |\langle 0 | \hat{\boldsymbol{\mu}} | k \rangle|^2 \\ &= \frac{2m \cdot \Delta E}{3\hbar^2 e^2} |\langle 0 | \hat{\boldsymbol{\mu}} | k \rangle|^2. \end{aligned}$$

where  $m$  is the mass of electron,  $e$  is the electron charge,  $\nu$  is the frequency of the incident light,  $\langle 0 | \hat{\boldsymbol{\mu}} | k \rangle$  is the transition moment between the ground state  $|0\rangle$  and excited state  $|k\rangle$  and  $\Delta E$  is the transition energy. The oscillator strength is dimensionless. In this program,

$$f_{0 \rightarrow k} = \frac{2}{3} \Delta E |\langle 0 | \hat{\boldsymbol{\mu}} | k \rangle|^2,$$

is used where atomic units are used throughout.

Oscillator strength is often used to indicate the degree of photo-absorption. For example, if the horizontal axis represents the wave number and the vertical axis represents the molar extinction coefficient, then the area under the absorption peak is proportional to the oscillator strength. If in particular the unit of the molar extinction coefficient is taken as  $\text{mol}^{-1} \cdot \text{cm}^{-1} \cdot \text{dm}^3$  and  $\text{cm}^{-1}$  is used for the wave number, the measured value for the oscillator strength  $f^{\text{exp}}$  will be given as

$$f^{\text{exp}} \simeq 4.3 \times 10^{-9} \times \text{Area under absorption peak} (\text{mol}^{-1} \cdot \text{dm}^3).$$

### 5.4.5 Atomic Charges

The wave function obtained from the calculation of an excited state with the CIS method may be used to compute the electron density for that excited state.

In the RHF method, if  $n_j$  is the orbital occupation number for  $\psi_j$  (2 when occupied, 0 when unoccupied), all the electrons of the system  $N_{\text{elec}}$  is given by,

$$\begin{aligned} N_{\text{elec}} &= \sum_j^N n_j \sum_{\mu,\nu}^{\text{nbasis}} C_{\mu j} C_{\nu j} S_{\mu\nu} \\ &= \sum_{\mu,\nu}^{\text{nbasis}} P_{\mu\nu} S_{\mu\nu}, \end{aligned}$$

where  $N$  is the number of all the orbitals,  $S_{\mu\nu}$  is the overlap integral and  $P_{\mu\nu}$  is the density matrix. If the spin-adapted CSF for one-electron excitation from an occupied orbital  $\psi_i$  to a virtual orbital  $\psi_a$  is represented by  $\Phi_{i \rightarrow a}$ , then  $N_{\text{elec}}$  for  $\Phi_{i \rightarrow a}$  is given by,

$$N_{\text{elec}} = \sum_{\mu,\nu}^{\text{nbasis}} S_{\mu\nu} (P_{\mu\nu} - C_{\mu i} C_{\nu i} + C_{\mu a} C_{\nu a}).$$

The  $k$ -th excitation will have a CIS wave function  $\Psi_e^k$  which is given by

$$\Psi_e^k = \sum_{i,a} C_{i \rightarrow a}^k \Phi_{i \rightarrow a},$$

and  $N_{\text{elec}}$  therefore can be rearranged,

$$\begin{aligned} N_{\text{elec}} &= \sum_{i,a} (C_{i \rightarrow a}^k)^2 \sum_{\mu,\nu}^{\text{nbasis}} S_{\mu\nu} (P_{\mu\nu} - C_{\mu i} C_{\nu i} + C_{\mu a} C_{\nu a}) \\ &= \sum_{\mu,\nu}^{\text{nbasis}} S_{\mu\nu} \left( P_{\mu\nu} + \sum_{i,a} (C_{i \rightarrow a}^k)^2 (C_{\mu a} C_{\nu a} - C_{\mu i} C_{\nu i}) \right). \end{aligned}$$

If

$$D_{\mu\nu}^k \equiv P_{\mu\nu} + \sum_{i,a} (C_{i \rightarrow a}^k)^2 (C_{\mu a} C_{\nu a} - C_{\mu i} C_{\nu i}),$$

then

$$N_{\text{elec}} = \sum_{\mu,\nu}^{\text{nbasis}} S_{\mu\nu} D_{\mu\nu}^k,$$

can be obtained. In the *ab initio* MO methods where the overlap integrals are explicitly evaluated, Mulliken population analysis can be performed for the  $k$ -th CIS excited state with  $D_{\mu\nu}^k$ .

For a method with the ZDO approximation, for example, if

$$\begin{aligned} \tilde{C}C &= \left( \tilde{C} \cdot \tilde{S}^{-\frac{1}{2}} \right) \cdot S \cdot \left( S^{-\frac{1}{2}} \cdot C \right) \\ &\equiv \tilde{C}' S C', \end{aligned}$$

non-orthogonalized  $C'$  is obtained. There are some programs which use  $C'$  to perform the Mulliken population analysis for ground state like MOPAC but this feature is not supported in this program. If the ZDO approximation is applied,  $S_{\mu\nu} = \delta_{\mu\nu}$  and hence further simplification is possible,

$$N_{\text{elec}} = \sum_{\mu}^{\text{nbasis}} D_{\mu\mu}^k = \sum_A^{\text{all}} \sum_{\mu \in A} D_{\mu\mu}^k \equiv \sum_A^{\text{all}} D_A^k,$$

where  $D_A^k$  is the electron density for atom A in the  $k$ -th excited state. With this electron density and nuclear charge, just as for the ground state, and the charge density can be computed. For the charge density of ground state please refer to [Section 5.3.5](#).

### 5.4.6 Dipole Moment

From [Section 5.4.3](#), the electronic contribution to the dipole moment for the CIS excited state  $\mu_e$  is given by

$$\langle e | \hat{\boldsymbol{\mu}} | e \rangle = -e \left( \sum_{a,b} T_{ab} \sum_i C_{i \rightarrow a} C_{i \rightarrow b} - \sum_{i,j} T_{ij} \sum_a C_{i \rightarrow a} C_{j \rightarrow a} + 2 \sum_p^{\text{occ}} T_{pp} \right).$$

The nuclear contribution in the ground state applies to the excited state also therefore

$$\begin{aligned} \boldsymbol{\mu}_e &= \langle e | \hat{\boldsymbol{\mu}}^{\text{mol}} | e \rangle \\ &= -e \left( \sum_{a,b} T_{ab} \sum_i C_{i \rightarrow a} C_{i \rightarrow b} - \sum_{i,j} T_{ij} \sum_a C_{i \rightarrow a} C_{j \rightarrow a} + 2 \sum_p^{\text{occ}} T_{pp} \right) + e \sum_A^{\text{all}} Z_A \mathbf{R}_A \\ &= -e \left( \sum_{a,b} T_{ab} \sum_i C_{i \rightarrow a} C_{i \rightarrow b} - \sum_{i,j} T_{ij} \sum_a C_{i \rightarrow a} C_{j \rightarrow a} \right) + \boldsymbol{\mu}_g, \end{aligned}$$

where  $\boldsymbol{\mu}_g$  is the dipole moment for the ground state.

In this program, MO-based dipole integrals  $T_{ij}$  are used to calculate the dipole moment for the excited state. The dipole integrals used for calculating the transition moment are used to compute  $T_{ij}$  and **when Dipole=ZDO is specified, the Mulliken approximation is used even for the one-center integrals.**

## 5.5 Calculating Polarizability $\alpha$

The sum-over-states method shown below is used to compute polarizability  $\alpha$ .<sup>24</sup>

$$\begin{aligned} \langle \alpha \rangle &= \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}, \\ \alpha_{ij}(-\omega; \omega) &= \sum_{e \neq 0} \langle 0 | \hat{\mu}_i | e \rangle \langle e | \hat{\mu}_j | 0 \rangle \left[ \frac{1}{\Delta E_e - \hbar\omega} + \frac{1}{\Delta E_e + \hbar\omega} \right], \\ \hat{\mu}_i &= -e \sum_{s=1}^N i_s, \end{aligned}$$

where  $\omega$  is the angular frequency of the incident light,  $\Delta E_e$  is the transition energy,  $|0\rangle$  is the total wave function of the ground state,  $|e\rangle$  is the total wave function of the excited state,  $i$  and  $j$  indicate the components of the Cartesian coordinates,  $\hat{\mu}_i$  is the dipole moment operator of the  $i$ -component and  $N$  is the number of electrons considered.

## 5.6 First Hyperpolarizability $\beta$

The sum-over-states method is used to compute the first hyperpolarizability  $\beta$ . In this method, the formula for calculating  $\beta$  is shown below.<sup>25–29</sup>

$$\begin{aligned}\beta_{\text{total}}(-(\omega_1 + \omega_2); \omega_1, \omega_2) &= \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}, \\ \beta_{\text{vec}}(-(\omega_1 + \omega_2); \omega_1, \omega_2) &= \sum_{i=x,y,z} \frac{\beta_i \cdot \mu_i}{|\boldsymbol{\mu}|}, \\ \beta_i(-(\omega_1 + \omega_2); \omega_1, \omega_2) &= \frac{1}{3} \sum_k (\beta_{ikk} + \beta_{kik} + \beta_{kki}),\end{aligned}$$

$$\begin{aligned}\beta_{ijk}(-(\omega_1 + \omega_2); \omega_1, \omega_2) &= \frac{1}{4} \sum_{e,e' \neq g} \left[ \frac{\langle 0 | \tilde{\mu}_i | e \rangle \langle e | \tilde{\mu}_j | e' \rangle \langle e' | \tilde{\mu}_k | 0 \rangle}{(\Delta E_e - \hbar(\omega_1 + \omega_2))(\Delta E_{e'} - \hbar\omega_2)} + \frac{\langle 0 | \tilde{\mu}_i | e \rangle \langle e | \tilde{\mu}_k | e' \rangle \langle e' | \tilde{\mu}_j | 0 \rangle}{(\Delta E_e - \hbar(\omega_1 + \omega_2))(\Delta E_{e'} - \hbar\omega_1)} \right. \\ &+ \frac{\langle 0 | \tilde{\mu}_j | e \rangle \langle e | \tilde{\mu}_i | e' \rangle \langle e' | \tilde{\mu}_k | 0 \rangle}{(\Delta E_e + \hbar\omega_1)(\Delta E_{e'} - \hbar\omega_2)} + \frac{\langle 0 | \tilde{\mu}_j | e \rangle \langle e | \tilde{\mu}_k | e' \rangle \langle e' | \tilde{\mu}_i | 0 \rangle}{(\Delta E_e + \hbar\omega_1)(\Delta E_{e'} + \hbar(\omega_1 + \omega_2))} \\ &\left. + \frac{\langle 0 | \tilde{\mu}_k | e \rangle \langle e | \tilde{\mu}_i | e' \rangle \langle e' | \tilde{\mu}_j | 0 \rangle}{(\Delta E_e + \hbar\omega_2)(\Delta E_{e'} - \hbar\omega_1)} + \frac{\langle 0 | \tilde{\mu}_k | e \rangle \langle e | \tilde{\mu}_j | e' \rangle \langle e' | \tilde{\mu}_i | 0 \rangle}{(\Delta E_e + \hbar\omega_2)(\Delta E_{e'} + \hbar(\omega_1 + \omega_2))} \right].\end{aligned}$$

where

$$\begin{aligned}\tilde{\mu}_i &= \hat{\mu}_i - \langle 0 | \hat{\mu}_i | 0 \rangle, \\ \hat{\mu}_i &= -e \sum_{s=1}^N i_s,\end{aligned}$$

$\omega_1$  and  $\omega_2$  are the angular frequencies of the incident lights,  $\Delta E_e$  and  $\Delta E_{e'}$  are the transition energies,  $|0\rangle$  is the total wave function of the ground state,  $|e\rangle$  and  $|e'\rangle$  are the total wave functions of the excited states.  $i, j$  and  $k$  are the components of the Cartesian coordinates and  $\hat{\mu}_i$  is the dipole moment operator of the  $i$ -component.  $|\boldsymbol{\mu}|$  is the norm of  $\mu_i$  and  $N$  is the number of electrons of the system.

The following four types of  $\beta$  can be calculated in this program.

- Static
- Electro-optic Pockels effect (EOPE)
- Second harmonic generation (SHG)
- Optical rectification (OR)

The relation between each type of  $\beta$  and  $\omega$  is shown below.

$$\begin{aligned}\beta^{\text{static}} &= \beta(0; 0, 0), \\ \beta^{\text{SHG}} &= \beta(-2\omega; \omega, \omega), \\ \beta^{\text{EOPE}} &= \beta(-\omega; 0, \omega), \\ \beta^{\text{OR}} &= \beta(0; \omega, -\omega).\end{aligned}$$

Note that in this program, the equation by Ward<sup>27</sup> with a  $-1/4$  multiplier is used to calculate  $\beta$  for EOPE. This is to make it equal to  $\beta(-\omega; 0, \omega)$  in the limit  $\omega \rightarrow 0$ . It is important therefore **to take care when comparing the value of  $\beta$  with the experimentally measured one.**

## 5.7 Second Hyperpolarizability $\gamma$

The sum-over-states method<sup>29</sup> is used to compute the second hyperpolarizability  $\gamma$ .

$$\begin{aligned}
\langle \gamma \rangle &= \frac{1}{5} \left[ \sum_i \gamma_{iiii} + \frac{1}{3} \sum_{j \neq i} (\gamma_{iijj} + \gamma_{ijij} + \gamma_{ijji}) \right], \\
\gamma_{ijkl}(-(\omega_1 + \omega_2 + \omega_3); \omega_1, \omega_2, \omega_3) \\
&= \frac{1}{24} \hat{P}(i, j, k, l; -(\omega_1 + \omega_2 + \omega_3), \omega_1, \omega_2, \omega_3) \\
&\left[ \sum_{e \neq 0} \sum_{e' \neq 0} \sum_{e'' \neq 0} \frac{\langle 0 | \tilde{\mu}_i | e \rangle \langle e | \tilde{\mu}_j | e' \rangle \langle e' | \tilde{\mu}_k | e'' \rangle \langle e'' | \tilde{\mu}_l | 0 \rangle}{(\Delta E_e - \hbar\omega_1 - \hbar\omega_2 - \hbar\omega_3)(\Delta E_{e'} - \hbar\omega_2 - \hbar\omega_3)(\Delta E_{e''} - \hbar\omega_3)} \right. \\
&\left. - \sum_{e \neq 0} \sum_{e' \neq 0} \frac{\langle 0 | \tilde{\mu}_i | e \rangle \langle e | \tilde{\mu}_j | 0 \rangle \langle 0 | \tilde{\mu}_k | e' \rangle \langle e' | \tilde{\mu}_l | 0 \rangle}{(\Delta E_e - \hbar\omega_1 - \hbar\omega_2 - \hbar\omega_3)(\Delta E_{e'} - \hbar\omega_3)(\Delta E_{e'} + \hbar\omega_2)} \right] \\
&= \frac{1}{24} \sum_{e \neq 0} \sum_{e' \neq 0} \sum_{e'' \neq 0} \left[ \frac{\langle 0 | \tilde{\mu}_i | e \rangle \langle e | \tilde{\mu}_j | e' \rangle \langle e' | \tilde{\mu}_k | e'' \rangle \langle e'' | \tilde{\mu}_l | 0 \rangle}{(\Delta E_e - \hbar\omega_1 - \hbar\omega_2 - \hbar\omega_3)(\Delta E_{e'} - \hbar\omega_2 - \hbar\omega_3)(\Delta E_{e''} - \hbar\omega_3)} \right. \\
&\quad + \frac{\langle 0 | \tilde{\mu}_i | e \rangle \langle e | \tilde{\mu}_j | e' \rangle \langle e' | \tilde{\mu}_l | e'' \rangle \langle e'' | \tilde{\mu}_k | 0 \rangle}{(\Delta E_e - \hbar\omega_1 - \hbar\omega_2 - \hbar\omega_3)(\Delta E_{e'} - \hbar\omega_2 - \hbar\omega_3)(\Delta E_{e''} - \hbar\omega_2)} \\
&\quad + \frac{\langle 0 | \tilde{\mu}_i | e \rangle \langle e | \tilde{\mu}_k | e' \rangle \langle e' | \tilde{\mu}_j | e'' \rangle \langle e'' | \tilde{\mu}_l | 0 \rangle}{(\Delta E_e - \hbar\omega_1 - \hbar\omega_2 - \hbar\omega_3)(\Delta E_{e'} - \hbar\omega_1 - \hbar\omega_3)(\Delta E_{e''} - \hbar\omega_3)} \\
&\quad + \frac{\langle 0 | \tilde{\mu}_i | e \rangle \langle e | \tilde{\mu}_k | e' \rangle \langle e' | \tilde{\mu}_l | e'' \rangle \langle e'' | \tilde{\mu}_j | 0 \rangle}{(\Delta E_e - \hbar\omega_1 - \hbar\omega_2 - \hbar\omega_3)(\Delta E_{e'} - \hbar\omega_1 - \hbar\omega_3)(\Delta E_{e''} - \hbar\omega_1)} \\
&\quad + \frac{\langle 0 | \tilde{\mu}_i | e \rangle \langle e | \tilde{\mu}_l | e' \rangle \langle e' | \tilde{\mu}_j | e'' \rangle \langle e'' | \tilde{\mu}_k | 0 \rangle}{(\Delta E_e - \hbar\omega_1 - \hbar\omega_2 - \hbar\omega_3)(\Delta E_{e'} - \hbar\omega_1 - \hbar\omega_2)(\Delta E_{e''} - \hbar\omega_2)} \\
&\quad + \frac{\langle 0 | \tilde{\mu}_i | e \rangle \langle e | \tilde{\mu}_l | e' \rangle \langle e' | \tilde{\mu}_k | e'' \rangle \langle e'' | \tilde{\mu}_j | 0 \rangle}{(\Delta E_e - \hbar\omega_1 - \hbar\omega_2 - \hbar\omega_3)(\Delta E_{e'} - \hbar\omega_1 - \hbar\omega_2)(\Delta E_{e''} - \hbar\omega_1)} \\
&\quad + \frac{\langle 0 | \tilde{\mu}_j | e \rangle \langle e | \tilde{\mu}_i | e' \rangle \langle e' | \tilde{\mu}_k | e'' \rangle \langle e'' | \tilde{\mu}_l | 0 \rangle}{(\Delta E_e + \hbar\omega_1)(\Delta E_{e'} - \hbar\omega_2 - \hbar\omega_3)(\Delta E_{e''} - \hbar\omega_3)} \\
&\quad + \frac{\langle 0 | \tilde{\mu}_j | e \rangle \langle e | \tilde{\mu}_i | e' \rangle \langle e' | \tilde{\mu}_l | e'' \rangle \langle e'' | \tilde{\mu}_k | 0 \rangle}{(\Delta E_e + \hbar\omega_1)(\Delta E_{e'} - \hbar\omega_2 - \hbar\omega_3)(\Delta E_{e''} - \hbar\omega_2)} \\
&\quad + \frac{\langle 0 | \tilde{\mu}_k | e \rangle \langle e | \tilde{\mu}_i | e' \rangle \langle e' | \tilde{\mu}_j | e'' \rangle \langle e'' | \tilde{\mu}_l | 0 \rangle}{(\Delta E_e + \hbar\omega_2)(\Delta E_{e'} - \hbar\omega_1 - \hbar\omega_3)(\Delta E_{e''} - \hbar\omega_3)} \\
&\quad + \frac{\langle 0 | \tilde{\mu}_k | e \rangle \langle e | \tilde{\mu}_i | e' \rangle \langle e' | \tilde{\mu}_l | e'' \rangle \langle e'' | \tilde{\mu}_j | 0 \rangle}{(\Delta E_e + \hbar\omega_2)(\Delta E_{e'} - \hbar\omega_1 - \hbar\omega_3)(\Delta E_{e''} - \hbar\omega_1)}
\end{aligned}$$







$$\begin{aligned}
& + \frac{\langle 0 | \tilde{\mu}_k | e \rangle \langle e | \tilde{\mu}_l | 0 \rangle \langle 0 | \tilde{\mu}_j | e' \rangle \langle e' | \tilde{\mu}_i | 0 \rangle}{(\Delta E_e + \hbar\omega_2)(\Delta E_{e'} + \hbar\omega_1 + \hbar\omega_2 + \hbar\omega_3)(\Delta E_{e'} + \hbar\omega_1)} \\
& + \frac{\langle 0 | \tilde{\mu}_l | e \rangle \langle e | \tilde{\mu}_j | 0 \rangle \langle 0 | \tilde{\mu}_k | e' \rangle \langle e' | \tilde{\mu}_i | 0 \rangle}{(\Delta E_e + \hbar\omega_3)(\Delta E_{e'} + \hbar\omega_1 + \hbar\omega_2 + \hbar\omega_3)(\Delta E_{e'} + \hbar\omega_1)} \\
& + \left. \frac{\langle 0 | \tilde{\mu}_l | e \rangle \langle e | \tilde{\mu}_k | 0 \rangle \langle 0 | \tilde{\mu}_j | e' \rangle \langle e' | \tilde{\mu}_i | 0 \rangle}{(\Delta E_e + \hbar\omega_3)(\Delta E_{e'} + \hbar\omega_1 + \hbar\omega_2 + \hbar\omega_3)(\Delta E_{e'} + \hbar\omega_1)} \right],
\end{aligned}$$

$$\tilde{\mu}_i = \hat{\mu}_i - \langle 0 | \hat{\mu}_i | 0 \rangle,$$

$$\hat{\mu}_i = -e \sum_{s=1}^N i_s.$$

where  $\omega_1$ ,  $\omega_2$  and  $\omega_3$  are the angular frequencies of the incident lights,  $\Delta E_e$ ,  $\Delta E_{e'}$  and  $\Delta E_{e''}$  are the transition energies.  $|0\rangle$  is the total wave function of the ground state and  $|e\rangle$ ,  $|e'\rangle$  and  $|e''\rangle$  are the total wave functions of the excited states. The indices  $i, j, k$  and  $l$  represent the components of the Cartesian coordinates,  $\hat{\mu}_i$  is the dipole moment operator of the  $i$ -th component and  $N$  is the number of electrons of the system.  $\hat{P}(i, j, k, l; -(\omega_1 + \omega_2 + \omega_3), \omega_1, \omega_2, \omega_3)$  is an exchange operator, where upon exchanging  $k$  and  $l$ , for example,  $\omega_2$  and  $\omega_3$  are swapped.

In this program, the following six type of  $\gamma$  can be calculated.

- Static
- DC-electric field induced Kerr effect (EFIKE)
- DC-electric field induced second harmonic (DC-SHG)
- Third harmonic generation (THG)
- Degenerate four-wave mixing (DFWM)
- DC-electric field induced optical rectification (DC-OR)

The relation between each type of  $\gamma$  and  $\omega$  is as follows.

$$\begin{aligned}
\gamma^{\text{static}} &= \gamma(0; 0, 0, 0), \\
\gamma^{\text{EFIKE}} &= \gamma(-\omega; \omega, 0, 0), \\
\gamma^{\text{DC-SHG}} &= \gamma(-2\omega; \omega, \omega, 0), \\
\gamma^{\text{THG}} &= \gamma(-3\omega; \omega, \omega, \omega), \\
\gamma^{\text{DFWM}} &= \gamma(-\omega; -\omega, \omega, \omega), \\
\gamma^{\text{DC-OR}} &= \gamma(0; -\omega, \omega, 0).
\end{aligned}$$



## Appendix A

# Atomic Parameters

This chapter lists the internally stored values in MOS-F V4.2D used in INDO/S, CNDO/S, CNDO/S2, CNDO/S3, and CNDO/S. These values can be included in the output if the keyword `ParMOut=A11` is specified.

The atomic parameters stored in MOS-F V4.2D are all taken from various published literature. For the source of each parameter, please refer to the appropriate footnote.

Table A.1 Ionization Potentials Used in INDO/S<sup>a</sup>

Atom	$I_1$ (eV)			$I_2$ (eV)			$C$	
	<i>s</i>	<i>p</i>	<i>d</i>	<i>s</i>	<i>p</i>	<i>d</i>	$C_1$	$C_2$
H	13.060	—	—	—	—	—	—	—
He	—	—	—	—	—	—	—	—
Li	5.390	3.540	—	—	—	—	—	—
Be	9.320	5.960	—	—	—	—	—	—
B	14.050	8.300	—	—	—	—	—	—
C	19.440	10.670	—	—	—	—	—	—
N	25.580	13.190	—	—	—	—	—	—
O	32.380	15.850	—	—	—	—	—	—
F	40.200	18.660	—	—	—	—	—	—
Na	—	—	—	—	—	—	1.00000	0.00000
Mg	—	—	—	—	—	—	1.00000	0.00000
Al	—	—	—	—	—	—	1.00000	0.00000
Si	—	—	—	—	—	—	1.00000	0.00000
P	—	—	—	—	—	—	1.00000	0.00000
S	—	—	—	—	—	—	1.00000	0.00000
Cl	26.850	13.860	—	—	—	—	1.00000	0.00000
K	—	—	—	—	—	—	1.00000	0.00000
Ca	6.030	3.960	3.440	5.130	2.990	3.440	0.96080	0.03920
Sc	6.720	4.200	8.160	5.830	3.430	4.850	0.93990	0.06010
Ti	7.280	4.480	9.070	6.340	3.750	5.930	0.90690	0.09310
V	7.730	4.770	9.890	6.710	3.950	6.770	0.83950	0.16050
Cr	8.070	5.040	10.660	6.970	4.060	7.430	0.70520	0.29480
Mn	8.350	5.270	11.450	7.150	4.100	7.990	0.66520	0.33480
Fe	8.570	5.420	12.310	7.270	4.080	8.530	0.31430	0.68570
Co	8.760	5.480	13.300	7.380	4.020	9.100	0.20650	0.79350
Ni	8.940	5.410	14.460	7.510	3.930	9.790	0.14210	0.85790
Cu	9.130	5.180	15.870	7.690	3.840	10.670	0.09560	0.90440
Zn	9.360	4.770	17.570	9.360	4.770	17.570	0.00000	1.00000
Ga	—	—	—	—	—	—	1.00000	0.00000
Ge	—	—	—	—	—	—	1.00000	0.00000
As	—	—	—	—	—	—	1.00000	0.00000
Se	—	—	—	—	—	—	1.00000	0.00000
Br	—	—	—	—	—	—	1.00000	0.00000

<sup>a</sup>H-F: Refs. 10,55, Cl: Ref. 56, Ca-Cu: Refs. 11,57.

Table A.2 Values of the Resonance Integral  $\beta$  and One-Center Electron Repulsion Integrals  $\gamma$  Used in INDO/S

Atom	$-\beta$ (eV) <sup>a</sup>			$\gamma$ (eV) <sup>b</sup>		
	<i>s</i>	<i>p</i>	<i>d</i>	<i>ss</i>	<i>sd</i>	<i>dd</i>
H	12.000	—	—	12.850	—	—
He	—	—	—	—	—	—
Li	—	—	—	—	—	—
Be	—	—	—	—	—	—
B	—	—	—	—	—	—
C	17.000	17.000	—	11.110	—	—
N	26.000	26.000	—	12.010	—	—
O	34.000	34.000	—	13.000	—	—
F	—	—	—	—	—	—
Na	—	—	—	—	—	—
Mg	—	—	—	—	—	—
Al	—	—	—	—	—	—
Si	—	—	—	—	—	—
P	—	—	—	—	—	—
S	—	—	—	—	—	—
Cl	19.000	19.000	—	10.866	—	—
K	—	—	—	—	—	—
Ca	—	—	—	3.250	4.000	6.030
Sc	1.000	1.000	18.000	3.890	4.710	7.020
Ti	1.000	1.000	18.000	4.500	5.380	7.980
V	1.000	1.000	18.000	5.070	6.010	8.910
Cr	1.000	1.000	18.000	5.600	6.600	9.810
Mn	1.000	1.000	18.000	6.090	7.160	10.680
Fe	1.000	1.000	23.000	6.540	7.680	11.520
Co	1.000	1.000	39.000	6.960	8.160	12.320
Ni	1.000	1.000	45.000	7.340	8.610	13.100
Cu	1.000	1.000	62.000	7.680	9.010	13.840
Zn	—	—	—	7.980	9.390	14.550
Ga	—	—	—	—	—	—
Ge	—	—	—	—	—	—
As	—	—	—	—	—	—
Se	—	—	—	—	—	—
Br	—	—	—	—	—	—

<sup>a</sup>H: Ref. 13, C-O: Ref. 8, Cl: Ref. 56, Sc-Cu: Ref. 12.<sup>b</sup>H-O: Ref. 8, Cl: Ref. 56, Ca-Zn: Ref. 11.

Table A.3 Slater Exponent Used in INDO/S<sup>a</sup>

Atom	$\zeta$ (Bohr <sup>-1</sup> )				Contraction Coef.	
	<i>s</i>	<i>p</i>	<i>d1</i>	<i>d2</i>	CC1	CC2
H	1.20000	—	—	—	—	—
He	1.70000	—	—	—	—	—
Li	0.65000	0.65000	—	—	—	—
Be	0.97500	0.97500	—	—	—	—
B	1.30000	1.30000	—	—	—	—
C	1.62500	1.62500	—	—	—	—
N	1.95000	1.95000	—	—	—	—
O	2.27500	2.27500	—	—	—	—
F	2.60000	2.60000	—	—	—	—
Na	0.73333	0.73333	0.73333	—	—	—
Mg	0.95000	0.95000	0.95000	—	—	—
Al	1.16667	1.16667	1.16667	—	—	—
Si	1.38333	1.38333	1.38333	—	—	—
P	1.60000	1.60000	1.60000	—	—	—
S	1.81667	1.81667	1.81667	—	—	—
Cl	2.03333	2.03333	2.03333	—	—	—
K	0.87400	0.87400	—	—	—	—
Ca	1.21000	1.21000	—	—	—	—
Sc	1.23000	1.23000	4.22244	1.74647	0.35922	0.76601
Ti	1.30000	1.30000	4.67000	1.98614	0.36461	0.75561
V	1.30000	1.30000	5.05186	2.17279	0.37378	0.74564
Cr	1.32000	1.32000	5.13843	2.07723	0.40714	0.73242
Mn	1.36000	1.36000	5.76739	2.50969	0.38984	0.72965
Fe	1.37000	1.37000	6.06828	2.61836	0.40379	0.71984
Co	1.42300	1.42300	6.38612	2.74495	0.41333	0.71262
Ni	1.47300	1.47300	6.70551	2.87381	0.42120	0.70658
Cu	1.48200	1.48200	6.79466	2.76527	0.44729	0.69683
Zn	1.50900	1.50900	—	—	—	—
Ga	1.35100	1.35100	1.35100	—	—	—
Ge	1.52700	1.52700	1.52700	—	—	—
As	1.70200	1.70200	1.70200	—	—	—
Se	1.87800	1.87800	1.87800	—	—	—
Br	2.05400	2.05400	2.05400	—	—	—

<sup>a</sup>H-Cl: Values with the Slater rule (Ref. 58), K: Ref. 59, Ca: Ref. 10, Sc-Cu: Refs. 10, 12, Ga-Br: Ref. 62.

Table A.4 Slater-Condon Parameter Used in INDO/S <sup>a</sup> (eV)

Atom	$G^1(sp)$	$F^2(pp)$	$G^2(sd)$	$G^1(pd)$	$F^2(pd)$	$G^3(pd)$	$F^2(dd)$	$F^4(dd)$
Li	2.50374	1.35688	—	—	—	—	—	—
Be	3.82814	2.65636	—	—	—	—	—	—
B	5.40150	3.48086	—	—	—	—	—	—
C	6.89786	4.50993	—	—	—	—	—	—
N	8.95848	6.45958	—	—	—	—	—	—
O	11.81545	6.90282	—	—	—	—	—	—
F	14.48483	8.59335	—	—	—	—	—	—
Na	1.66759	0.74391	0.37716	1.14363	1.36383	0.68266	0.92703	0.60455
Mg	2.47646	3.27318	0.48168	0.38063	0.54751	0.22726	0.92703	0.60455
Al	3.35911	1.60250	0.17680	0.23507	0.42911	0.14010	0.92703	0.60455
Si	4.81232	2.26271	1.79728	0.31070	2.43939	1.46649	2.41001	1.57175
P	1.05895	2.94773	2.36574	3.14102	2.87346	1.87514	2.96632	1.93453
S	3.07568	4.53782	3.22012	4.27572	3.61699	2.55246	3.52252	2.29730
Cl	8.80288	6.44718	2.12397	0.28194	0.63257	0.16837	1.59444	1.03986
K	1.11412	0.49594	—	—	—	—	—	—
Ca	1.56220	0.28826	0.46246	0.73027	0.55545	—	2.34330	1.17785
Sc	1.50021	0.61992	0.72779	0.70051	1.36383	0.27401	3.65754	1.81017
Ti	1.62419	0.68191	0.76870	0.90756	1.69858	1.27704	5.56689	3.68233
V	1.87216	0.74391	0.77366	0.64224	1.38862	0.21201	6.29840	4.38904
Cr	1.78537	0.80590	0.64720	0.69183	1.41342	0.03682	7.87300	4.56262
Mn	2.34330	0.86789	0.75754	0.15374	0.99311	0.61620	8.18296	4.69900
Fe	2.02094	0.92988	0.82326	0.30376	0.62240	0.43642	7.56304	4.76099
Co	2.81444	0.99187	0.78606	0.39303	0.77986	0.28020	7.99698	5.96364
Ni	2.40529	1.05387	0.83069	0.37319	0.75010	0.40295	9.89394	6.60836
Cu	2.56647	1.11586	0.55297	0.69679	1.32663	0.85921	10.66017	7.18675
Zn	2.52928	1.17785	—	—	—	—	—	—
Ga	—	—	—	—	—	—	—	—
Ge	—	—	—	—	—	—	—	—
As	—	—	—	—	—	—	—	—
Se	—	—	—	—	—	—	—	—
Br	—	—	—	—	—	—	—	—

<sup>a</sup>Ref. 9.

Table A.5 Atomic Parameters Used in CNDO/S (I)

Atom	$(I + A)/2$ (eV) <sup>a</sup>			$-\beta_{\mu}$ (eV) <sup>b</sup>		
	<i>s</i>	<i>p</i>	<i>d</i>	<i>s</i>	<i>p</i>	<i>d</i>
H	7.175	—	—	12.000	—	—
Li	3.105	2.050	—	3.000	3.000	—
Be	6.550	3.435	—	4.000	4.000	—
B	10.305	4.370	—	5.000	5.000	—
C	14.960	5.805	—	17.500	17.500	—
N	20.485	8.480	—	26.000	26.000	—
O	27.255	10.965	—	30.000 <sup>c</sup>	30.000 <sup>c</sup>	—
F	28.480	12.180	—	50.000	50.000	—
Na	2.805	1.565	—	5.000	5.000	5.000
Mg	5.875	2.290	—	1.000	1.000	1.000
Al	8.595	3.920	—	1.500	1.500	1.500
Si	12.125	6.005	—	5.250	5.250	5.250
P	14.340	7.235	—	7.800	7.800	7.800
S	15.810	8.410	—	13.500	13.500	13.500
Cl	17.500	9.380	—	15.000	15.000	15.000

<sup>a</sup>H-F: Ref. 15. Na-Cl: Ref. 60.

<sup>b</sup>H-F: Ref. 15. O: Ref. 16. Li, Be, Na-Cl: Ref. 60.

<sup>c</sup>  $-\beta_{\mu} = 45.0$  eV, if the keyword, 01d0xygenBeta, was specified. (Ref. 15)



Table A.6 Atomic Parameters Used in CNDO/S (II)

Atom	$\zeta$ (Bohr <sup>-1</sup> ) <sup>a</sup>			$\gamma_{AA}$ (eV) <sup>b</sup>
	<i>s</i>	<i>p</i>	<i>d</i>	
H	1.200	—	—	12.850
Li	0.650	0.650	—	2.980
Be	0.975	0.975	—	5.350
B	1.300	1.300	—	8.100
C	1.625	1.625	—	10.930
N	1.950	1.950	—	11.880
O	2.275	2.275	—	15.130
F	2.600	2.600	—	17.360
Na	0.733	0.733	0.733	2.950
Mg	0.950	0.950	0.950	4.460
Al	1.167	1.167	1.167	5.100
Si	1.383	1.383	1.383	6.370
P	1.600	1.600	1.600	9.310
S	1.817	1.817	1.817	10.010
Cl	2.033	2.033	2.033	11.300

<sup>a</sup>Values with the Slater rule.

<sup>b</sup>H-F: Ref. 15. O: Ref. 16. Li, Be, Na-Cl: Ref. 60.

Table A.7 Atomic Parameters Used in CNDO/S2 and CNDO/S3 (I)

Atom	$I$ (eV) <sup>a</sup>			$-\beta_{\mu}$ (eV) <sup>b</sup>		
	<i>s</i>	<i>p</i>	<i>d</i>	<i>s</i>	<i>p</i>	<i>d</i>
H	13.600	—	—	10.000	—	—
C	21.340	11.540	—	20.000	17.000	—
N	27.510	14.340	—	25.000	20.000	—
O	35.500	17.910	—	31.000	26.000	—
F	43.700	20.890	—	39.330	18.800	—
S	21.020	10.970	2.000	18.000	15.000	3.000
Cl	25.020	13.960	—	22.520	12.560	—
Br	23.480	12.470	—	21.130	11.230	—

<sup>a</sup>H-Br: Ref. 18. O: Ref. 54. S: Ref. 19.

<sup>b</sup>H-Br: Ref. 18. N, O: Refs. 20–22. S: Ref. 19.

Table A.8 Atomic Parameters Used in CNDO/S2 and CNDO/S3 (II)

Atom	$\zeta$ (Bohr <sup>-1</sup> ) <sup>a</sup>			$\gamma_{AA}$ (eV) <sup>b</sup>
	<i>s</i>	<i>p</i>	<i>d</i>	
H	1.233	—	—	12.850
C	2.000 <sup>c</sup>	2.000 <sup>c</sup>	—	10.630
N	1.704	1.704	—	12.370
O	2.286	2.286	—	13.100
F	2.381	2.381	—	15.180
S	2.313	2.011	1.588	9.670
Cl	2.350	2.037	—	10.920
Br	2.641	2.260	—	8.820

<sup>a</sup>H-Br: Ref. 18. N, O: Refs. 21, 22. S: Ref. 19.

<sup>b</sup>H-Br: Ref. 18. N, O: Refs. 20–22. S: Ref. 19.

<sup>c</sup> $\zeta$  of *sp*<sup>3</sup> carbon in the CNDO/S3 method: 1.625 Bohr<sup>-1</sup>

Table A.9 Atomic Parameters Used in CNDO/2

Atom	$(I + A)/2$ (eV) <sup>a</sup>			$-\beta_{\mu}$ (eV) <sup>b</sup>			$\zeta$ (Bohr <sup>-1</sup> ) <sup>c</sup>		
	<i>s</i>	<i>p</i>	<i>d</i>	<i>s</i>	<i>p</i>	<i>d</i>	<i>s</i>	<i>p</i>	<i>d</i>
H	7.176	—	—	9.000	—	—	1.200	—	—
Li	3.106	1.258	—	9.000	9.000	—	0.650	0.650	—
Be	5.946	2.563	—	13.000	13.000	—	0.975	0.975	—
B	9.594	4.001	—	17.000	17.000	—	1.300	1.300	—
C	14.051	5.572	—	21.000	21.000	—	1.625	1.625	—
N	19.316	7.275	—	25.000	25.000	—	1.950	1.950	—
O	25.390	9.111	—	31.000	31.000	—	2.275	2.275	—
F	32.272	11.080	—	39.000	39.000	—	2.600	2.600	—
Na	2.804	1.302	0.150	7.720	7.720	7.720	0.733	0.733	0.733
Mg	5.125	2.052	0.162	9.447	9.447	9.447	0.950	0.950	0.950
Al	7.771	2.995	0.224	11.301	11.301	11.301	1.167	1.167	1.167
Si	10.033	4.133	0.337	13.065	13.065	13.065	1.383	1.383	1.383
P	14.033	5.464	0.500	15.070	15.070	15.070	1.600	1.600	1.600
S	17.650	6.989	0.713	18.150	18.150	18.150	1.817	1.817	1.817
Cl	21.591	8.708	0.977	22.330	22.330	22.330	2.033	2.033	2.033
Sc	3.657	0.558	3.793	2.000	2.000	15.000	—	—	—
Ti	3.770	0.690	4.140	9.333	9.333	24.000	—	—	—
V	3.822	0.777	4.475	12.000	12.000	21.000	—	—	—
Cr	3.909	0.876	4.822	17.000	17.000	23.000	—	—	—
Mn	3.983	0.975	5.157	22.000	22.000	25.000	—	—	—
Fe	4.120	1.062	5.504	26.000	26.000	27.000	—	—	—
Co	4.170	1.160	5.839	29.000	29.000	28.000	—	—	—
Ni	4.306	1.260	6.182	32.000	32.000	29.000	—	—	—
Cu	4.567	1.347	6.520	35.000	35.000	30.000	—	—	—
Ge	11.435	4.080	—	10.000	10.000	10.000	1.527	1.527	1.527
As	13.335	5.345	—	13.000	13.000	13.000	1.702	1.702	1.702
Se	16.315	7.100	—	16.000	16.000	16.000	1.878	1.878	1.878
Br	19.630	8.400	—	22.000	22.000	22.000	2.054	2.054	2.054

<sup>a,b</sup>H-Cl: Ref. 1. Sc-Cu: Ref. 61. Ge-Br: Ref. 62. <sup>c</sup>Values with the Slater rule.

Table A.10 Van der Waals Radii<sup>a</sup> in Å

H	1.200	He	1.400	Li	1.820
C	1.700	N	1.550	O	1.520
F	1.470	Ne	1.540	Na	2.270
Mg	1.730	Si	2.100	P	1.800
S	1.800	Cl	1.750	Ar	1.880
K	2.750	Ni	1.630	Cu	1.400
Zn	1.390	Ga	1.870	Ge	2.100
As	1.850	Se	1.900	Br	1.850
Kr	2.020	Pd	1.630	Ag	1.720
Cd	1.580	In	1.930	Sn	2.170
Sb	2.200	Te	2.060	I	1.980
Xe	2.160	Pt	1.750	Au	1.660
Hg	1.550	Tl	1.960	Pb	2.020
Rn	2.400	U	1.860		

<sup>a</sup>Sb, Rn: Pauling's value, Others: Ref. 63.



## Appendix B

# Electron Repulsion Integrals for the INDO/S Method

### B.1 One-Center Electron Repulsion Integrals

The INDO/S method with  $3d$ -type orbitals requires the following one-center repulsion integral with the Slater-Condon parameter.<sup>9</sup>

For  $s$ ,  $p$  and  $d$  orbital, however, the following notation applies.

$$\begin{aligned} 1 &= s, & 2 &= p_x, & 3 &= p_y, & 4 &= p_z, \\ 5 &= d_{z^2}, & 6 &= d_{zx}, & 7 &= d_{yz}, & 8 &= d_{x^2-y^2}, & 9 &= d_{xy}. \end{aligned}$$

$$\begin{aligned} (11|11) &= F_0(ss) \\ (21|21) = (31|31) = (41|41) &= G_1(sp) \\ (22|11) = (33|11) = (44|11) &= F_0(ss) \\ (22|22) = (33|33) = (44|44) &= F_0(ss) + 4F_2(pp) \\ (32|32) = (42|42) = (43|43) &= 3F_2(pp) \\ (33|22) = (44|22) = (44|33) &= F_0(ss) - 2F_2(pp) \\ (51|51) = (61|61) = (71|71) = (81|81) = (91|91) &= G_2(sd) \\ (52|52) = (53|53) &= G_1(pd) + 18G_3(pd) \\ (54|54) &= 4G_1(pd) + 27G_3(pd) \\ (55|11) = (66|11) = (77|11) = (88|11) = (99|11) &= F_0(sd) \\ (55|22) = (55|33) &= F_0(sd) - 2F_2(pd) \\ (55|44) &= F_0(sd) + 4F_2(pd) \\ (55|55) = (66|66) = (77|77) = (88|88) = (99|99) &= F_0(dd) + 4F_2(dd) + 36F_4(dd) \\ (62|54) = (73|54) &= 2\sqrt{3}G_1(pd) - 9\sqrt{3}G_3(pd) \end{aligned}$$

$$\begin{aligned}
(62|62) &= (64|64) = (73|73) = (74|74) = (82|82) \\
&= (83|83) = (92|92) = (93|93) &= 3G_1(pd) + 24G_3(pd) \\
(63|63) &= (72|63) = (72|72) = (84|62) = (84|84) \\
&= (94|63) = (94|72) = (94|94) &= 15G_3(pd) \\
(64|52) &= (74|53) &= -\sqrt{3}G_1(pd) + 12\sqrt{3}G_3(pd) \\
(65|42) &= (75|43) &= \sqrt{3}F_2(pd) \\
(65|65) &= (75|75) &= F_2(dd) + 30F_4(dd) \\
(66|22) &= (66|44) = (77|33) = (77|44) = (88|22) \\
&= (88|33) = (99|22) = (99|33) &= F_0(sd) + 2F_2(pd) \\
(66|33) &= (77|22) = (88|44) = (99|44) &= F_0(sd) - 4F_2(pd) \\
(66|55) &= (77|55) &= F_0(dd) + 2F_2(dd) - 24F_4(dd) \\
(73|62) &= (82|64) = (92|74) = (93|64) &= 3G_1(pd) - 6G_3(pd) \\
(76|32) &= (86|42) = (96|43) = (97|42) &= 3F_2(pd) \\
(76|76) &= (86|86) = (87|87) = (96|96) = (97|97) &= 3F_2(dd) + 20F_4(dd) \\
(77|66) &= (88|66) = (88|77) = (99|66) = (99|77) &= F_0(dd) - 2F_2(dd) - 4F_4(dd) \\
(82|52) &= (92|53) = (93|52) &= -\sqrt{3}G_1(pd) - 3\sqrt{3}G_3(pd) \\
(83|53) & &= \sqrt{3}G_1(pd) + 3\sqrt{3}G_3(pd) \\
(83|74) & &= -3G_1(pd) + 6G_3(pd) \\
(84|73) & &= -15G_3(pd) \\
(85|22) &= (95|32) &= -2\sqrt{3}F_2(pd) \\
(85|33) & &= 2\sqrt{3}F_2(pd) \\
(85|66) &= (95|76) &= -2\sqrt{3}F_2(dd) + 10\sqrt{3}F_4(dd) \\
(85|77) & &= 2\sqrt{3}F_2(dd) - 10\sqrt{3}F_4(dd) \\
(85|85) &= (95|95) &= 4F_2(dd) + 15F_4(dd)
\end{aligned}$$



$$\begin{aligned}
(86|65) &= (96|75) = (97|65) &= \sqrt{3}F_2(dd) - 5\sqrt{3}F_4(dd) \\
(87|43) &&= -3F_2(pd) \\
(87|75) &&= -\sqrt{3}F_2(dd) + 5\sqrt{3}F_4(dd) \\
(88|55) &= (99|55) &= F_0(dd) - 4F_2(dd) + 6F_4(dd) \\
(92|83) &&= -3G_1(pd) + 21G_3(pd) \\
(93|82) &&= 3G_1(pd) - 21G_3(pd) \\
(96|87) &&= -3F_2(dd) + 15F_4(dd) \\
(97|86) &&= 3F_2(dd) - 15F_4(dd) \\
(98|98) &&= 35F_4(dd) \\
(99|88) &&= F_0(dd) + 4F_2(dd) - 34F_4(dd)
\end{aligned}$$

## B.2 Two-Center Electron Repulsion Integrals

In INDO/S, the formula by Nishimoto-Mataga-Weiss is used to evaluate the two-center electron repulsion integrals.<sup>39</sup>

$$\gamma_{\mu\nu}^{AB} = \frac{f_r}{R_{AB} + \frac{2f_r k}{\gamma_{\mu\mu}^A + \gamma_{\nu\nu}^B}}.$$

In the formula above,  $f = 1.2$ . If  $f = 1$  and  $k = 1$ , the standard Nishimoto-Mataga formula<sup>39</sup> is used. When  $f = 1$  and  $k \neq 1$ , the modified version of Nishimoto-Mataga formula<sup>40</sup> is applied. In INDO/S involving the first series of the transition metals, there will be  $3d$ -type orbitals to be considered and the following four types of two-center repulsion integrals need to be evaluated.

### Nishimoto-Mataga-Weiss

$$\begin{aligned}
\gamma_{ss}^{AB} (= \gamma_{sp}^{AB} = \gamma_{ps}^{AB} = \gamma_{pp}^{AB}) &= \frac{f_r}{R_{AB} + \frac{2f_r k}{\gamma_{ss}^A + \gamma_{ss}^B}}, \\
\gamma_{sd}^{AB} (= \gamma_{pd}^{AB}) &= \frac{f_r}{R_{AB} + \frac{2f_r k}{\gamma_{ss}^A + \gamma_{dd}^B}}, \\
\gamma_{ds}^{AB} (= \gamma_{dp}^{AB}) &= \frac{f_r}{R_{AB} + \frac{2f_r k}{\gamma_{dd}^A + \gamma_{ss}^B}}, \\
\gamma_{dd}^{AB} &= \frac{f_r}{R_{AB} + \frac{2f_r k}{\gamma_{dd}^A + \gamma_{dd}^B}}.
\end{aligned}$$

In MOS-F V4.2D, INDO/S for molecules with the first series of transition metals can be used for Ohno,<sup>41</sup> Ohno-Klopman<sup>42</sup> and DasGupta-Huzinaga<sup>43</sup> formula. They are shown below.

**Ohno**

$$\begin{aligned}
\gamma_{ss}^{AB} (= \gamma_{sp}^{AB} = \gamma_{ps}^{AB} = \gamma_{pp}^{AB}) &= \frac{1}{\sqrt{R_{AB}^2 + \left(\frac{2}{\gamma_{ss}^A + \gamma_{ss}^B}\right)^2}}, \\
\gamma_{sd}^{AB} (= \gamma_{pd}^{AB}) &= \frac{1}{\sqrt{R_{AB}^2 + \left(\frac{2}{\gamma_{ss}^A + \gamma_{dd}^B}\right)^2}}, \\
\gamma_{ds}^{AB} (= \gamma_{dp}^{AB}) &= \frac{1}{\sqrt{R_{AB}^2 + \left(\frac{2}{\gamma_{dd}^A + \gamma_{ss}^B}\right)^2}}, \\
\gamma_{dd}^{AB} &= \frac{1}{\sqrt{R_{AB}^2 + \left(\frac{2}{\gamma_{dd}^A + \gamma_{dd}^B}\right)^2}}.
\end{aligned}$$

**Ohno-Klopman**

$$\begin{aligned}
\gamma_{ss}^{AB} (= \gamma_{sp}^{AB} = \gamma_{ps}^{AB} = \gamma_{pp}^{AB}) &= \frac{1}{\sqrt{R_{AB}^2 + \left(\frac{1}{2\gamma_{ss}^A} + \frac{1}{2\gamma_{ss}^B}\right)^2}}, \\
\gamma_{sd}^{AB} (= \gamma_{pd}^{AB}) &= \frac{1}{\sqrt{R_{AB}^2 + \left(\frac{1}{2\gamma_{ss}^A} + \frac{1}{2\gamma_{dd}^B}\right)^2}}, \\
\gamma_{ds}^{AB} (= \gamma_{dp}^{AB}) &= \frac{1}{\sqrt{R_{AB}^2 + \left(\frac{1}{2\gamma_{dd}^A} + \frac{1}{2\gamma_{ss}^B}\right)^2}}, \\
\gamma_{dd}^{AB} &= \frac{1}{\sqrt{R_{AB}^2 + \left(\frac{1}{2\gamma_{dd}^A} + \frac{1}{2\gamma_{dd}^B}\right)^2}}.
\end{aligned}$$

**DasGupta-Huzinaga**

$$\begin{aligned}
\gamma_{ss}^{AB} (= \gamma_{sp}^{AB} = \gamma_{ps}^{AB} = \gamma_{pp}^{AB}) &= \frac{1}{R_{AB} + \frac{1}{\frac{\gamma_{ss}^A}{2} e^{k_A R_{AB}} + \frac{\gamma_{ss}^B}{2} e^{k_B R_{AB}}}}, \\
\gamma_{sd}^{AB} (= \gamma_{pd}^{AB}) &= \frac{1}{R_{AB} + \frac{1}{\frac{\gamma_{ss}^A}{2} e^{k_A R_{AB}} + \frac{\gamma_{dd}^B}{2} e^{k_B R_{AB}}}}, \\
\gamma_{ds}^{AB} (= \gamma_{dp}^{AB}) &= \frac{1}{R_{AB} + \frac{1}{\frac{\gamma_{dd}^A}{2} e^{k_A R_{AB}} + \frac{\gamma_{ss}^B}{2} e^{k_B R_{AB}}}}, \\
\gamma_{dd}^{AB} &= \frac{1}{R_{AB} + \frac{1}{\frac{\gamma_{dd}^A}{2} e^{k_A R_{AB}} + \frac{\gamma_{dd}^B}{2} e^{k_B R_{AB}}}}.
\end{aligned}$$

Where  $k$  is the Klondike parameter and is in the range  $0.4 \leq k \leq 0.8$ . In MOS-F V4.2D, the default value of  $k$  is 0.4 for all the atoms.



# Appendix C

## Fundamental Constants

The fundamental constants used in this program are listed below.

$\pi$

It is numerically defined as  $4 \tan^{-1}(1)$  and evaluated in the program.<sup>65</sup>

### Conversion Factor from Bohr to Å

The factor used is 0.529177249.

### Conversion Factor from Hartree to eV

Conversion factor AUtoEr from Hartree to erg and EVtoEr from eV to erg are used together as follows.

$$10 \times \text{AUtoEr}/\text{EVtoEr} \quad (\simeq 27.2113961318)$$

where, AUtoEr = 4.3597482, EVtoEr = 1.60217733.

### Planck's Constant

6.6260755 ( $10^{-34}$  (J·s))

### Speed of Light

2.99792458 ( $10^8$  (m/s))

### Conversion Factor from EV to Erg

1.60217733 ( $10^{-12}$ )

### Conversion Factor from EV to KCal/Mol

EVtoEr for conversion between eV and erg, the Avogadro number Avogdr and ToCal for conversion between Joules and Calories are used together in the following manner and program follows the formula.

$$10 \times \text{EVtoEr} \times \text{Avogdr}/\text{ToCal} \quad (\simeq 23.0605423014)$$

where, EVtoEr = 1.60217733, Avogdr = 6.0221367, ToCal = 4.184.

**Conversion Factor from Hartree to Erg**4.3597482 ( $10^{-11}$ )**The Wavelength of Nd+3 YAG Laser**

1064.8 (nm)

**The Wavelength of He-Ne Laser**

632.82 (nm)

**Avogadro's Number**6.0221367 ( $10^{23}$ )**Conversion Factor from Joules to Calories**

4.184

**Conversion Factor from Debye to the Atomic Unit for Dipole Moment**

The following formula built in the program uses the speed of light SLight, conversion factors ToAng (Bohr to Å) and EVtoEr (eV to erg).

$$\text{SLight} \times \text{ToAng} \times \text{EVtoEr} \quad (\simeq 2.54174776034)$$

where, SLight = 2.99792458, ToAng = 0.529177249, EVtoEr = 1.60217733.

**Conversion Factor from Atomic Units to ESU for First Hyperpolarizability**

Atomic units are used throughout the calculation of first hyperpolarizability and the result in atomic units is converted to  $10^{-30}\text{cm}^5/\text{esu}$  at the output stage. The following formula with the speed of light, and the conversion factors from Bohr to Å and from eV to erg is built in the program.

$$\text{ToAng}^5/(\text{EVtoEr} \times \text{SLight}) \quad (\simeq 0.00863922004455)$$

**Conversion Factor from Atomic Units to ESU for Second Hyperpolarizability**

Atomic units are used throughout the calculation of second hyperpolarizability and the result in atomic units is converted to  $10^{-36}\text{cm}^6/\text{erg}$  at the output stage. The following formula with the conversion factors from Bohr to Å and from Hartree to erg is built in the program.

$$0.1 \times \text{ToAng}^6/\text{AUtoEr} \quad (\simeq 0.000503669413736)$$

where, AUtoEr = 4.3597482.

**Conversion Factor from Hartree to  $\text{cm}^{-1}$** 

The conversions factor from eV to erg, from Hartree to eV, the speed of light and Planck's constant are used in the following manner to form a formula for conversion.

$$(10^5 \times \text{EVtoEr} \times \text{AUtoEV})/(\text{Planck} \times \text{SLight}) \quad (\simeq 219474.629232)$$

## Appendix D

# List of Solvent Data

Table D.1 Dielectric Constant and Refractive Index of Solvent

Solvent		Dielectric Constant		Refractive Index	
Name	Alias	$\epsilon$	Temp. ( $^{\circ}\text{C}$ )	$n$	Temp. ( $^{\circ}\text{C}$ )
1-Butanol		17.5100	25.0	1.39931	20.0
1-Chloronaphthalene		5.0400	25.0	1.63321	20.0
1-Methyl-2-pyrrolidinone	N-Methylpyrrolidone	32.0000	—	1.47000	25.0
1-Pentanol		13.9000	25.0	1.41173	15.0
1-Propanol		20.3300	25.0	1.38543	20.0
1.1.2-Trichlorotrifluoroethane		2.4100	25.0	1.35400	25.0
1.2-Dichlorobenzene		9.9300	—	1.54920	25.0
1.2-Dichloroethane		10.6490	20.0	1.44439	20.0
1.2-Dichloroethane-25C		10.3350	25.0	1.44439	20.0
1.2.4-Trichlorobenzene		3.9800	20.0	1.56933	25.0
1.4-Dioxane		2.1020	20.0	1.42240	20.0
2-Butanol		16.5600	25.0	1.39743	19.1
2-Butanone	MEK	15.4500	20.0	1.37850	20.0
2-Methylbutane	Isopentane	1.8430	20.0	1.35080	25.0
2-Propanol		19.9200	25.0	1.38126	20.0
2.2.4-Trimethylpentane	Isooctane	1.9430	20.0	1.38900	25.0
4-Methyl-2-pentanone	MIBK	13.1100	20.0	1.39580	20.0
Acetaldehyde	CH <sub>3</sub> CHO	21.1000	21.0	1.33157	20.0
Acetone	CH <sub>3</sub> COCH <sub>3</sub>	20.7000	25.0	1.35886	19.4
Acetonitrile	CH <sub>3</sub> CN	37.5000	20.0	1.34596	16.5
Acetophenone	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	17.3900	25.0	1.53427	19.1
Acetylacetone		25.7000	20.0	1.45178	18.5
Aniline	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	6.8900	20.0	1.58629	20.0
Anisole	C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	4.3300	25.0	1.51503	21.8
Benzaldehyde	C <sub>6</sub> H <sub>5</sub> CHO	17.8000	20.0	1.54638	20.0
Benzene	C <sub>6</sub> H <sub>6</sub>	2.2840	20.0	1.47439	20.0
Benzene-25C	C <sub>6</sub> H <sub>6</sub> -25C	2.2740	25.0	1.47439	20.0
Benzonitrile	C <sub>6</sub> H <sub>5</sub> CN	25.2000	25.0	1.52570	25.5
Benzylamine	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NH <sub>2</sub>	4.6000	21.0	1.54406	19.5
Bromobenzene	C <sub>6</sub> H <sub>5</sub> Br	5.4000	25.0	1.55977	20.0
Butylacetate		5.0100	20.0	1.39420	20.0
CarbonDisulfide	CS <sub>2</sub>	2.6400	—	1.62803	20.1
CarbonTetrachloride	CCl <sub>4</sub>	2.2380	20.0	1.46072	20.0
CarbonTetrachloride-25C	CCl <sub>4</sub> -25C	2.2280	25.0	1.46072	20.0
Chlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	5.7080	20.0	1.52479	20.0
Chlorobenzene-25C	C <sub>6</sub> H <sub>5</sub> Cl-25C	5.6210	25.0	1.52479	20.0
Chloroform	CHCl <sub>3</sub>	4.8060	20.0	1.44671	20.0

Cyclohexane		2.0228	20.0	1.42680	20.0
Cyclohexane-25C		2.0152	25.0	1.42680	20.0
Cyclohexanol		15.0000	25.0	1.46055	37.0
Cyclohexanone		18.3000	20.0	1.45070	20.0
Dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	7.7700	10.0	1.42721	15.0
DiethylEther	C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>5</sub>	4.3350	20.0	1.35420	16.5
Dimethylsulfoxide	DMSO	48.9000	20.0	1.47830	20.0
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	24.5500	25.0	1.36232	20.0
EthylAcetate		6.0530	20.0	1.37239	20.0
EthylBromide	C <sub>2</sub> H <sub>5</sub> Br	9.3900	20.0	1.42406	20.0
EthyleneDiamine		12.9000	25.0	1.45400	26.1
EthyleneGlycol		37.7000	25.0	1.42743	20.0
Formamide	HCONH <sub>2</sub>	111.0000	20.0	1.44530	22.7
FormicAcid	HCOOH	58.5000	16.0	1.37137	20.0
Furfural		41.9000	20.0	1.52608	20.0
Glycerin	Glycerol	42.5000	25.0	1.47460	20.0
Heptane		1.9240	20.0	1.38777	20.0
Hexane		1.8900	20.0	1.37230	25.0
IsobutylAlcohol	2-Methyl-1-Propanol	17.9300	25.0	1.39396	25.6
Isoquinoline		10.7000	25.0	1.62233	25.1
m-Xylene		2.3740	20.0	1.49962	14.9
Methanol	CH <sub>3</sub> OH	32.6300	25.0	1.33001	18.0
Methylcyclohexane		2.0200	25.0	1.42310	25.0
MethylFormate	HCOOCH <sub>3</sub>	8.2300	—	1.34400	20.0
N,N-Dimethylformamide	DMF	36.7100	—	1.42690	25.0
Nitrobenzene	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	35.7040	20.0	1.55319	20.0
Nitrobenzene-25C	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> -25C	34.7420	25.0	1.55319	20.0
Nitromethane	CH <sub>3</sub> NO <sub>2</sub>	35.8700	30.0	1.38133	21.6
o-Toluidine		6.3400	18.0	1.57276	20.0
o-Xylene		2.5680	20.0	1.50777	15.5
p-Xylene		2.2700	20.0	1.49734	16.2
Pentane		1.8440	20.0	1.35470	25.0
Phenol	C <sub>6</sub> H <sub>5</sub> OH	9.7800	60.0	1.54247	40.6
Pyridine	C <sub>5</sub> H <sub>5</sub> N	12.3000	25.0	1.50919	21.0
Quinoline		9.0000	25.0	1.62450	24.9
Styrene		2.4300	25.0	1.54382	20.0
Tetrachloroethylene		2.3000	25.0	1.50547	20.0
Tetrahydrofuran	THF	8.2000	20.0	1.40500	20.0
Toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	2.3790	25.0	1.49782	16.4
Trichloroethylene	Trichlen	3.4200	16.0	1.47820	20.0
TrifluoroaceticAcid	CFC-113	42.1000	25.0	1.28500	20.0
Water	H <sub>2</sub> O	80.1000	20.0	1.33335	20.0
Water-25C	H <sub>2</sub> O-25C	78.3000	25.0	1.33287	25.0



## Appendix E

# Differences between MOS-F V4.2D and older versions

### E.1 Differences between MOS-F V4.2D and V1

#### E.1.1 New Features

- INDO/S method
- Frequency-dependent polarizability  $\alpha$
- Frequency-dependent second hyperpolarizability  $\gamma$
- Prediction of the following molecular properties in the presence of a solvent using the SCRF calculation by means of the Onsager model:
  - Electronic spectrum
  - Electron density and dipole moment in excited states
  - Frequency-dependent polarizability,  $\alpha$ , first hyperpolarizability,  $\beta$ , and second hyperpolarizability,  $\gamma$
- Level-shift method
- Add the parameters of S, Cl, and Br for CNDO/S2 and CNDO/S3
- Coordinate input format equivalent to that of Gaussian symbolic Z-matrix
- Dynamic memory allocation
- Different exponents for  $s$ ,  $p$  and  $d$ -type orbitals can be specified separately.
- WinMOPAC IO interface (except WinMOPAC V1)
- SCRF calculation for an ionic molecule
- Automatic calculation of the cavity radius for a solute
- Automatic input system of dielectric constant and refractive index by specifying a solvent name
- Output control of the difference density matrices between ground and excited states for WinMOPAC file
- Displaying of the process of the MOS-F calculation on the standard error output (except the calculation on WinMOPAC)

## E.1.2 Changes

- Input for user-defined atomic parameters
- Default switch on the calculation of hyperpolarizability  $\beta$  (yes  $\rightarrow$  no)
- Default CI dimension (CI(5 5)  $\rightarrow$  CI(10 10))
- Default output for MO coefficients and densities (5  $\rightarrow$  10)
- Frequency increment setting for the frequency dependent first hyperpolarizability  $\beta$  (0.02 eV  $\rightarrow$  0.2 eV)
- Output format of molecular coordinates
- Output format of first hyperpolarizability  $\beta$
- Full original source code
- Evaluation of the overlap integrals for Slater-type orbitals
- Method of diagonalization of real symmetric matrix
- Some of the atomic parameters are changed (e.g. the value of resonance integral for oxygen in CNDO/S)
- Fundamental constants
- Improved performance
- Minor bug fixed

## E.1.3 Keywords Added in MOS-F V4.2D

- |                         |  |
|-------------------------|--|
| • Alpha                 | Calculates static polarizability.  |
| • AlphaDispersion       | Calculates frequency dispersion of the polarizability.   |
| • AlphaDynamic          | As AlphaDispersion.  |
| • AlphaFreqStep=X.XXXXX | Input incremental value of frequency in the dynamic polarizability calculation in eV.            |
| • AlphaStatic           | As Alpha.  |
| • AUtoEr=X.XXXXXXX      | Input conversion factor from Hartree to erg (Default value: 4.3597482).                          |
| • Avogdr=X.XXXXXXX      | Input Avogadro's number (Default value: 6.0221367).  |
| • Beta                  | Calculates static first hyperpolarizability.   |
| • BetaDispersionEO      | As BetaDispersionEOPE.   |
| • BetaDispersionEOPE    | Calculates frequency dispersion of the first hyperpolarizability for EOPE.                       |
| • BetaDispersionOR      | Calculates frequency dispersion of the first hyperpolarizability for OR.                         |
| • BetaDispersionSHG     | Calculates frequency dispersion of the first hyperpolarizability for SHG.                        |
| • BetaEO                | As BetaEOPE.   |
| • BetaEOPE              | Calculates first hyperpolarizability for EOPE (Incident light: He-Ne laser)                      |
| • BetaFreqStep=X.XXXXX  | Input incremental value of frequency in the dynamic first hyperpolarizability calculation in eV. |

- `BetaOR` Calculates first hyperpolarizability for OR (Incident light: He-Ne laser).
- `BetaSHG` Calculates first hyperpolarizability for SHG (Incident light: YAG laser).
- `BetaStatic` As Beta.
- `CavityRadius=vdW` Compute the cavity radius of the solute using its approximate molar volume obtained from the van der Waals radii of the constituent atoms.
- `CavityRadius=vdW+0.5` Add empirical value 0.5 Å to the value obtained from `CavityRadius=vdW`.
- `CavityRadius=vdW_cube` Compute the cavity radius of the solute using its approximate molar volume with the cube shape obtained from the van der Waals radii of the constituent atoms.
- `CavityRadius=XXX.XXX` Specifies the cavity radius of the solute in Å.
- `Charges=n` Specifies the charge on the molecule.
- `CheckParm` Check whether the atomic parameters are sufficient or not.
- `CI=All` Specifies that all orbitals obtained from SCF calculation be used in CIS calculation (requires memory space to the order of the fourth power of the number of molecular orbitals for CIS calculation).
- `Coord=MCart` Specifies that the coordinate input format of MOPAC's Cartesian coordinate be used.
- `Coord=Z` Specifies that the coordinate input format of Gaussian's symbolic Z-matrix be used.
- `D-Delta=X.XXXXX` Specifies the scale factor for  $d\delta$ -type overlap integrals (default: 1.0). Only effective with INDO/S.
- `D-Pi=X.XXXXX` Specifies the scale factor for  $d\pi$ -type overlap integrals (default: 1.0). Only effective with INDO/S.
- `D-Sigma=X.XXXXX` Specifies the scale factor for  $d\sigma$ -type overlap integrals (default: 1.0). Only effective with INDO/S.
- `Diag=Inv` Specifies that for matrix diagonalization the QL method is used for eigenvalue calculation and the inverse iteration method is used for eigenvector calculation.
- `Diag=QL` Specifies that for matrix diagonalization the QL method is used for both eigenvalue and eigenvector calculation.
- `DielectricConstant=X.XXX` Specifies the dielectric constant of the solvent.
- `Display=S` As `Display=Silent`.
- `Display=Silent` Suppress displaying the progress of the MOS-F process on the standard error output.
- `Display=V` As `Display=Verbose`.
- `Display=Verbose` Verbosely display the progress of the MOS-F process on the standard error output.

- `Gamma`                               Calculates static second hyperpolarizability.
- `GammaDCOR`                        Calculates second hyperpolarizability for DC-OR (Incident light: He-Ne laser).
- `GammaDCSHG`                        Calculates second hyperpolarizability for DC-SHG (Incident light: YAG laser).
- `GammaDFWM`                         Calculates second hyperpolarizability for DFWM (Incident light: He-Ne laser).
- `GammaDispersionDCOR`             Calculates the frequency dispersion of second hyperpolarizability for DC-OR.
- `GammaDispersionDCSHG`            Calculates the frequency dispersion of second hyperpolarizability for DC-SHG.
- `GammaDispersionDFWM`            Calculates the frequency dispersion of second hyperpolarizability for DFWM.
- `GammaDispersionKerr`             Calculates the frequency dispersion of second hyperpolarizability for EFIKE.
- `GammaDispersionTHG`             Calculates the frequency dispersion of second hyperpolarizability for THG.
- `GammaFreqStep=X.XXXXX`           Input incremental value of frequency in the dynamic second hyperpolarizability calculation in eV.
- `GammaKerr`                         Calculates second hyperpolarizability for EFIKE (Incident light: He-Ne laser).
- `GammaStatic`                        As `Gamma`.
- `GammaTHG`                         Calculates second hyperpolarizability for THG (Incident light: 1907 nm).
- `HeNeNM=XXX.XXXXXXXX`            Specifies the wavelength of He-Ne laser in nm (Default: 632.82).
- `INDO/S`                             Specifies that INDO/S is used as the model Hamiltonian.
- `MinorBetaTensor`                 Computes all the tensor elements of the first hyperpolarizability.
- `MinorGammaTensor`                Computes all the tensor elements of the second hyperpolarizability.
- `NoCheckParm`                       Do not check whether the atomic parameters are sufficient or not.
- `NoShift`                            Do not apply the level-shift method in the SCF calculation.
- `OldOxygenBeta`                    Uses the old value of resonance integral for oxygen in CNDO/S (-45.0 eV).
- `Plane=X-Y`                         Places the second atom on the x-axis and third on x-y plane when Z-Matrix is used for coordinate input.
- `P-Pi=X.XXXXX`                     Specifies a scale factor for  $p\pi$ -type overlap integrals, as for `FP=X.XXXXX`.
- `P-Sigma=X.XXXXX`                 Specifies a scale factor for  $p\sigma$ -type overlap integrals, as for `FS=X.XXXXX`.
- `Plane=Z-X`                        Places the second atom on the Z-axis and third on Z-X plane when Z-Matrix is used for coordinate input.
- `Plane=Z-Y`                        Places the second atom on the Z-axis and third on Z-Y plane when Z-Matrix is used for coordinate input.
- `PrintSolvent`                     Requests the list of the program-defined name, alias, dielectric constant, and refractive index of the solvent in the output.
- `RefractiveIndex=X.XXX`            Specifies the refractive index of the solvent.

- SCF=NoExtrap Do not extrapolate the density matrix in the SCF calculation.
- SCRF Perform the SCRF calculation using the Onsager model with model B proposed by Zerner.
- SCRF=Onsager Perform the SCRF calculation using the Onsager model.
- SCRF=Onsager\_A Perform the SCRF calculation using the Onsager model with model A proposed by Zerner.
- SCRF=Onsager\_B As SCRF.
- SCRF=Onsager\_B1 Perform the SCRF calculation using the Onsager model with model B1 proposed by Zerner.
- Shift As Shift=0.5.
- Shift=X.XXXXXXXXX Specifies the amount by which the virtual orbital energies are shifted in Hartree.
- Solvent=XXXXXX Specifies the solvent name to use the program-defined dielectric constant and refractive index of the solvent.
- ToCal=X.XXXXXXXXX Input conversion factor from Joules to Calories (Default: 4.184)
- UseCNDOParm Use atomic parameters for CNDO/S and CNDO/S2 in the INDO/S calculation.
- UseTripletParm Use atomic parameters for triplet excited states in the INDO/S calculation.
- Weiss=XX.XXXX Specifies the Weiss factor  $f_r$  for Nishimoto-Mataga-Weiss formula (Default: 1.2).
- WinMOPAC An output file for WinMOPAC V3 (.wms file) is generated.
- wms=CIDens(m n) Output the difference density matrices from the m-th excited state to the n-th one on the WinMOPAC file.
- wms=CIDens=ECharge Output the difference density matrices for excited states with their number specified by the keyword ECharge.
- wms=CIDens=XX[KMG](B) Output the difference density matrices for excited states with the specified size.
- wms=NoCIDens Do not output the difference density matrices for excited states on the WinMOPAC file.
- YAGNM=XXXX.XXXXXXXXX Inputs the wavelength of Nd+3 YAG laser in nm (Default: 1064.8).

#### E.1.4 Obsolete Keywords in MOS-F V4.2D

- E0 Calculates the frequency dispersion of the first hyperpolarizability for EOPE.  
Alternative Keyword: BetaDispersionEOPE.
- E0=Rev Calculates the frequency dispersion of the energy difference between the  $S_1$  excited state and incident light for the first hyperpolarizability for EOPE.  
Alternative Keyword: None.

- EOPE As EO.
- EOPE=Rev As EO=Rev.
- NoBeta Specifies that the first hyperpolarizability  $\beta$  shall not be computed.  
Alternative Keyword: None (The default setting in this version will not calculate it).
- OR Computes the frequency dispersion of the first hyperpolarizability for OR.  
Alternative Keyword: BetaDispersionOR.
- OR=Rev Calculates the frequency dispersion for the energy difference between the  $S_1$  excited state and incident light for the first hyperpolarizability for OR.  
Alternative Keyword: None.
- SHG Computes the frequency dispersion for the first hyperpolarizability for SHG.  
Alternative Keyword: BetaDispersionSHG.
- SHG=Rev Computes the frequency dispersion for the energy difference between the  $S_1$  excited state and incident light for the first hyperpolarizability for SHG.  
Alternative Keyword: None.
- SlaCon Outputs the Slater-Condon parameters.  
Alternative Keyword: combination of INDO/S and ParmOut=XXXX.

## E.2 Differences between MOS-F V4.2D and V4.1

Let us now go through the difference between the current version MOS-F V4.2D and V4.1, which is bundled in WinMOPAC V2.

### E.2.1 New Features

- Add the parameters of CI for INDO/S
- Use atomic parameters for CNDO/S and CNDO/S2 in the INDO/S calculation via keyword
- Prediction of the following molecular properties in the presence of a solvent using the SCRF calculation by means of the Onsager model:
  - Electronic spectrum
  - Electron density and dipole moment in excited states
  - Frequency-dependent polarizability,  $\alpha$ , first hyperpolarizability,  $\beta$ , and second hyperpolarizability,  $\gamma$
- SCRF calculation for an ionic molecule
- Automatic calculation of the cavity radius for a solute
- Automatic input system of dielectric constant and refractive index by specifying a solvent name
- Output control of the difference density matrices between ground and excited states for WinMOPAC file.
- Displaying of the process of the MOS-F calculation on the standard error output (except the calculation on WinMOPAC)

## E.2.2 Changes

- Part of output format
- Improved performance
- Minor bug fixed
- Modification of command line input
- Modification of input for MOPAC internal coordinates
- Computational functionality for a molecule containing atoms with atomic number more than 35

## E.2.3 Keywords Added in MOS-F V4.2D

- `CavityRadius=vdW` Compute the cavity radius of the solute using its approximate molar volume obtained from van der Waals radii of the constituent atoms.
- `CavityRadius=vdW+0.5` Add empirical value, 0.5 Å to the value obtained from `CavityRadius=vdW`.
- `CavityRadius=vdW_cube` Compute the cavity radius of the solute using its approximate molar volume with cube shape obtained from van der Waals radii of the constituent atoms.
- `CavityRadius=XXX.XXX` Specifies the cavity radius of the solute in Å.
- `CheckParm` Check if the atomic parameters are sufficient or not.
- `DielectricConstant=X.XXX` Specifies the dielectric constant of the solvent.
- `Display=S` As `Display=Silent`.
- `Display=Silent` Suppress displaying the progress of the MOS-F process on the standard error output.
- `Display=V` As `Display=Verbose`.
- `Display=Verbose` Verbosely display the progress of the MOS-F process on the standard error output.
- `NoCheckParm` Do not check if the atomic parameters are sufficient or not.
- `PrintSolvent` Requests the list of the program-defined name, alias, dielectric constant and refractive index of the solvent in output.
- `RefractiveIndex=X.XXX` Specifies the refractive index of the solvent.
- `SCF=NoExtrap` Do not extrapolate the density matrix in the SCF calculation.
- `SCRF` Perform the SCRF calculation using the Onsager model with the model B proposed by Zerner.
- `SCRF=Onsager` Perform the SCRF calculation using the Onsager model.
- `SCRF=Onsager_A` Perform the SCRF calculation using the Onsager model with the model A proposed by Zerner.
- `SCRF=Onsager_B` As `SCRF`.

- `SCRf=Onsager_B1` Perform the SCRf calculation using the Onsager model with the model B1 proposed by Zerner.
- `Solvent=XXXXXX` Specifies the solvent name to use the program-defined dielectric constant and refractive index of the solvent.
- `UseCNDOParm` Use atomic parameters for CNDO/S and CNDO/S2 in the INDO/S calculation.
- `UseTripletParm` Use atomic parameters for triplet excited states in the INDO/S calculation.
- `WinMOPAC` An output file for WinMOPAC V3 (`.wms` file) is generated.
- `wms=CIDens(m n)` Output the difference density matrices from m-th excited state to n-th one on WinMOPAC file.
- `wms=CIDens=ECharge` Output the difference density matrices for excited states with its number specified by the keyword `ECharge`.
- `wms=CIDens=XX[KMG](B)` Output the difference density matrices for excited states with specified size.
- `wms=NoCIDens` Do not output the difference density matrices for excited states on WinMOPAC file.

## E.2.4 Keywords for Atomic Parameters Added in MOS-F V4.2D

### Available Keywords for `Parm=Type`

- `vdW` Van der Waals radius in Å



## Appendix F

# Error Messages

Here are the warning and error messages possible in MOS-F V4.2D listed in alphabetical order. Both warning and error messages indicate flaws in input or possibility of malfunctioning, but the warnings let the computation continue whereas the errors will terminate it completely. Warnings and errors both show the corresponding program unit's name and an explanation.

A typical message is listed below.

**ADynam: Too little transition energy ... Cannot calculate frequency dispersion.**

This example shows that a problem "Too little transition energy ... Cannot calculate frequency dispersion." has resulted in the unit ADynam.

Here are the warning and error messages and their meanings with possible remedies.

### F.1 Warnings

**ADynam: Too little transition energy ... Cannot calculate frequency dispersion.**

**Explanation:** For evaluating the frequency-dependent  $\alpha$ , the energy denominator is the energy difference between the transition energy to the  $S_1$  state and incident light. Therefore, if the  $S_1$  transition energy is less than that of the incident light (0.2 eV by default), the frequency-dependent  $\alpha$  is not calculated. Please refer to [Section 5.5](#) for more details of the calculation of polarizability.

**Solution:** None. Other calculations are unaffected.

**Angled: Dihedral angle not definable. Forced to zero.**

**Solution:** Not explicitly given and other calculations are unaffected. This message is given for linear molecules where dihedral angles cannot be defined.

**AtPrms: Do not check atomic parameters by external request.**

**Explanation:** When specifying the keyword `NoCheckParm`, this message will result.

**Solution:** None.

**CToZ: Failed to find the atom lc to define the dihedral angle.**

**Solution:** Not explicitly given and other calculations are unaffected. This message is given for linear molecules where dihedral angles cannot be defined.

**ERI: Analytic or PP gamma is not available for the INDO/S method involving d orbitals. Use NMW gamma instead.**

**Explanation:** In MOS-F V4.2D, analytic or Pariser-Parr formulae cannot be used for INDO/S involving *d*-type orbitals. PP: Pariser-Parr. NMW: Nishimoto-Mataga-Weiss.

**Solution:** Use the default formula NMW or specify `G=NM`, `G=O`, `G=OK` or `G=DH`.

**ExitMOS: Date ... don't work fine.**

**Explanation:** The date function has not functioned properly.

**Solution:** None, but the result will not be affected by this problem.

**GetCnt: Specified atomic identifier too long. Ignore extra characters.**

**Explanation:** A string is sometimes used to identify particular atoms for Z-matrix generation or atomic parameter input. Such a string is called an atom identifier in this manual (see [page 20](#)). This string may not exceed eight characters in size or this message will result.

**Solution:** Cut down to equal to or fewer than eight characters.

**GetIAN: Specified atomic name too long. Ignore extra characters.**

**Explanation:** A string is sometimes used to identify particular atoms for Z-matrix generation or atomic parameter input. Such a string is called an atom identifier in this manual (see [page 20](#)). This string may not exceed eight characters in size or this message will result.

**Solution:** Cut down to equal to or fewer than eight characters.

**GetPrm: XXXX ... Only Parm=Type**

**Explanation:** If the keyword `Parm=Atom` for atomic parameter input is in use, the Slater-Condon parameter, for example, should not be included or else this message will appear.

**Solution:** Use `Parm=Type` for atomic parameter input.

**GetZ: Specified variable too long. Ignore extra characters.**

**Explanation:** Within the Gaussian symbolic Z-Matrix, a string variable (called *Z-matrix variables* in the manual) starting with an alphabetical character may be used for a bond length, a bond angle and so on. It should not exceed eight characters in size or else this message will result.

**Solution:** Cut down to equal to or fewer than eight characters.

**GetZ: Specified variable not found. Ignore.**

**Explanation:** Within the Gaussian symbolic Z-Matrix, the values for the variables are specified after the Z-Matrix input. If the variables are not in the Z-Matrix this message will appear.

**Solution:** Check the Z-Matrix again.

**H1EOPE: Too little transition energy ... Cannot calculate beta (He-Ne).**

**Explanation:** For calculating the first hyperpolarizability for EOPE, the energy difference between the transition energy to the  $S_1$  state and incident light is used as the denominator. Therefore, if the  $S_1$  transition energy is smaller than that of the incident light (He-Ne laser), it is not computed. Please refer to [Section 5.6](#) for more details on the calculation of first hyperpolarizability.

**Solution:** None. Other calculations unaffected.

**H1EOPE: Too little transition energy ... Cannot calculate frequency dispersion.**

**Explanation:** For calculating the frequency dispersion of the first hyperpolarizability for EOPE, the energy difference between the transition energy to the  $S_1$  state and incident light is used as the denominator. Therefore, if the  $S_1$  transition energy is smaller than that of the incident light (0.2 eV by default), it is not computed. Please refer to [Section 5.6](#) for more details on the calculation of first hyperpolarizability.

**Solution:** None. Other calculations unaffected.

**H1OR: Too little transition energy ... Cannot calculate beta (He-Ne).**

**Explanation:** For calculating the first hyperpolarizability for OR, the energy difference between the transition energy to the  $S_1$  state and incident light is used as the denominator. Therefore, if the  $S_1$  transition energy is smaller than that of the incident light (He-Ne laser), it is not computed. Please refer to [Section 5.6](#) for more details on the calculation of first hyperpolarizability.

**Solution:** None. Other calculations unaffected.

**H1OR: Too little transition energy ... Cannot calculate frequency dispersion.**

**Explanation:** For calculating the frequency dispersion of the first hyperpolarizability for OR, the energy difference between the transition energy to the  $S_1$  state and incident light is used as the denominator. Therefore, if the  $S_1$  transition energy is smaller than that of the incident light (0.2 eV by default), it is not computed. Please refer to [Section 5.6](#) for more details on the calculation of first hyperpolarizability.

**Solution:** None. Other calculations unaffected.

**H1SHG: Too little transition energy ... Cannot calculate beta (YAG).**

**Explanation:** For calculating the first hyperpolarizability for SHG, the energy difference between the transition energy to the  $S_1$  state and twice that of the incident light is used as the denominator. Therefore, if the  $S_1$  transition energy is smaller than twice that of the incident light (YAG laser), it is not computed. Please refer to [Section 5.6](#) for more details on the calculation of first hyperpolarizability.

**Solution:** None. Other calculations unaffected.

**H1SHG: Too little transition energy ... Cannot calculate frequency dispersion.**

**Explanation:** For calculating the frequency dispersion of the first hyperpolarizability for SHG, the energy difference between the transition energy to the  $S_1$  state and twice that of the incident light is used as the denominator. Therefore, if the  $S_1$  transition energy is smaller than twice that of the incident light (twice 0.2 eV by default), it is not computed. Please refer to [Section 5.6](#) for more details on the calculation of first hyperpolarizability.

**Solution:** None. Other calculations unaffected.

**H2DFWM: Too little transition energy ... Cannot calculate frequency dispersion.**

**Explanation:** For calculating the frequency dispersion of the second hyperpolarizability for DFWM, the energy difference between the transition energy to the  $S_1$  state and twice that of the incident light is used as the denominator. Therefore, if the  $S_1$  transition energy is smaller than twice that of the incident light (twice 0.2 eV by default), it is not computed. Please refer to [Section 5.7](#) for more details on the calculation of second hyperpolarizability.

**Solution:** None. Other calculations unaffected.

**H2DFWM: Too little transition energy ... Cannot calculate gamma (He-Ne).**

**Explanation:** For calculating the second hyperpolarizability for DFWM, the energy difference between the transition energy to the  $S_1$  state and twice that of the incident light is used as the denominator. Therefore, if the  $S_1$  transition energy is smaller than twice that of the incident light (He-Ne laser), it is not computed. Please refer to [Section 5.7](#) for more details on the calculation of second hyperpolarizability.

**Solution:** None. Other calculations unaffected.

**H2Kerr: Too little transition energy ... Cannot calculate frequency dispersion.**

**Explanation:** For calculating the frequency dispersion of the second hyperpolarizability for EFIKE, the energy difference between the transition energy to the  $S_1$  state and that of the incident light is used as the denominator. Therefore, if the  $S_1$  transition energy is smaller than that of the incident light (0.2 eV by default), it is not computed. Please refer to [Section 5.7](#) for more details on the calculation of second hyperpolarizability.

**Solution:** None. Other calculations unaffected.

**H2Kerr: Too little transition energy ... Cannot calculate gamma (He-Ne).**

**Explanation:** For calculating the second hyperpolarizability for EFIKE, the energy difference between the transition energy to the  $S_1$  state and that of the incident light is used as the denominator. Therefore, if the  $S_1$  transition energy is smaller than that of the incident light (He-Ne laser), it is not computed. Please refer to [Section 5.7](#) for more details on the calculation of second hyperpolarizability.

**Solution:** None. Other calculations unaffected.

**H2OR: Too little transition energy ... Cannot calculate frequency dispersion.**

**Explanation:** For calculating the frequency dispersion of the second hyperpolarizability for DC-OR, the energy difference between the transition energy to the  $S_1$  state and that of the incident light is used as the denominator. Therefore, if the  $S_1$  transition energy is smaller than that of the incident light (0.2 eV by default), it is not computed. Please refer to [Section 5.7](#) for more details on the calculation of second hyperpolarizability.

**Solution:** None. Other calculations unaffected.

**H2OR: Too little transition energy ... Cannot calculate gamma (He-Ne).**

**Explanation:** For calculating the second hyperpolarizability for DC-OR, the energy difference between the transition energy to the  $S_1$  state and that of the incident light is used as the denominator. Therefore, if the  $S_1$  transition energy is smaller than that of the incident light (He-Ne laser), it is not computed. Please refer to [Section 5.7](#) for more details on the calculation of second hyperpolarizability.

**Solution:** None. Other calculations unaffected.

**H2SHG: Too little transition energy ... Cannot calculate frequency dispersion.**

**Explanation:** For calculating the frequency dispersion of the second hyperpolarizability for DC-SHG, the energy difference between the transition energy to the  $S_1$  state and twice that of the incident light is used as the denominator. Therefore, if the  $S_1$  transition energy is smaller than twice that of the incident light (twice 0.2 eV by default), it is not computed. Please refer to [Section 5.7](#) for more details on the calculation of second hyperpolarizability.

**Solution:** None. Other calculations unaffected.

**H2SHG: Too little transition energy ... Cannot calculate gamma (YAG).**

**Explanation:** For calculating the second hyperpolarizability for DC-SHG, the energy difference between the transition energy to the  $S_1$  state and twice that of the incident light is used as the denominator. Therefore, if the  $S_1$  transition energy is smaller than twice that of the incident light (YAG laser), it is not computed. Please refer to [Section 5.7](#) for more details on the calculation of second hyperpolarizability.

**Solution:** None. Other calculations unaffected.

**H2THG: Too little transition energy ... Cannot calculate frequency dispersion.**

**Explanation:** For calculating the frequency dispersion of the second hyperpolarizability for THG, the energy difference between the transition energy to the  $S_1$  state and triple that of the incident light is used as the denominator. Therefore, if the  $S_1$  transition energy is smaller than triple that of the incident light (triple 0.2 eV by default), it is not computed. Please refer to [Section 5.7](#) for more details on the calculation of second hyperpolarizability.

**Solution:** None. Other calculations unaffected.

**H2THG: Too little transition energy ... Cannot calculate gamma.**

**Explanation:** For calculating the second hyperpolarizability for THG, the energy difference between the transition energy to the  $S_1$  state and triple that of the incident light is used as the denominator. Therefore, if the  $S_1$  transition energy is smaller than triple that of the incident light, it is not computed. Please refer to [Section 5.7](#) for more details on the calculation of second hyperpolarizability.

**Solution:** None. Other calculations unaffected.

**InitMOS: SetBuf ... don't work fine.**

**Explanation:** The SetBuf function (setvbuf function) has not functioned properly.

**Solution:** None, but the result will not be affected by this problem.

**MDef: Multi-defined data block was detected. The latter is used.**

**Explanation:** If the keyword is repeated in atomic parameter input, this warning message will appear.

**Solution:** Check the atomic parameter input.

**MOInfo: MO number out of range ... ignored MO XXXX**

**Explanation:** When specifying the serial number of MO's to be considered in CI calculation with CI=Read, giving 0 or any other invalid number, this message will result.

**Solution:** Check the option input data for CI=Read.

**MOInfo: Number of active occupied MOs out of range. Maximum value is assumed.**

**Explanation:** When specifying the MO's for CI calculation with CI(m n), giving a value for m corresponding to a case which is beyond the program's capability, this message will appear.

**Solution:** Check the CI keyword.

**MOInfo: Number of active virtual MOs out of range. Maximum value is assumed.**

**Explanation:** When specifying the MO's for CI calculation with CI(m n), giving a value for n corresponding to a case which is beyond the program's capability, this message will appear.

**Solution:** Check the CI keyword.

**MOInfo: The same MO number exists in the input deck.**

**Explanation:** When specifying the MO's for CI calculation CI=Read in the option section, repeating the same number inappropriately will lead to this message.

**Solution:** Check the option input data for CI=Read.

**OptSet: AlphaFreqStep out of range. Default value is assumed.**

**Explanation:** When calculating the frequency dispersion of the polarizability, the user can specify the incremental value of frequency of incident light in eV as AlphaFreqStep=X.XXXXX. If the value for X.XXXXX is less than or equal to 0.0, this message will appear. By default, the value for X.XXXXX is 0.2, namely the incremental value of frequency is 0.2 eV.

**Solution:** Check the value for AlphaFreqStep=X.XXXXX.

**OptSet: BetaFreqStep out of range. Default value is assumed.**

**Explanation:** When calculating the frequency dispersion of the first hyperpolarizability, the user can specify the incremental value of frequency of incident light in eV as BetaFreqStep=X.XXXXX. If the value for X.XXXXX is less than or equal to 0.0, this message will appear. By default, the value for X.XXXXX is 0.2, namely the incremental value of frequency is 0.2 eV.

**Solution:** Check the value for BetaFreqStep=X.XXXXX.

**OptSet: CavityRadius not specified. Do not perform the SCRF calculation.**

**Explanation:** The SCRF calculation requires the cavity radius of the solute via CavityRadius=XXX.XXX in Å.

**Solution:** Specify the cavity radius of the solute using CavityRadius=XXX.XXX.

**OptSet: CavityRadius out of range. Do not perform the SCRF calculation.**

**Explanation:** If the value for CavityRadius=XXX.XXX is less than or equal to 0.0, this message will appear. This message means that an illegal cavity radius is specified; it should be larger than 0.0.

**Solution:** Check the value for CavityRadius=XXX.XXX.

**OptSet: CI state is singlet. Use singlet parameters for the INDO/S method.**



**Explanation:** When specifying `UseTripletParm` without the keyword `Triplet`, this message will appear. The user can use atomic parameters for triplet excited states with `UseTripletParm` in the INDO/S calculation.

**Solution:** When specifying `UseTripletParm`, the user should also specify `INDO/S` and `Triplet`.

**OptSet: DielectricConstant not specified. Do not perform the SCRF calculation.**

**Explanation:** The SCRF calculation requires the dielectric constant of the solvent via `DielectricConstant=X.XXX`.

**Solution:** Specify the dielectric constant of the solvent via `DielectricConstant=X.XXX`.

**OptSet: DielectricConstant out of range. Do not perform the SCRF calculation.**

**Explanation:** If the value for `DielectricConstant=X.XXX` is less than 1.0, this message will appear.

**Solution:** Check the value for `DielectricConstant=X.XXX`. Note that the results are the same as those in a vacuum if the value for `X.XXX` is 1.0.

**OptSet: ECharge out of range. Default value is assumed.**

**Explanation:** The keyword `ECharge=n` will prompt the program to calculate the charge density of excited states. If the value for `n` is smaller than -1, this warning message will appear. The default value depends on the keyword `NStates=n`. If `n=-1` is specified, the charge density of all the excited states will be computed. If `n` is positive, it will not be detected by the error trap in `OptSet`.

**Solution:** Check the value for `ECharge=n`.

**OptSet: GammaFreqStep out of range. Default value is assumed.**

**Explanation:** When calculating the frequency dispersion of the second hyperpolarizability, the user can specify the incremental value of frequency of incident light in eV as `GammaFreqStep=X.XXXXX`. If the value for `X.XXXXX` is less than or equal to 0.0, this message will appear. By default, the value for `X.XXXXX` is 0.2, namely the incremental value of frequency is 0.2 eV.

**Solution:** Check the value for `GammaFreqStep=X.XXXXX`.

**OptSet: K factor for new NM gamma out of range. Default value is assumed.**

**Explanation:** This message will appear if the value specified with the keyword `k-NM=XX.XXXX` for  $k$  in Nishimoto-Mataga formula is invalid. The allowed range of  $k$  in MOS-F V4.2D is as follows.

$$0.01 \leq k \leq 100$$

`k-NM=1.0` by default.

**Solution:** Check the value specified with the keyword `k-NM=XX.XXXX`.

**OptSet: Keyword UseCNDOParm is only available for the INDO/S method.**

**Solution:** When specifying `UseCNDOParm`, the user should also specify `INDO/S`.

**OptSet: Keyword UseTripletParm is only available for the INDO/S method.**

**Solution:** When specifying `UseTripletParm`, the user should also specify `INDO/S`.

**OptSet: MOCcoef out of range. Default value is assumed.**

**Explanation:** This message will be prompted if a value smaller than -1 for  $n$  is specified with the keyword `MOCcoef=n` for MO's listings in output. The default value is `MOCcoef=10`. When -1 is specified, all the MO will be listed in the output. If  $n$  is positive but larger than the actual number of MO's, it will be automatically changed to -1.

**Solution:** Check the value specified with the keyword `MOCcoef=n`.

**OptSet: MODens out of range. Default value is assumed.**

**Explanation:** If the value given for  $n$  in the keyword `MODens=n` used for electron density analysis by an orbital is smaller than -1, then this message will appear. The default value is 10. When -1 is specified, all the MO's electron density will be listed in the output. If  $n$  is positive but larger than the actual number of MO's, it will be automatically changed to -1.

**Solution:** Check the value specified with the keyword `MODens=n`.

**OptSet: NStates out of range. Default value is assumed.**

**Explanation:** This message will appear if the value given for  $n$  in the keyword `NStates= $n$`  used to include information on excited state such as transition energy and oscillator strength in output is 0 or smaller than -1. The default value is 10. When -1 is specified, the information on all the excited states will be listed in the output. If  $n$  is positive but larger than the number of CSF's, it will be automatically changed to -1.

**Solution:** Check the value specified with the keyword `NStates= $n$` .

**OptSet: Number of active occupied MOs out of range. Default value is assumed.**

**Explanation:** This message will result if the value given for  $m$  in the keyword `CI( $m$   $n$ )` used to specify MO's to be considered in CI calculation is smaller than -1. The default is  $m=10$ . If  $m=-1$ , all the occupied orbitals are considered. When the given value exceeds the maximum number of occupied orbitals defined by the system, a warning so indicating will be prompted and the system's maximum value is automatically assumed.

**Solution:** Check the values in the keyword `CI( $m$   $n$ )`.

**OptSet: Number of active occupied MOs out of range. Maximum value is assumed.**

**Explanation:** If the value given for  $m$  in the keyword `CI( $m$   $n$ )` used to specify the orbitals to be considered in a CI calculation exceeds the maximum defined by the system, this message will appear.

**Solution:** Check the values in the keyword `CI( $m$   $n$ )`.

**OptSet: Number of active virtual MOs out of range. Default value is assumed.**

**Explanation:** If the value given for  $n$  in the keyword `CI( $m$   $n$ )` used to specify the orbitals to be considered in a CI calculation is smaller than -1, this message will appear. The default is  $n=10$ . If  $n=-1$ , all the virtual orbitals are considered. When the given value exceeds the maximum number of virtual orbitals defined by the system, a warning so indicating will be prompted and the system's maximum value is automatically assumed.

**Solution:** Check the values in the keyword `CI( $m$   $n$ )`.

**OptSet: Number of active virtual MOs out of range. Maximum value is assumed.**

**Explanation:** If the value given for  $n$  in the keyword `CI( $m$   $n$ )` used to specify the orbitals to be considered in a CI calculation exceeds the maximum defined by the system, this message will appear.

**Solution:** Check the values in the keyword `CI( $m$   $n$ )`.

**OptSet: RefractiveIndex not specified. No SCRF correction for electron polarization performed.**

**Explanation:** The SCRF calculation with SCRF, SCRF=Onsager\_A, and SCRF=Onsager\_B requires the refractive index of the solvent via RefractiveIndex=X.XXX.

**Solution:** Specify the refractive index of the solvent via RefractiveIndex=X.XXX.

**OptSet: RefractiveIndex out of range. No SCRF correction for electron polarization performed.**

**Explanation:** If the value for RefractiveIndex=X.XXX is less than or equal to 0.0, this message will appear. In this case, RefractiveIndex=1.0 will be assumed.

**Solution:** Check the value for RefractiveIndex=X.XXX.

**OptSet: Right parenthesis insufficient ... near CI keyword.**

**Explanation:** Missing the closing parenthesis will prompt this message.

**Solution:** Check the parenthesis in the keyword CI(m n).

**OptSet: SCFCrt out of range. Default value is assumed.**

**Explanation:** If the value (floating point number) specified in the keyword SCFCrt=X.XXXXXXXXXX for SCF convergence threshold is not in the following range, this message will appear.

$$0.000000001 \leq \text{SCFCrt} \leq 0.01$$

By default, SCFCrt=0.00003(=3.0e-05).

**Solution:** Check the keyword SCFCrt=X.XXXXXXXXXX.

**OptSet: SCFCyc out of range. Default value is assumed.**

**Explanation:** If the value specified for n in the keyword SCFCyc=n for SCF iteration is not in the following range, this message will appear.

$$1 \leq n \leq 999$$

By default, SCFCyc=100.

**Solution:** Check the keyword SCFCyc=n.

**OptSet: Unrecognized keywords.**

**Explanation:** Keywords not recognized by the program are listed in the output. They are ignored.

**Solution:** Check all the keywords.

**OptSet: Weiss factor out of range. Default value is assumed.**

**Explanation:** The value for the Weiss factor  $f_r$  in Nishimoto-Mataga-Weiss formula specified by the keyword `Weiss=XX.XXXX` is invalid. The range of  $f_r$  in MOS-F V4.2D is as follows.

$$0.01 \leq f_r \leq 100$$

By default, `Weiss=1.2`.

**Solution:** Check `Weiss=XX.XXXX`.

**Orthog: Bond angle almost 180 deg.**

**Explanation:** Bond angles in Z-Matrix section must be smaller than 180 degrees. If not, the Schmidt orthogonalization scheme used to convert the Z-Matrix into Cartesian coordinates will not function properly.

**Solution:** Check the bond angles in the Z-Matrix section.

**PrHdr: Date ... don't work fine.**

**Explanation:** The date function has not functioned properly.

**Solution:** None, but the result will not be affected by this problem.

**PrHdr: Time ... don't work fine.**

**Explanation:** The time function has not functioned properly.

**Solution:** None, but the result will not be affected by this problem.

**PrHdr: UTSNam ... don't work fine.**

**Explanation:** The UTSNam function (uname function) has not functioned properly.

**Solution:** None, but the result will not be affected by this problem.

**RdDeck: Number of arguments .gt. 1. Assume the first argument as an input file.**

**Explanation:** When executing MOS-F V4.2D with the number of command-line arguments as the input file greater than 1, this message will appear.

**Solution:** Specify one command-line argument as the input file.

**RHFClo: Density converged but energy not the lowest. Delta E =X.XXXXX**

**Explanation:** In MOS-F V4.2D, judgment on SCF convergence is done on density matrix. Theoretically speaking, the minimum energy is attained upon convergence, but the energy may be higher by a minute amount due to numerical error.

**Solution:** Use the keyword SCFCrt=X.XXXXXXXXXX to change the criterion of SCF convergence.

**RHFClo: Shift .lt. Zero. Default value is assumed.**

**Explanation:** By shifting the energies of virtual orbitals, SCF convergence may be improved. If the shift is a downward one, some negative effect is likely. The default setting is Shift=0.5 (Hartree).

**Solution:** Check the keyword Shift=X.XXXXX.

**RdParm: Atomic parameters unchanged because of imperfect input data.**

**Explanation:** With Parm=Atom Or Parm=Type, some atomic parameter is invalid and left unchanged.

**Solution:** Check the input section for atomic parameters.

**RdParm: Blank card was detected.**

**Explanation:** The section for atomic parameters is blank.

**Solution:** Check the input section for atomic parameters.

**RdParm: EOF was detected.**

**Explanation:** End of File is detected in the atomic parameter section. The section is terminated by a blank line.

**Solution:** Check the input section for atomic parameters.

**Symm: Dummy routine now.**

**Explanation:** This message will appear if a string `Symm` is included in the keyword section.

**Solution:** Check all the keywords again.

**WinEP: Size of WinMOPAC file for CIS delta-density matrices exceeds 100 MB. Approximate size = XXXXXXXX.XX MB.**

**Explanation:** If the size of the difference density matrices between ground and excited states for the WinMOPAC file is greater than 100 MB, this warning message will appear.

**Solution:** If the disk space is sufficient for the approximate size, the user needs not to do anything. If not so, the user should decrease the number of output matrices using the keywords `ECharge=n` or `wms=CIDens`.

**WinEP: Size of WinMOPAC file for CIS delta-density matrices exceeds 100 MB. Number of output matrices reduced to XXXXX**

**Explanation:** If the size of the difference density matrices between ground and excited states for the WinMOPAC file is greater than 100 MB, this warning message will appear.

**Solution:** The following are possible.

- Decrease the number of output matrices using the keywords `ECharge=n` or `wms=CIDens`.
- Increase the size of the matrices for the WinMOPAC file using the keyword `wms=CIDens`.

**WinEP: Specified WinMOPAC file size is too small. Number of output CIS delta-density matrices reduced to XXXXX**

**Explanation:** When specifying `wms=CIDens=XX [KMG] (B)`, this warning message will be prompted if the specified size is smaller than the actual one.

**Solution:** The following are possible.

- Decrease the number of output matrices using the keywords `ECharge=n` or `wms=CIDens`.
- Increase the size of the matrices for the WinMOPAC file using the keyword `wms=CIDens`.

**ZAtm: Specified atomic identifier too long. Ignore extra characters.**

- Explanation:** Some strings may be added for particular atoms so that they are better distinguished when making a Z-matrix or input for atomic parameters. Such strings are called atom identifiers in this manual (see [page 20](#)). They must not exceed eight characters in size or else this warning message will be prompted.
- Solution:** Cut down to equal to or shorter than eight characters.

**ZVar: Specified variable too long. Ignore extra characters.**

- Explanation:** For Gaussian symbolic Z-matrix, string variables (called *Z-matrix variables* in the manual) starting with an alphabetical character may be used to represent bond lengths for example. If they exceed eight characters in size, this warning message will appear.
- Solution:** Cut down to equal to or shorter than eight characters.

## F.2 Errors

**AtPrms: Cannot calculate an atom.**

- Explanation:** MOS-F V4.2D cannot run on an isolated atom.
- Solution:** Do the calculation on a molecule.

**AtoF: XXXXXXXXXXXX ... Illegal string.**

- Explanation:** A function AtoF is for converting a string representing a floating point number into a genuine number recognized by the system. If it does not represent a real number, this error message will appear. The function AtoF is used to process data on molecular structure and atomic parameters.
- Solution:** Check the section for molecular structure and atomic parameters.

**Atol: XXXXXXXXXXXX ... Illegal string.**

- Explanation:** A function Atol is for converting a string representing an integer into a genuine number recognized by the system. If it does not represent an integer, this error message will appear. The function Atol is used to process data on molecular structure and atomic parameters.
- Solution:** Check the section for molecular structure and atomic parameters.

**BasInf: Atomic number .gt. 103.**



**Explanation:** An atom with the atomic number higher than 103 is not allowed in MOS-F V4.2D.

**Solution:** Run on atoms with the atomic number smaller than 103.

**BasInf: Cannot calculate a molecule with noble gas.**

**Explanation:** MOS-F V4.2D cannot run on a molecule with noble gas.

**Solution:** Do the calculation on a molecule without noble gas.

**BasInf: Cannot calculate an open-shell molecule.**

**Explanation:** Open shell calculation, namely as a system with an odd number of electrons, is not allowed in MOS-F V4.2D.

**Solution:** Check the section for the molecular structure or keyword `Charges=n`.

**BasInf: f function not supported.**

**Explanation:** An atom with an *f*-type orbital is not allowed in MOS-F V4.2D.

**Solution:** Run on a molecule with atoms with the atomic orbital up to the *d*-type.

**BasInf: Number of basis functions .gt. XXXX**

**Explanation:** The number of basis functions is greater than the maximum defined by the system.

**Solution:** Reduce the number of basis functions.

**CToZ: Too short atomic distance R21.**

**Explanation:** When converting the Cartesian coordinates into Z-matrix form, the distance between the atoms 1 and 2 is found to be too short. This error occurs for Cartesian coordinate input.

**Solution:** Check the Cartesian coordinate input section.

**CToZ: Too short atomic distance R31.**

**Explanation:** When converting the Cartesian coordinates into Z-matrix form, the distance between the atoms 1 and 3 is found to be too short. This error occurs for Cartesian coordinate input.

**Solution:** Check the Cartesian coordinate input section.

**CToZ: Too short atomic distance R32.**

**Explanation:** When converting the Cartesian coordinates into Z-matrix form, the distance between the atoms 2 and 3 is found to be too short. This error occurs for Cartesian coordinate input.

**Solution:** Check the Cartesian coordinate input section.

**CToZ: Too short atomic distance RmAB.**

**Explanation:** When converting the Cartesian coordinates into Z-matrix form, the distance between the atoms A and B is found to be too short. This error occurs for Cartesian coordinate input.

**Solution:** Check the Cartesian coordinate input section.

**ChkKey: Keyword is multi-defined.**

**Explanation:** The following case exemplifies the cause.

```
CI=Read CI(10 15)
```

In this case, the ambiguity is created by the fact that, (1) whether to read in the orbitals to be considered in the CI calculation (2) whether to take in 10 occupied and 15 virtual orbitals to be considered in CI calculation. It is trying to define two parameters for each of which a separate keyword is required.

**Solution:** Check the keyword once.

**DiagF1: Too many iterations in Invltr.**

**Explanation:** If the eigenvector does not converge within the iteration limit in the inverse iteration procedure, this error message appears.

**Solution:** None specifically given. Diag=QL may help.

**DiagF1: Too many iterations in QLRat.**

**Explanation:** If the eigenvalue does not converge within the iteration limit in the rational QL procedure, this error message appears.

**Solution:** None specifically given. Diag=QL may help.

**DiagF2: Too many iterations in QLiSft.**

**Explanation:** If the eigenvector or eigenvalue does not converge within the iteration limit in the QL diagonalization procedure, this error message appears.

**Solution:** None specifically given. `Diag=Inv` may help.

**GaussC: Number of data fields insufficient.**

**Explanation:** With the keyword `Coord=Cart`, four data fields per line are required (atomic number, x-coordinate, y-coordinate, z-coordinate). If there are only three or fewer data per line, this error message will appear.

**Solution:** Check the section for the molecular structure or all the keywords.

**GaussZ: Number of data fields insufficient.**

**Explanation:** With the keyword `Coord=Z`, if the number of data falls short of the required number, this error message will appear.

**Solution:** Check the section for the molecular structure or all the keywords.

**GetCnt: Illegal atomic name, XXXXXXXX**

**Explanation:** Some strings may be used to allow clear and easy distinction on particular atoms when making Z-matrix or input for atomic parameters. They may be called atom identifiers (see [page 20](#)). If some invalid data is specified in such strings, this error message appears.

**Solution:** Check the section for the molecular structure or atomic parameters.

**GetCnt: Specified center number out of range. iAtNum = XXXX**

**Explanation:** This error occurs if the serial number for atoms includes 0 or any other invalid number such as one larger than the total number of atoms.

**Solution:** Check the section for the molecular structure or atomic parameters.

**GetCnt: Unrecognized atomic identifier, XXXXXXXX**

**Explanation:** Some strings may be used to allow clear and easy distinction on particular atoms when making Z-matrix or input for atomic parameters. They may be called atom identifiers (see [page 20](#)). If it does not match with the one in the first field in the molecular structure input, this error message appears.

**Solution:** Check the section for the molecular structure or atomic parameters.

**GetIAN: Illegal atomic name, XXXXXXXX**

**Explanation:** Some strings may be used to allow clear and easy distinction on particular atoms when making Z-matrix or input for atomic parameters. They may be called atom identifiers (see [page 20](#)). If some invalid data is specified in such strings, this error message appears.

**Solution:** Check the section for the molecular structure or atomic parameters.

**GetIAN: Specified atomic number out of range. iAtNum = XXXX**

**Explanation:** This error message is caused by specifying a number other than in the range from 1 to 99 for the atomic number.

**Solution:** Check the atomic number.

**GetIAN: Unrecognized atomic name, XXXXXXXX**

**Explanation:** Some strings may be used to allow clear and easy distinction on particular atoms when making Z-matrix or input for atomic parameters. They may be called atom identifiers (see [page 20](#)). If some invalid data is specified in such strings, this error message appears.

**Solution:** Check the section for the molecular structure or atomic parameters.

**GetMem: Failed in the allocation.**

**Explanation:** MOS-F V4.2D dynamically allocates the appropriate amount of memory space taking account of the molecule's size and number of orbitals to be considered in the CI calculation. If the required size exceeds the amount available in the system, allocation fails.

**Solution:** The followings are possible.

- Reduce the size of the molecule.
- Cut down on the number of orbitals to be used in the CI calculation.
- Add more memory.

**GetPrm: Unrecognized keyword, XXXX**

**Explanation:** When specifying atomic parameters with the keyword `Prm=Atom` or `Prm=Type`, this error message will be prompted if an invalid keyword is used.

**Solution:** Check the section for the atomic parameters.

**GetVal: Value out of range.**

**Explanation:** When specifying values for keyword arguments, if they exceed 9 figures above and 17 figures below the decimal point, this error message will appear.

**Solution:** Check the keyword again.

**GetZ: Blank card was detected.**

**Explanation:** This error message is caused by leaving equal to or more than two blank lines between Z-matrix and Z-matrix data section.

**Solution:** They must be separated by only one blank line.

**GetZ: EOF was detected.**

**Explanation:** This error message will appear when End of File is detected when reading in the data for the Z-matrix (called *Z-matrix variables* in the manual). The data section for the Z-matrix variables must be terminated by one blank line.

**Solution:** Check if there is a blank line at the end of the Z-matrix variable section.

**GetZ: Number of data fields insufficient.**

**Explanation:** The format for the Z-matrix requires at least the Z-matrix variable and its value which must be separated with a comma, a space or an equal sign.

**Solution:** Check the input section for Z-matrix variables.

**GetZ: Variable insufficient.**

**Explanation:** This error message will appear if there is a variable with no corresponding value in Z-matrix.

**Solution:** Check the input section for Z-matrix variables or the Z-matrix itself.

**IRead: Card contains too large integer value.**

**Explanation:** This error message will appear if a number greater than  $(2^{31} - 1)/10$  is specified when giving the serial number for MO's with the keyword CI=Read.

**Solution:** Check the option section with CI=Read.

**IRead: No data block.**

**Explanation:** This message will appear if there is no integer is given for the serial number for MO's with the keyword CI=Read.

**Solution:** Check the option section with CI=Read.

**IRead: Non-integer type.**

**Explanation:** This message will appear if a string corresponding to a non-integer is given for the serial number for MO's with the keyword CI=Read.

**Solution:** Check the option section with CI=Read.

**IRead: Number of data exceeds maximum size. MDim = XXXXX**

**Explanation:** This message will appear if a number exceeding the maximum defined by the system is given for the serial number for MO's with the keyword CI=Read.

**Solution:** Reduce the number of MO's to be considered in the CI calculation.

**MOInfo: CIS calculation cancelled because nCSFs .lt. 1.**

**Explanation:** The number of CIS configuration state functions is less than 1 and CIS calculation cannot be performed.

**Solution:** Specify the range of MO's so as to increase the number of CSF's equal to or greater than 1.

**MOInfo: No occupied MO specified.**

**Explanation:** When specifying the MO's to be used for CI calculation with the keyword CI=Read, not even a single occupied orbital has been given.

**Solution:** Check the option data entry for CI=Read.

**MOInfo: No virtual MO specified.**

**Explanation:** When specifying the MO's to be used for CI calculation with the keyword CI=Read, not even a single virtual orbital has been given.

**Solution:** Check the option data entry for CI=Read.

**MOInfo: Too many occupied MOs. Maximum size = XXX**

**Explanation:** When specifying the MO's to be used for CI calculation with the keyword CI=Read, the number of occupied orbitals exceeded the maximum defined by the system XXXX has been given.

**Solution:** Check the option data entry for CI=Read.

**MOInfo: Too many virtual MOs. Maximum size = XXX**

**Explanation:** When specifying the MO's to be used for CI calculation with the keyword CI=Read, the number of virtual orbitals exceeded the maximum defined by the system XXXX has been given.

**Solution:** Check the option data entry for CI=Read.

**MopacC: Number of data fields insufficient.**

**Explanation:** With the keyword Coord=MCart, seven data entries are required per line (atomic number, x-coordinate, dummy data, y-coordinate, dummy data, z-coordinate, dummy data). This error will appear if there are only six or less data entries per line.

**Solution:** Check the molecular structure or keyword input section.

**MopacZ: Number of data fields insufficient.**

**Explanation:** With a molecular structure input in MOPAC internal coordinate format, this error message will be prompted if there are not enough data entries.

**Solution:** Check the molecular structure or keyword input section.

**OptSet: Bad operand for wms=CIDens.**

**Explanation:** When the operand of wms=CIDens is not specified properly, this message will result.

**Solution:** Check the keyword wms=CIDens again.

**OptSet: CavityRadius is not properly specified.**

**Explanation:** When the operand of `CavityRadius` is not specified properly, this message will result.

**Solution:** Check the keyword `CavityRadius` again.

**OptSet: Illegal character was found ... near CI keyword.**

**Explanation:** An invalid character has been found near the `CI(m n)` keyword.

**Solution:** Check the vicinity of `CI(m n)`.

**OptSet: Invalid window definition for wms=CIDens(m n).**

**Explanation:** If `m` or `n` for `wms=CIDens(m n)` is invalid, this message will result. The value for `m` must be less than or equal to that for `n` and both values must be positive.

**Solution:** Check the keyword `wms=CIDens(m n)` again.

**OptSet: Operand for wms=CIDens is too long.**

**Explanation:** When specifying `wms=CIDens`, this error message will be prompted if an operand with more than 32 characters is used.

**Solution:** Check the keyword `wms=CIDens` again.

**OptSet: Right parenthesis insufficient for wms=CIDens.**

**Explanation:** Missing the closing parenthesis for `wms=CIDens(m n)` will prompt this message.

**Solution:** Check the keyword `wms=CIDens(m n)` again.

**OptSet: Size of CIDens out of range.**

**Explanation:** When specifying the keyword `wms=CIDens=XX [KMG] (B)` with a value for `XX` less than or equal to 0.0, this message will appear.

**Solution:** Check the keyword `wms=CIDens=XX [KMG] (B)` again.



**OptSet: Solvent name is not specified.**

**Explanation:** When specifying the keyword `Solvent` with no operand, this message will result.

**Solution:** Check the keyword `Solvent=XXXXXX` and [Table D.1](#) again.

**OptSet: Specified CavityRadius is too long.**

**Explanation:** When specifying `CavityRadius`, this error message will be prompted if an operand with more than 32 characters is used.

**Solution:** Check the keyword `CavityRadius` again.

**OptSet: Specified m or n for `wms=CIDens(m n)` is not an integer.**

**Explanation:** When the specified type of `m` or `n` for `wms=CIDens(m n)` is not an integer, this message will result.

**Solution:** Check the keyword `wms=CIDens(m n)` again.

**OptSet: Specified solvent name is too long.**

**Explanation:** When specifying a solvent with the keyword `Solvent=XXXXXX`, this error message will be prompted if a solvent name with more than 32 characters is used.

**Solution:** Check the keyword `Solvent=XXXXXX` and [Table D.1](#) again.

**OptSet: XXXXXXXX ... Undefined method for CavityRadius.**

**Explanation:** When specifying `CavityRadius` with an undefined operand in the program, this message will result.

**Solution:** Check the operand of `CavityRadius` again.

**OptSet: XXXXXX ... Unknown solvent name is specified.**

**Explanation:** When specifying a solvent with the keyword `Solvent=XXXXXX`, this error message will be prompted if a program-undefined solvent name is used.

**Solution:** Check the keyword `Solvent=XXXXXX` and [Table D.1](#) again.

**Orthog: Bond angle 180 deg.**

**Explanation:** With Z-matrix, bond angles must be less than 180 degrees. If not, the Schmidt orthogonalization procedure will not function properly when converting into the Cartesian coordinate form from Z-matrix form.

**Solution:** Check all the bond angles in Z-matrix.

**Overlap: Too short distance, Atoms XXXXX and YYYYY ... R = Z.ZZZZZZZZZZZZ Angstroms**

**Explanation:** This error message will appear if there is an internuclear distance shorter than 0.3 Å.

**Solution:** Check the input data for the molecular structure or use the optimized structure generated by MOPAC in which case this error is very unlikely.

**PrmChk: Atomic parameters XXXX for center number YYYY are insufficient. Check atomic parameters in the outlist.**

**Explanation:** This error will occur if there is an atom with a center number YYYY for which the parameters XXXX are insufficient in the molecule. See [Appendix H](#) for XXXX.

**Solution:** The following measures are possible.

- Eliminate atoms for which atomic parameters are undefined.
- Give the atomic parameters with the keyword `Parm=Type` or `Parm=Type`.

Another method is specifying the keyword `NoCheckParm` (except the van der Waals radii of the constituent atoms which are used in molar volume calculation). However, only an expert in semiempirical MO calculation should use this method.

**RCoord: EOF was detected.**

**Explanation:** In the molecular structure section, End of File has been detected. Molecular structure input section is terminated by a blank line.

**Solution:** Check whether there is a blank line at the end of the molecular structure input section.

**RCoord: Number of atoms .gt. XXXX**

**Explanation:** The number of atoms including the dummies has exceeded the maximum allowed by the system.

**Solution:** Cut down on the number of atoms for the calculation.

**RCoord: Number of atoms .lt. 2.**

**Explanation:** The number of atoms is less than two. MOS-F V4.2D cannot run calculation on an atom.

**Solution:** Run a calculation on a molecule.

**RdDeck: File XXXXXX not found.**

**Explanation:** If the specified file name does not exist, this message will appear.

**Solution:** Check the input file name.

**RdDeck: File name XXXXXX invalid.**

**Explanation:** There are several file names that MOS-F V4.2D can not handle as an input file. For example, MOS-F V4.2D can not handle a file name with a length greater than 255 bytes. Please refer to [Section 2.1.1](#) for details of the input file names that MOS-F V4.2D can not handle.

**Solution:** Check the input file name.

**RdDeck: Too many input lines. System maximum = XXXXX**

**Explanation:** MOS-F V4.2D can handle an input file within 5120 lines.

**Solution:** Decrease the number of lines in the input file.

**RHFCl0: Density not converged.**

**Explanation:** SCF convergence not achieved within the iteration limit.

**Solution:** The following measures are possible.

- Increase the maximum number of iterations with the keyword SCFCyc=n.

- Increase the shift on the virtual orbital energies with the keyword `Shift=X.XXXXX`.
- Loosen the convergence criterion with the keyword `SCFCrt=X.XXXXXXXXXX`.
- Use the optimized molecular geometry such as the one generated by MOPAC.
- Use different formula to evaluate electron repulsion integrals.
- If the modified version of Nishimoto-Mataga formula is in use, alter the value for  $k$  with the keyword `k-NM=XX.XXXX`.

**RdOpt: No card to read.**

**Explanation:** This error will be prompted if the first line in the input is blank or End of File is encountered. Specify at least one keyword in the first line.

**Solution:** Make sure that the first line in the input is not blank or End of File.

**RdOpt: Too many option cards. MaxCrd = XX**

**Explanation:** The number of lines in the keyword input section has exceeded the maximum allowed by the system.

**Solution:** Put in fewer lines in the keyword input.

**RdParm: Dummy atom specified.**

**Explanation:** Changing the parameters for the dummy atoms has no meaning, and it is possibly intended for another atom.

**Solution:** Check the input for the atomic parameters.

**RdParm: No atom in molecule.**

**Explanation:** When changing the atomic parameters, the corresponding atom is not in the molecule.

**Solution:** Check the input for the atomic parameters.

**RdParm: Number of data fields insufficient.**

**Explanation:** There are not enough data entries in the atomic parameter input.

**Solution:** Check the input for the atomic parameters.

**RdParm: Specified atomic number out of range. iAtNum = XXXX**

**Explanation:** This error message will appear if the atomic number does not fall in the range from 1 to 99 when giving the atomic parameters.

**Solution:** Check the data entries on the atomic numbers in the atomic parameter input.

**RdTitl: No title card.**

**Explanation:** This message will be shown if the title section has been left blank or End of File is encountered.

**Solution:** Check the title section.

**RdTitl: Too many title cards. MaxCrd = XXX**

**Explanation:** The number of lines in the title input has exceeded the maximum allowed by the system.

**Solution:** Reduce the number of lines.

**vdWVol: van der Waals radius not defined. Atomic number = XXX**

**Explanation:** When calculating the molar volume using the van der Waals radii of the constituent atoms, this error message will be prompted if there is an atom with an undefined radius.

**Solution:** Add the radius using the keyword Parm=Type.

**XGausJ: Specified alpha and beta illegal.**

**Explanation:** With 1 or -1 specified for the Gaussian  $j$ -value, this error message will appear if the first bond angle  $\alpha$  and second bond angle  $\beta$  are not in the following range.

$$0^\circ < \alpha < 180^\circ \qquad 0^\circ < \beta < 180^\circ$$

Refer to [Figure 3.6](#) on  $\alpha$  and  $\beta$  with the Gaussian  $j$ -value.

**Solution:** Check the molecular structure input and keywords.

**ZSyml: The same variable name is used in length and angle.**

**Explanation:** The same name is given to Z-matrix variables for a bond length and angle.

**Solution:** Use different names for length and angle.

**ZVal: Variables are multi-defined.**

**Explanation:** The values for Z-matrix variables are repeated.

**Solution:** Check Z-matrix variable section.

**ZtoC: Gaussian J value illegal. J = XX**

**Explanation:** This error will be prompted if a value other than -1, 0 or 1 is specified for the Gaussian  $j$ -value with keyword `Coord=Z`.

**Solution:** Check the Z-matrix and keywords.

**ZtoC: Specified Z-matrix illegal. Center number = XXXX**

**Explanation:** A definition in the Z-matrix for the serial number on atoms is invalid.

**Solution:** Check the data entry for the atom with a serial number XXXX.

**ZtoC: Specified bond angle illegal. Center number = XXXX**

**Explanation:** This error message will appear if the value of a bond angle  $\alpha$  in Z-matrix does not fall in the range shown below.

$$0^\circ < \alpha < 180^\circ$$

**Solution:** Check the bond angle on the atom with a serial number XXXX.

**ZtoC: Specified bond angle-2 illegal. Center number = XXXX**

**Explanation:** With 1 or -1 specified for the Gaussian  $j$ -value, if the second bond angle  $\beta$  does not fall in the following range, this error will be prompted.

$$0^\circ < \beta < 180^\circ$$

**Solution:** Check the value of the second bond angle on the atom with a serial number XXXX.

**ZtoC: Specified bond length illegal. Center number = XXXX**

**Explanation:** This error message will appear if the bond length is shorter than  $1 \times 10^{-8}$  Å.

**Solution:** Check the data given for the atom with a serial number XXXX.

**ZtoC: Specified dihedral angle illegal. Center number = XXXX**

**Explanation:** If a dihedral angle  $\beta$  does not fall in the following range, this error message will result.

$$-360^\circ \leq \beta \leq 360^\circ$$

**Solution:** Check the dihedral angle on the atom with a serial number XXXX.

**ZtoC: Specified na illegal. Center number = XXXX**

**Explanation:** If the atom with a serial number XXXX used to fix the bond angle is invalid, this message will appear.

**Solution:** Check the input data on the atom with a serial number XXXX.

**ZtoC: Specified na, nb illegal. Center number = XXXX**

**Explanation:** If the atom with a serial number XXXX used to fix the bond length and bond angle is invalid, this message will appear.

**Solution:** Check the input data on the atom with a serial number XXXX.

**ZtoC: Specified na, nb, nc illegal. Center number = XXXX**

**Explanation:** If the atom with a serial number XXXX used to fix the bond length, bond angle and dihedral angle is invalid, this message will appear.

**Solution:** Check the input data on the atom with a serial number XXXX.





# Appendix G

## List of Available Keywords

### G.1 Purpose-Related List

#### G.1.1 Model Hamiltonians

- `CNDO/2` Use CNDO/2 by Pople *et al.*
  - `CNDO/S` Use CNDO/S by Jaffé *et al.*
  - `CNDO/S2` Use CNDO/S2 by Lipari and Duke.
  - `CNDO/S3` Use CNDO/S3 by Lipari and Duke.
  - `INDO/S` Use INDO/S by Zerner *et al.*
- Default Use CNDO/S

The exponent used for the *sp*<sup>3</sup>-hybrid is not the same as the one used for the *sp*<sup>2</sup> or *sp*-hybrids in CNDO/S3. When using CNDO/S3, check the values of Slater exponents by using the keyword `ParmOut=Atom`. The values for Slater exponents can be modified with the keyword `Parm=Atom`.

#### G.1.2 Molecular Charge

- `Charge=n` The molecule has a charge *n*.
  - `Charges=n` AS Charge=*n*.
- Default *n* = 0 (neutral molecule)

#### G.1.3 Molecular Specification

For more details, refer to [Section 3.4](#).

Note: Molecular geometry for WinMOPAC V3 can be prepared only in the MOPAC compatible formats (`Coord=Inter` and `Coord=MCart`). The Z-matrix used in Gaussian (`Coord=Z`) and the standard Cartesian coordinates (`Coord=Cart`) are not available at present. These formats are available for running MOS-F V4.2D independently.

- `Coord=Inter` Use MOPAC internal coordinate compatible format.
- `Coord=Z` Use Gaussian symbolic Z-matrix compatible format.

- `Coord=MCart` Cartesian coordinate input from MOPAC data or equivalent.
  - `Coord=Cart` Standard Cartesian coordinate input.
- Default      `Coord=Inter`

### G.1.4 Molecular Orientation

This keyword is effective only when the input is based on internal coordinate (Z-matrix) and will be ignored for Cartesian coordinate input.

- `Plane=X-Y` Place the second atom on positive x-axis, third on x-y plane.
  - `Plane=Z-X` Place the second atom on positive z-axis, third on z-x plane.
  - `Plane=Z-Y` Place the second atom on positive z-axis, third on z-y plane.
- Default      `Plane=X-Y`

### G.1.5 Atomic Parameters Input and Modification

See [Section 3.5.1](#) for more details on atomic parameter input. For the default values, refer to [Appendix A](#).

- `Parm=Type` Input by atom type.
  - `Parm=Atom` Input for a particular atom. For assigning different values for the same type of atoms in a molecule.
- Default      Use the program-defined values.

### G.1.6 Resonance Integral for Oxygen in CNDO/S

- `OldOxygenBeta` Use the old value for the resonance integral ( $-45.0$  eV).<sup>13</sup>
- Default       $-30.0$  eV<sup>16</sup>

### G.1.7 Specification of atomic parameters in INDO/S

#### Use of CNDO Parameters in the INDO/S Calculation

- `UseCNDOParam` Use atomic parameters for CNDO/S and CNDO/S2 which are absent in INDO/S in MOS-F V4.2D. These parameters are available for F and S.
- Default      Do not use the parameters for CNDO.

#### Parameters for Triplet Excited States

- `UseTripletParam` Use atomic parameters for triplet excited states in the INDO/S calculation. These parameters are available for H, C, N, and O.
- Default      Use parameters for a singlet.

### G.1.8 Keywords for *d*-Orbitals

#### Second Row Atoms

- Don2     Add *d*-type orbital on the second row atoms.  
     Default     Do not add *d*-type orbital.

#### Third Row Atoms

- Don3     Add *d*-type orbital on the third row atoms.  
     Default     Do not add *d*-type orbital.

### G.1.9 Scale Factor for Overlap Integrals in Local Coordinates

#### *pσ*-Type Overlap

- FS=X.XXXXX     Scale factor for *pσ*-type overlap.
- P-Sigma=X.XXXXX     As FS=X.XXXXX.
- Default     INDO/S: FS=1.267, Others: FS=1.0

#### *pπ*-Type Overlap

- FP=X.XXXXX     Scale factor for *pπ*-type overlap.
- P-Pi=X.XXXXX     As FP=X.XXXXX.
- Default     INDO/S, CNDO/S: FP=0.585, Others: FP=1.0

#### *dσ*-Type Overlap

- D-Sigma=X.XXXXX     Scale factor for *dσ*-type overlap. Only effective with INDO/S.
- Default     D-Sigma=1.0

#### *dπ*-Type Overlap

- D-Pi=X.XXXXX     Scale factor for *dπ*-type overlap. Only effective with INDO/S.
- Default     D-Pi=1.0

#### *dδ*-Type Overlap

- D-Delta=X.XXXXX     Scale factor for *dδ*-type overlap. Only effective with INDO/S.
- Default     D-Delta=1.0

#### Overlap Integrals Involving *d*-Type Orbitals

- FD=X.XXXXX     Scale factor for overlap integrals involving *d*-type orbital.
- Default     CNDO/S: FD=0.3, Others: FD=1.0

### G.1.10 Checking of atomic parameters

- `CheckParm`      Check whether the atomic parameters are sufficient or not.  
If one of the parameters required in the calculation is zero, MOS-F V4.2D invokes the error message and the process is terminated.
  - `NoCheckParm`    Do not check whether the atomic parameters are sufficient or not.  
MOS-F V4.2D invokes the warning message by specifying this keyword.
- Default            `CheckParm`

### G.1.11 Evaluation of Two-Center Electron Repulsion Integrals

- `G=A`            Use analytical formula for *s*-type orbital (Roothaan formula).
  - `G=PP`           Use Pariser-Parr formula.
  - `G=NM`           Use Nishimoto-Mataga formula. When using its modified version, specify the *k*-value with the keyword `k-NM`.
  - `G=NMW`        Use Nishimoto-Mataga-Weiss formula. This keyword permits `k-NM` to be specified simultaneously.
  - `G=O`            Use Ohno formula.
  - `G=OK`          Use Ohno-Klopman formula.
  - `G=DH`          Use DasGupta-Huzinaga formula.
- Default    CNDO/2: `G=A`  
           CNDO/S + singlet-CI: `G=NM`  
           CNDO/S + triplet-CI: `G=PP`  
           CNDO/S2 and CNDO/S3: `G=NM`  
           INDO/S + singlet-CI: `G=NMW`  
           INDO/S + triplet-CI: `G=PP`

### G.1.12 *k*-value for Nishimoto-Mataga Formula

- `k-NM=XX.XXXX`    *k*-value for the modified version of Nishimoto-Mataga formula.
- Default            `k-NM=1.0` (as for the conventional formula)

### G.1.13 Weiss Factor $f_r$ for Nishimoto-Mataga-Weiss Formula

- `Weiss=XX.XXXX`    Weiss factor  $f_r$  for Nishimoto-Mataga-Weiss formula.
- Default            `Weiss=1.2`

### G.1.14 SCF Calculation

#### Maximum Number of Iterations

- `SCFCyc=n`      The maximum number of iterations for SCF calculation ( $1 \leq n \leq 999$ ).
- Default            `SCFCyc=100`

**Convergence Criterion**

- SCFCrt=X.XXXXXXXXXX Criterion of SCF Convergence on density matrix, range from  $10^{-2}$  to  $10^{-9}$ .  
Default SCFCrt=0.00003 (3.0d-05)

**Level Shifting**

- Shift=X.XXXXXXXXXX Level-shift method is applied to the SCF calculation with the given amount of shift (unit: Hartree).
- Shift As Shift=0.5.
- NoShift No level-shift applied.
- Default Level-shift applied with Shift=0.5 only when an energy increase is observed during the SCF calculation.

**Extrapolation of a Density Matrix**

- SCF=NoExtrap Do not extrapolate the density matrix in the SCF calculation.
- Default Perform the 3-point or 4-point extrapolation on an appropriate condition during the SCF calculation.

**G.1.15 Solvation Model****SCRF Calculation**

- SCRF Perform the SCRF calculation using the Onsager model and correct the transition energies using the model B proposed by Zerner.<sup>32</sup>
- SCRF=Onsager Perform the SCRF calculation using the Onsager model and add neither solvent cost terms nor electron relaxation terms to the transition energies.<sup>32</sup>
- SCRF=Onsager\_A Perform the SCRF calculation using the Onsager model and correct the transition energies using the model A proposed by Zerner.<sup>32</sup>
- SCRF=Onsager\_B As SCRF.
- SCRF=Onsager\_B1 Perform the SCRF calculation using the Onsager model and correct the transition energies using the model B1 proposed by Zerner.<sup>32</sup>
- Default Do not perform the SCRF calculation.

**Cavity Radius of Solute**

- CavityRadius=XXX.XXX Specifies the cavity radius of the solute in Å.
- CavityRadius=vdW Compute the cavity radius of the solute using its approximate molar volume obtained from the van der Waals radii of the constituent atoms.  
In this method, the cavity radius of the solute,  $a_0$ , is expressed as the following:

$$a_0 = \left( \frac{3V}{4\pi} \right)^{\frac{1}{3}}.$$

- `CavityRadius=vdW+0.5` Add the empirical value 0.5 Å to the value obtained from the keyword `CavityRadius=vdW` to account for the nearest approach of solvent molecules.<sup>64</sup>

In this method, the cavity radius of the solute,  $a_0$ , is expressed as the following:

$$a_0 = \left( \frac{3V}{4\pi} \right)^{\frac{1}{3}} + 0.5.$$

- `CavityRadius=vdW_cube` Compute the cavity radius of the solute using its approximate molar volume with the cube shape obtained from the van der Waals radii of the constituent atoms.<sup>32</sup>

In this method, the cavity radius of the solute,  $a_0$ , is expressed as the following:

$$a_0 = \frac{1}{2}V^{\frac{1}{3}}.$$

Default

`CavityRadius=vdW+0.5`

### Specification of Solvent

- `Solvent=XXXXXX` Specifies the solvent name to use the program-defined dielectric constant and refractive index of the solvent.

Please refer to [Table D.1](#) in Appendix D for the information on program-defined solvents.

Solvent is specified with its name or alias listed in [Table D.1](#)

Example:

```
Solvent=Water
```

```
Solvent=H2O
```

```
Solvent=DMF
```

```
Solvent=Benzene
```

Substitute commas “,” with periods “.” when specifying the solvent name including commas.

Example:

```
Solvent=1,2-Dichlorobenzene ... bad!
```

```
Solvent=1.2-Dichlorobenzene ... good!
```

### Dielectric Constant of Solvent

- `DielectricConstant=X.XXX` Specifies the dielectric constant of the solvent.

Default

`DielectricConstant=1.0` when not specifying the keyword `Solvent=XXXXXX`. This implies no SCRF calculation is performed.

This keyword has priority over `Solvent=XXXXXX` when specifying both.

**Refractive Index of Solvent**

- `RefractiveIndex=X.XXX` Specifies the refractive index of the solvent.

Default                      `RefractiveIndex=1.0`

This keyword has priority over `Solvent=XXXXXX` when specifying both.

Note that the keywords `SCRF`, `SCRF=Onsager_A`, `SCRF=Onsager_B`, and `SCRF=Onsager_B1` need to specify the following keywords when not specifying `Solvent=XXXXXX`:

- `DielectricConstant=X.XXX`
- `RefractiveIndex=X.XXX`

`SCRF=Onsager` needs to specify the following keywords:

- `DielectricConstant=X.XXX`

**G.1.16 CI Singles Calculation****CI Calculation**

- `CI(m n)` All possible singly excited CSF's formed from the  $m$ -highest occupied and the  $n$ -lowest virtual MO's are used in the CIS calculation. Thus the number of singly excited CSF's is  $m \times n$ .
  - `CI` As `CI(10 10)`.
  - `CI=All` All the orbitals obtained from SCF calculation are taken into the CIS calculation. The amount of memory required for CIS calculation is proportional to the quadruple of the number of orbitals involved and a care must be exercised on the molecular size when using this keyword.
  - `CI=Read` The serial numbers of the orbitals to be taken into CI calculation can be given. See [Section 3.5.2](#) for more details.
  - `NoCI` No CI calculation is performed. When used,  $\alpha$ ,  $\beta$  and  $\gamma$  are not calculated.
- Default      `CI`

**Spin Multiplicity in CIS Calculation**

- `Singlet` Do singlet CIS calculation.
  - `Triplet` Do triplet CIS calculation.
- Default      `Singlet`

**G.1.17 Dipole Integral and Transition Moment**

- `Dipole=ZDO` ZDO approximation  $\langle \chi_\mu | r | \chi_\nu \rangle = \delta_{\mu\nu} \langle \chi_\mu | r | \chi_\mu \rangle$  is used for evaluating one-center dipole integrals.
- Default              One-center dipole integrals are evaluated analytically.

### G.1.18 Polarizability $\alpha$

#### Polarizability $\alpha$

- Alpha                      Calculates the static polarizability.
- AlphaStatic              As Alpha.
- AlphaDynamic            Calculates the frequency dispersion of  $\alpha$ .
- AlphaDispersion        As AlphaDynamic.
- Default                    No  $\alpha$  calculated.

#### Incremental Value of Frequency

- AlphaFreqStep=X.XXXXX Specifies incremental value of frequency for frequency dispersion of  $\alpha$  in eV.
- Default                    AlphaFreqStep=0.2

### G.1.19 First Hyperpolarizability $\beta$

#### Static $\beta$

- Beta                      Calculates static  $\beta$ .
- BetaStatic              As Beta.
- Default                     $\beta$  not calculated.

#### $\beta$ for EOPE

- BetaEOPE                Calculates  $\beta$  for Electro-Optic Pockels Effect (EOPE) (Incident light: He-Ne laser).
- BetaEO                    As BetaEOPE.
- BetaDispersionEOPE    Calculates the frequency dispersion of  $\beta$  for EOPE.
- BetaDispersionEO        As BetaDispersionEOPE.
- Default                    Not calculated.

#### $\beta$ for SHG

- BetaSHG                 Calculates  $\beta$  for Second Harmonic Generation (SHG) (Incident light: YAG laser).
- BetaDispersionSHG     Requests the frequency dispersion of  $\beta$  for SHG.
- Default                    Not calculated.

#### $\beta$ for OR

- BetaOR                    Requests  $\beta$  for Optical Rectification (OR) (Incident light: He-Ne laser).
- BetaDispersionOR       Requests the frequency dispersion of  $\beta$  for OR.
- Default                    Not calculated.



**Tensor Elements of  $\beta$** 

- **MinorBetaTensor** All elements are computed.
- Default** Calculates the following.  
XXX, YYY, ZZZ, YYX, YXY, XYY, ZZX, ZXZ, XZZ, XXY, XYX, YXX, ZZY, ZYZ, YZZ, XXZ, XZX, ZXX, YYZ, YZY.

**Incremental Value of Frequency**

- **BetaFreqStep=X.XXXXX** Specifies incremental value of frequency for frequency dispersion of  $\beta$  in eV.
- Default** BetaFreqStep=0.2

**G.1.20 Second Hyperpolarizability  $\gamma$** **Static  $\gamma$** 

- **Gamma** Requests static  $\gamma$ .
- **GammaStatic** AS Gamma.
- Default** Not calculated.

 **$\gamma$  for EFIKE**

- **GammaKerr** Requests  $\gamma$  for DC-electric field Kerr induced effect (EFIKE) (Incident light : He-Ne laser).
- **GammaDispersionKerr** Computes the frequency dispersion of  $\gamma$  for EFIKE.
- Default** Not calculated.

 **$\gamma$  for DC-SHG**

- **GammaDCSHG** Computes  $\gamma$  for DC-electric field induced second harmonic (DC-SHG) (Incident light : YAG laser).
- **GammaDispersionDCSHG** Computes the frequency dispersion of  $\gamma$  for DC-SHG.
- Default** Not calculated.

 **$\gamma$  for THG**

- **GammaTHG** Computes  $\gamma$  for third harmonic generation (THG) (Incident light: 1907 nm).
- **GammaDispersionTHG** Requests the frequency dispersion of  $\gamma$  for THG.
- Default** Not calculated.

 **$\gamma$  for DFWM**

- **GammaDFWM** Computes  $\gamma$  for degenerate four-Wave mixing (DFWM) (Incident light: He-Ne laser).
- **GammaDispersionDFWM** Requests the frequency dispersion on  $\gamma$  for DFWM.
- Default** Not calculated.

**$\gamma$  for DC-OR**

- **GammaDCOR**                      Computes  $\gamma$  for DC-electric field induced rectification (DC-OR) (Incident light : He-Ne laser).
- **GammaDispersionDCOR**      Requests the frequency dispersion on  $\gamma$  for DC-OR.
- Default**                              Not calculated.

**Tensor elements of  $\gamma$** 

- **MinorGammaTensor**      Requests that all elements are computed.
- Default**                              The following components are computed.  
XXXX, YYYY, ZZZZ, XXYY, XYXY, XYYX, XXZZ, XZXZ, XZZX, YYXX, YXYX, YXXY, YYZZ, YZYZ, YZZY, ZZXX, ZXZX, ZXXZ, ZZYY, ZYZY, ZYYZ.

**Incremental Value of Frequency**

- **GammaFreqStep=X.XXXXX**      Specifies incremental value of frequency for frequency dispersion of  $\gamma$  in eV.
- Default**                              GammaFreqStep=0.2

**G.1.21 WinMOPAC File**

- **WinMOPAC**      An output file for WinMOPAC V3 (.wms file) is generated.
- Default**      Do not generate.

**G.1.22 Output Control for WinMOPAC File**

This keyword is related to the output control of the difference density matrices between ground and excited states for the WinMOPAC file. The following keywords are available when the keyword ECharge is specified.

- **wms=CIDens(m n)**                      Output the matrices from the m-th excited state to the n-th one.  
If the size of the matrices is greater than 100 MB, output the approximate size as a warning message.
- **wms=CIDens=ECharge**                      Output the matrices with their number specified by the keyword ECharge.  
If the size of the matrices is greater than 100 MB, output the approximate size as a warning message.
- **wms=CIDens=XX [KMG] (B)**                      Output the matrices of the specified size.  
If the actual size of matrices is greater than user-specified size, reduce the number of the output matrices. Then output the actual number of the matrices output as a warning message.

Example:

```
wms=CIDens=2048KB
wms=CIDens=20.5M
wms=CIDens=1.3GB
wms=CIDens=0.5G
```

- `wms=NoCIDens` Do not output the matrices in the WinMOPAC file.
- Default Output the matrices with the N-lowest excited states when `ECharge=N` is specified. If the size of the matrices exceeds 100 MB, a warning message is invoked and the number of the output matrices is reduced.

### G.1.23 Keywords for Output

#### Displaying of the MOS-F Process

- `Display=Silent` Suppress displaying the progress of the MOS-F process on the standard error output. An example of the standard error output given by specifying this keyword is shown below.

```

Entering MOS-F system at Sun Jul  9 14:29:02 2000
MOS-F version 4.2D ... Linux Release 2.2.9 i686/az.
MOS-F> JCtrl entering.
Silent mode on the stderr output specified.
MOS-F> ExitMOS entering.
Leaving MOS-F system at Sun Jul  9 14:29:02 2000
Process terminated normally in ExitMOS.

```

- `Display=S` As `Display=Silent`.
- `Display=Verbose` Verbosely display the progress of the MOS-F process on the standard error output.
- `Display=V` As `Display=Verbose`.
- Default `Display=Silent`

#### Output Columns

- `TSS` The maximum columns in output is suppressed to 80.
- `L/P` The maximum columns in output is suppressed to 133.
- Default `TSS`

#### Keywords and Options

- `PrtIOp` Requests a list of options showing the keywords in their code form.
- Default No option list given.

#### Dielectric Constant and Refractive Index of Solvent

- `PrintSolvent` Requests the list of the program-defined name, alias, dielectric constant and refractive index of the solvent in the output.
- Default None requested.

#### Atomic Parameters

- `ParmOut=Type` Requests atomic parameters for each constituent atom in output.
- `ParmOut=Atom` Requests atomic parameters of all constituent atoms.
- `ParmOut=All` Requests atomic parameters of all atoms internally stored in the program.
- Default None requested.

### Interatomic Distances

- `AtDist` Requests interatomic distances to be included in output.  
Default Not included.

### Overlap Integrals

- `SOut` Requests integrals which are transformed into molecular coordinate based ones, after scaling them in local coordinates, to be included in output. If non-scaled integrals are desired, use the keyword `FS=1.0 FP=1.0 FD=1.0`. Care must be exercised with these keywords as other integrals may also be unscaled in the calculation.  
Default Not included.

### Electron Repulsion Integrals

- `GOut` Requests repulsion integrals  $\gamma_{AB}$  to be included in output.  
Default Not included.

### Orbital Initial Guess

- `Guess` Requests initial Hückel guess orbitals and Hückel Hamiltonian to be included in output.  
Default Not included.

### Core Hamiltonian

- `HCore` Core Hamiltonian matrix will be given in output.  
Default No.

### Fock Matrix

- `Fock` Fock matrix upon SCF convergence will be given in output.  
Default Not given

### Density Matrix

- `Dens` Density matrix upon SCF convergence will be given in output.  
Default No.

### MO Coefficients

- `MOCoeff=n` The  $n$ -highest occupied and the  $n$ -lowest virtual MO coefficients will be given in output. If  $n = -1$ , all MO coefficients will be given.
- `MOCoeff=All` All MO coefficients will be given in output.
- `MOCoeff` `MOCoeff=10`  
Default Not given.

**MO Densities**

- MODens=n      The  $n$ -highest occupied and the  $n$ -lowest virtual MO densities will be given in output. If  $n = -1$ , all MO densities will be given. MO density is normalized to unity.
- MODens=All    All MO densities will be given in output.
- MODens        MODens=10
- Default        Not given.

**Molecular Integrals**

- MOInt        Requests that molecular integrals for electron repulsion integrals calculated by integral transformation to be given in output. This option is primarily for debugging. If this option is used with more than 100 serial numbers for orbitals for CI calculation, format overflow will occur. The unit for molecular integral is Hartree.
- Default        Not requested.

**CI Matrix**

- CIMat        Requests that the CIS matrix is included in output. This option is primarily for debugging. If this option is used with a CIS matrix dimension larger than 100, format overflow will occur. The unit for matrix element is Hartree.
- Default        Not requested.

**Eigenvalues and Eigenvectors of CI Matrix**

- CIVec        Requests that the eigenvalues and eigenvectors of the CIS matrix are included in the output. This option is primarily for debugging. If this option is used with the size of the CIS matrix larger than 100, format overflow will occur. The unit for matrix element is Hartree.
- Default        Not requested.

**Dipole Integrals**

- Dipole        MO-based dipole integrals in atomic units are printed in output.
- Default        Not printed.

**Transition Moment**

- TMom        The transition moment between ground and excited states  $\langle 0 | \hat{\mu} | e \rangle$  in atomic units is given in output.
- TMom=All    The transition moment between ground and excited states  $\langle 0 | \hat{\mu} | e \rangle$  and the quantity corresponding to those between excited states  $\langle e | -\tilde{\mu} | e' \rangle$  in atomic units are given in output. Only when the keyword requesting hyperpolarizability is used, will the transition moment for excited-excited state be given.
- Default        Not given.

**Excited States**

- `NStates=n` Requests that the transition energies and oscillator strengths for  $n$  CIS excited states starting from the one with the lowest transition energy are given in output.
  - `NStates=All` Requests the transition energies and oscillator strengths of all the CIS excited states.
- Default `NStates=10`

**Excited States Charge**

- `ECharge=n` The charge differences between ground and excited states and charges for  $n$  CIS excited states starting from the one with the lowest transition energy are calculated and given in output.
  - `ECharge` As `ECharge=NStates`. See keyword `NStates`.
  - `ECharge=All` The charge differences between ground and excited states and charges for all CIS excited states are calculated and given in output.
- Default Do not calculate.

**G.1.24 Fundamental Constants** $\pi$ 

- `Pi=X.XXXXXXXXXX`  $\pi$
- Default The value obtained from internally evaluating  $4 \tan^{-1}(1)$  is used.

**Bohr to Å**

- `ToAng=X.XXXXXXXXXX` Conversion factor from Bohr to Å.
- Default 0.529177249

**Hartree to EV**

- `AUtoEV=XX.XXXXXXXXXX` Conversion factor from Hartree to eV.
- Default  $10 \times \text{AUtoEr}/\text{EVtoEr} \simeq 27.2113961318$

**Planck's Constant**

- `Planck=X.XXXXXXXXXX` Planck's constant (without  $10^{-34}(\text{J}\cdot\text{s})$ ).
- Default 6.6260755

**Speed of Light**

- `SLight=X.XXXXXXXXXX` Speed of light (without  $10^8(\text{m/s})$ ).
- Default 2.99792458

**EV to Erg**

- EVtoEr=X.XXXXXXXXXX Conversion factor from eV to erg (without  $10^{-12}$ ).
- Default 1.60217733

**EV to KCal/Mol**

- EVtoKC=XX.XXXXXXXXXX Conversion factor from eV to kcal/mol.
- Default  $10 \times \text{EVtoEr} \times \text{Avogdr}/\text{ToCal} \simeq 23.0605423014$

**Hartree to Erg**

- AUtoEr=X.XXXXXXXXXX Conversion factor from Hartree to erg (without  $10^{-11}$ ).
- Default 4.3597482

**Nd+3 YAG Laser**

- YAGNM=XXXX.XXXXXXXXXX Wavelength of Nd+3 YAG laser (in nm).
- Default 1064.8

**He-Ne Laser**

- HeNeNM=XXX.XXXXXXXXXX Wavelength of He-Ne laser (in nm).
- Default 632.82

**Avogadro's Number**

- Avogdr=X.XXXXXXXXXX Avogadro's number (without  $10^{23}$ ).
- Default 6.0221367

**Joules to Calories**

- ToCal=X.XXXXXXXXXX Conversion factor from Joules to Calories.
- Default 4.184

**G.1.25 Other Keywords****Matrix Diagonalization**

- Diag=Inv For diagonalizing real symmetric matrix, use the QL method for eigenvalue calculation and the inverse iteration method for eigenvector calculation.<sup>66-68</sup>
- Diag=QL Use the QL method for eigenvalue and eigenvector calculation.<sup>66-68</sup>
- Default Diag=Inv

**ANCHOR II Output**

- ANCHOR Output file for 3D Molecular Design Assistance System ANCHOR II<sup>69</sup> is generated. For this keyword to work, an output file name needs to be assigned for the environmental variable File10 beforehand.

Default Do not generate.

**PCNOE Calculation**

- PCNOE DO PCNOE calculation. This keyword is useful for checking input data.

Default No calculation performed.



## G.2 Quick Alphabetical Reference

For details on keywords, see [the previous section](#) or [Chapter 3](#).

- `Alpha` Computes static polarizability.
- `AlphaDispersion` Requests frequency dispersion of polarizability.
- `AlphaDynamic` As `AlphaDispersion`.
- `AlphaFreqStep=X.XXXXX` Specifies incremental value of frequency for frequency dispersion of polarizability in eV.
- `AlphaStatic` As `Alpha`.
- `ANCHOR` Generates an output file for 3D Molecular Design Assistance System ANCHOR II.
- `AtDist` Requests interatomic distances in output.
- `AUtoEr=X.XXXXXXXX` Specifies the conversion factor from Hartree to erg (Default: 4.3597482).
- `AUtoEV=XX.XXXXXXXX` Specifies the conversion factor from Hartree to eV (Default:  $\simeq 27.2113961318$ ).
- `Avogdr=X.XXXXXXXX` Specifies Avogadro's number to be used (Default: 6.0221367).
- `Beta` Requests static first hyperpolarizability.
- `BetaDispersionEO` As `BetaDispersionEOPE`.
- `BetaDispersionEOPE` Requests the frequency dispersion of first hyperpolarizability for EOPE.
- `BetaDispersionOR` Requests the frequency dispersion of first hyperpolarizability for OR.
- `BetaDispersionSHG` Requests the frequency dispersion for first hyperpolarizability for SHG.
- `BetaEO` As `BetaEOPE`.
- `BetaEOPE` Requests first hyperpolarizability for EOPE (Incident light: He-Ne laser).
- `BetaFreqStep=X.XXXXX` Specifies incremental value of frequency for frequency dispersion of first hyperpolarizability in eV.
- `BetaOR` Requests first hyperpolarizability for OR (Incident light: He-Ne laser).
- `BetaSHG` Requests first hyperpolarizability for SHG (Incident light: YAG laser).
- `BetaStatic` As `Beta`.
- `CavityRadius=vdW` Compute the cavity radius of the solute using its approximate molar volume obtained from the van der Waals radii of the constituent atoms.
- `CavityRadius=vdW+0.5` Add empirical value 0.5 Å to the value obtained from `CavityRadius=vdW`.
- `CavityRadius=vdW_cube` Compute the cavity radius of the solute using its approximate molar volume with the cube shape obtained from the van der Waals radii of the constituent atoms.

- CavityRadius=XXX.XXX      Specifies the cavity radius of the solute in Å.
- Charge=n      As Charges=n.
- Charges=n      Specifies the charge on a molecule.
- CheckParm      Check whether the atomic parameters are sufficient or not.
- CI      As CI(10 10).
- CI(m n)      Takes the *m*-highest occupied and the *n*-lowest virtual MO's for CIS calculation.
- CI=All      Requests that all SCF orbitals are used for CIS calculation.
- CI=Read      For specifying the serial numbers on orbitals to be used for CI calculation.
- CIMat      Requests CIS matrix in output.
- CIVec      Requests the eigenvalues and eigenvectors of CIS matrix in output.
- CNDO/2      CNDO/2 will be used as the model Hamiltonian.
- CNDO/S      CNDO/S will be used as the model Hamiltonian.
- CNDO/S2      CNDO/S2 will be used as the model Hamiltonian.
- CNDO/S3      CNDO/S3 will be used as the model Hamiltonian.
- Coord=Cart      Specifies the standard Cartesian coordinate format.
- Coord=Inter      Specifies the format compatible with MOPAC Internal Coordinate.
- Coord=MCart      Specifies the format compatible with MOPAC Cartesian Coordinate.
- Coord=Z      Specifies the format compatible with Gaussian symbolic Z-matrix.
- D-Delta=X.XXXXX      Specifies the scale factor for  $d\delta$ -type overlap integral.
- D-Pi=X.XXXXX      Specifies the scale factor for  $d\pi$ -type overlap integral.
- D-Sigma=X.XXXXX      Specifies the scale factor for  $d\sigma$ -type overlap integral.
- Dens      Requests density matrix upon SCF convergence in output.
- Diag=Inv      Requests that, for matrix diagonalization, the QL method is used for eigenvalue calculation and the inverse iteration method is used for eigenvector calculation.
- Diag=QL      Requests that, for matrix diagonalization, the QL method is used for eigenvalue and eigenvector calculation.
- DielectricConstant=X.XXX      Specifies the dielectric constant of the solvent.
- Display=S      As Display=Silent.
- Display=Silent      Suppress displaying the progress of the MOS-F process on the standard error output.
- Display=V      As Display=Verbose.
- Display=Verbose      Verbosely display the progress of the MOS-F process on the standard error output.

- Dipole Requests MO-based dipole moment integrals in output.
- Dipole=ZDO Requests that ZDO approximation is used for evaluating one-center dipole integrals for transition moment.
- Don2 Adds  $3d$ -type orbital on the second row atoms.
- Don3 Adds  $3d$ -type orbital on the third row atoms.
- ECharge As ECharge=NStates.
- ECharge=All Requests that the charges and charge differences from the ground state for all CIS excited states are computed.
- ECharge=n Requests that the charges and charge differences from the ground state for the  $n$ -lowest transition energy CIS excited states are computed.
- EVtoEr=X.XXXXXXXXXX Specifies the conversion factor from eV to erg to be used (Default: 1.60217733).
- EVtoKC=XX.XXXXXXXXXX Specifies the conversion factor from eV to kcal/mol to be used (Default:  $\simeq$  23.0605423014).
- FD=X.XXXXX Specifies the scale factor for overlap integrals involving  $d$ -type orbitals.
- Fock Requests Fock matrix upon SCF convergence in output.
- FP=X.XXXXX Specifies the scale factor for overlap integrals of  $p\pi$ -type.
- FS=X.XXXXX Specifies the scale factor for overlap integrals of  $p\sigma$ -type.
- G=A The analytical formula for  $s$ -type orbitals is used for evaluating two-center electron repulsion integrals.
- G=DH The formula by DasGupta and Huzinaga is used for evaluating two-center electron repulsion integrals.
- G=NM The formula by Nishimoto and Mataga is used for evaluating two-center electron repulsion integrals.
- G=NMW The formula by Nishimoto and Mataga with Weiss modification is used for evaluating two-center electron repulsion integrals.
- G=O The formula by Ohno is used for evaluating two-center electron repulsion integrals.
- G=OK The formula by Ohno and Klopman is used for evaluating two-center electron repulsion integrals.
- G=PP The formula by Pariser and Parr is used for evaluating two-center electron repulsion integrals.
- Gamma Requests that static second hyperpolarizability is computed.
- GammaDCOR Requests that second hyperpolarizability for DC-OR is computed (Incident light: He-Ne laser).
- GammaDCSHG Requests that second hyperpolarizability for DC-SHG is computed (Incident Light: YAG laser).

- `GammaDFWM` Requests that second hyperpolarizability for DFWM is computed (Incident light: He-Ne laser).
- `GammaDispersionDCOR` Requests the frequency dispersion of second hyperpolarizability for DC-OR.
- `GammaDispersionDCSHG` Requests the frequency dispersion of second hyperpolarizability for DC-SHG.
- `GammaDispersionDFWM` Requests the frequency dispersion of second hyperpolarizability for DFWM.
- `GammaDispersionKerr` Requests the frequency dispersion of second hyperpolarizability for EFIKE.
- `GammaDispersionTHG` Requests the frequency dispersion of second hyperpolarizability for THG.
- `GammaKerr` Computes second hyperpolarizability for EFIKE (Incident light: He-Ne laser).
- `GammaFreqStep=X.XXXXX` Specifies incremental value of frequency for frequency dispersion of second hyperpolarizability in eV.
- `GammaStatic` As `Gamma`.
- `GammaTHG` Computes second hyperpolarizability for THG (Incident light: 1907 nm).
- `GOut` Requests electron repulsion integrals in output.
- `Guess` Requests Hückel initial guess MO coefficients and Hückel Hamiltonian matrix in output.
- `HCore` Requests core Hamiltonian matrix in output.
- `HeNeNM=XXX.XXXXXXXX` Specified the wavelength of He-Ne laser to be used in nm (Default: 632.82).
- `INDO/S` Requests that INDO/S model Hamiltonian is used.
- `k-NM=XX.XXXX` Specifies the  $k$ -value of modified Nishimoto-Mataga formula.
- `L/P` The maximum number of output columns is suppressed to 133.
- `MinorBetaTensor` All the tensor elements of the first hyperpolarizability are computed.
- `MinorGammaTensor` All the tensor elements of the second hyperpolarizability are computed.
- `MOCcoef` As `MOCcoef=10`.
- `MOCcoef=All` All the MO coefficients are given in output.
- `MOCcoef=n` The  $n$ -highest occupied and the  $n$ -lowest virtual MO coefficients are given in output. If  $n = -1$ , all MO coefficients are given.
- `MODens` As `MODens=10`.
- `MODens=All` All the MO densities are given in output.
- `MODens=n` The  $n$ -highest occupied and the  $n$ -lowest virtual MO densities are given in output. If  $n = -1$ , all MO densities are given.
- `MOInt` Molecular integrals for electron repulsion integrals are listed in output.
- `NoCI` Requests that no CI calculation is performed. This implies that  $\alpha$ ,  $\beta$  and  $\gamma$  are not computed.

- `NoCheckParm` Do not check whether the atomic parameters are sufficient or not.
- `NoShift` No Level shifting is applied for SCF calculation.
- `NStates=All` Transition energy and oscillator strength for all CIS excited states are listed in output.
- `NStates=n` Transition energy and oscillator strength for the  $n$ -lowest transition energy CIS excited states are listed in output.
- `OldOxygenBeta` Use the old value ( $-45.0$  eV) for the resonance integral of oxygen in CNDO/S.
- `P-Pi=X.XXXXX` As `FP=X.XXXXX`.
- `P-Sigma=X.XXXXX` As `FS=X.XXXXX`.
- `Parm=Atom` For assigning atomic parameters for a particular atom. Different parameters may be assigned to the same kind of atoms.
- `Parm=Type` Assigns atomic parameters for each type of atom.
- `ParmOut=All` Requests that the atomic parameters of all the internally stored atoms are listed in output.
- `ParmOut=Atom` Requests that the atomic parameters of all the constituent atoms are listed in output.
- `ParmOut=Type` Requests that the atomic parameters are listed for each type of constituent atom.
- `PCNOE` Performs PCNOE calculation.
- `Pi=X.XXXXXXXXXX` Specifies the value of  $\pi$  to be used (Default:  $4 \tan^{-1}(1)$ ).
- `Planck=X.XXXXXXXXXX` Specifies the value of Planck's constant to be used (Default: 6.6260755).
- `Plane=X-Y` Places the second atom on positive x-axis and third atom on x-y plane when coordinate input is for Z-matrix.
- `Plane=Z-X` Places the second atom on positive z-axis and third atom on z-x plane when coordinate input is for Z-matrix.
- `Plane=Z-Y` Places the second atom on positive z-axis and third atom on z-y plane when coordinate input is for Z-matrix.
- `PrintSolvent` Requests the list of the program-defined name, alias, dielectric constant, and refractive index of the solvent in the output.
- `PrtIOp` Requests that the keywords in use are listed with their numerical code.
- `RefractiveIndex=X.XXX` Specifies the refractive index of the solvent.
- `SCF=NoExtrap` Do not extrapolate the density matrix in the SCF calculation.
- `SCFCrt=X.XXXXXXXXXX` Specifies density matrix convergence threshold for SCF calculation ( $1.0d-02$  to  $1.0d-09$ ).

- SCFCyc=n                      Specifies the maximum number of iterative cycles in SCF calculation ( $1 \leq n \leq 999$ ).
- SCRF                              Perform the SCRF calculation using the Onsager model with model B proposed by Zerner.
- SCRF=Onsager                  Perform the SCRF calculation using the Onsager model.
- SCRF=Onsager\_A                Perform the SCRF calculation using the Onsager model with model A proposed by Zerner.
- SCRF=Onsager\_B                As SCRF.
- SCRF=Onsager\_B1               Perform the SCRF calculation using the Onsager model with model B1 proposed by Zerner.
- Shift                              As Shift=0.5.
- Shift=X.XXXXXXXXX              Specifies the amount of shift on virtual orbitals in the level-shift method in Hartree.
- Singlet                            Singlet CIS calculation is performed.
- SLight=X.XXXXXXXXXXX          Specifies the speed of light to be used (Default: 2.99792458).
- Solvent=XXXXXX                Specifies the solvent name to use the program-defined dielectric constant and refractive index of the solvent.
- SOut                              Requests that the overlap integrals transformed into molecular coordinates after scaling them in local coordinates are listed in output.
- TMom                              Transition moment in atomic units between the ground and the excited states  $\langle 0 | \hat{\mu} | e \rangle$  is given in output.
- TMom=All                        Transition moment between the ground and the excited states  $\langle 0 | \hat{\mu} | e \rangle$  and quantity corresponding to those between excited states  $\langle e | -\tilde{\mu} | e' \rangle$  in atomic units are given in output.
- ToAng=X.XXXXXXXXXXX          Specifies the conversion factor from Bohr to Å (Default: 0.529177249).
- ToCal=X.XXXXXXXXX              Specifies the conversion factor from Joules to Calories (Default: 4.184).
- Triplet                            Triplet CIS calculation is performed.
- TSS                                Suppresses the maximum number of columns in output to 80.
- UseCNDOParm                    Use atomic parameters for CNDO/S and CNDO/S2 in the INDO/S calculation.
- UseTripletParm                  Use atomic parameters for triplet excited states in the INDO/S calculation.
- Weiss=XX.XXXX                  Specifies the value for  $f_r$ , the Weiss factor, in Nishimoto-Mataga-Weiss formula.
- WinMOPAC                        An output file for WinMOPAC V3 (.wms file) is generated.

- `wms=CIDens(m n)` Output the difference density matrices from the m-th excited state to the n-th one on the WinMOPAC file.
- `wms=CIDens=ECharge` Output the difference density matrices for excited states with their number specified by the keyword `ECharge`.
- `wms=CIDens=XX[KMG](B)` Output the difference density matrices for excited states with the specified size.
- `wms=NoCIDens` Do not output the difference density matrices for excited states on the WinMOPAC file.
- `YAGNM=XXXX.XXXXXXXXXX` Specifies the wavelength of Nd+3 YAG laser in nm (Default: 1064.8).





# Appendix H

## Keywords for Atomic Parameters

The keywords related to atomic parameters may be used with `Parm=Type` or `Parm=Atom` in the keyword section. There are two categories in the atomic parameter keywords, namely, there are some which can be used with both `Parm=Type` and `Parm=Atom` and the rest can be used only with `Parm=Type`. Users are directed to [Section 3.5](#) for more details on specifying atomic parameters and to [page 58](#) for the ionization process.

### H.1 Common Keywords

- `Es` This is the ionization potential for *s*-type orbitals. In INDO/S, it is the ionization potential of Process II for the transition metals.<sup>†</sup>
- `Es1` As `Es`.
- `Ep` This is the ionization potential for *p*-type orbitals.<sup>†</sup> In INDO/S, it is the ionization potential of Process II for the transition metals.
- `Ep1` As `Ep`.
- `Ed` This is the ionization potential for *d*-type orbitals.<sup>†</sup> In INDO/S, it is the ionization potential of Process II for the transition metals.
- `Ed1` As `Ed`.
- `Es2` This is the ionization potential for *s*-type orbitals in Process I. Only effective in INDO/S with the transition metals.
- `Ep2` This is the ionization potential for *p*-type orbitals in Process I. Only effective in INDO/S with the transition metals.
- `Ed2` This is the ionization potential for *d*-type orbitals in Process I. Only effective in INDO/S with the transition metals.
- `CSq1` The weight of Process II (The value of  $C_1^2$ )
- `Bs` Resonance integral for *s*-type orbitals  $-\beta_s$
- `Bp` Resonance integral for *p*-type orbitals  $-\beta_p$
- `Bd` Resonance integral for *d*-type orbitals  $-\beta_d$
- `Bsp` Requests that the same value is used for the resonance integral of both *s* and *p*-type.

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<sup>†</sup>For CNDO/S2, CNDO/S3, and INDO/S. It is the average between the ionization potential and electron affinity in CNDO/2 and CNDO/S.

- Bspd Requests that the same value is used for the resonance integral of  $s$ ,  $p$  and  $d$ -type.
- Zs Slater exponent for  $s$ -type orbital.
- Zp Slater exponent for  $p$ -type orbital.
- Zd Slater exponent for  $d$ -type orbital. In INDO/S, it is for one of the two primitive  $d$ -type orbitals for the transition metal.
- Zd1 As Zd.
- Zd2 The one other than Zp1 in the two primitive orbitals. Only effective in INDO/S for the transition metals.
- CC1 Contraction coefficient for Zd1. Only effective in INDO/S for the transition metals.
- CC2 Contraction coefficient for Zd2. Only effective in INDO/S for the transition metals.
- Zsp Requests that the same value is used for the Slater exponent of both  $s$  and  $p$ -type.
- Zspd Requests that the same value is used for the Slater exponent of  $s$ ,  $p$  and  $d$ -type.
- G One-center electron repulsion integral  $\gamma_{AA}$
- Gss As G.
- F0ss As G
- Gsd One-center electron repulsion integral between  $s$  and  $d$ -type orbitals. Only effective in INDO/S for the transition metals.
- F0sd As Gsd.
- Gdd One-center electron repulsion integral between  $d$ -type orbitals. Only effective in INDO/S for the transition metals.
- F0dd As Gdd.
- Pk Klondike parameter in DasGupta-Huzinaga formula.

## H.2 Available Keywords for Parm=Type

- G1sp Slater-Condon parameter  $G^1(sp)$
- F2pp Slater-Condon parameter  $F^2(pp)$
- G2sd Slater-Condon parameter  $G^2(sd)$
- G1pd Slater-Condon parameter  $G^1(pd)$
- F2pd Slater-Condon parameter  $F^2(pd)$
- G3pd Slater-Condon parameter  $G^3(pd)$
- F2dd Slater-Condon parameter  $F^2(dd)$
- F4dd Slater-Condon parameter  $F^4(dd)$
- vdW Van der Waals radius in Å

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