

# **NDOL v. 7.0.1**

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## ***Theoretical Introduction***

It is well known the importance and necessity of the theoretical prediction of the energy and the general characteristics of excitons to model spectra of interaction of light with nanoscopic systems because the imminent necessities of mankind on energy saving and recovering<sup>1</sup> and understanding important biological processes for applications on human needs<sup>2</sup>. It allows an explanation of the state transitions that are really happening, as well as the modeling of substances and materials with specific properties. The main characteristic is that the calculations of excited electronic states only can be made with approximations and procedures of quantum mechanics that is the only formalism that can explain them to the present time.

Hamiltonians that are used nowadays for calculations of electron transitions in molecules are either *semiempirical*<sup>3</sup>, *time-dependent density functional theories (TD-DFT)*<sup>4</sup> or *ab initio SCF*<sup>5</sup>.

The calculations with *semiempirical* or *parametrical* methods are not expensive and acceptable for routine work, although results are always subject to the inclusion of arbitrary parameters in the Hamiltonians to guarantee that they reproduce the experimental compound data taken as references. This type of method is known like *a posteriori* parameterized.

On the other hand, the *ab initio SCF* calculation methods are theoretically consistent and considered as *a priori* type, since the approaches that are made are selected rigorously and without considering experimental results as references. It means that any new and unknown polyatomic system will be modeled according a consistent and unique basis. Nevertheless, shortcomings arise because the very expensive nature of calculations due to high requirements in computational resources. In addition, because the rigorous nature of the procedures, systematic errors are rarely cancelled, and sometimes results are very far from expected when procedures do not cover all possible factors influencing electron excitations in molecules.

*Time-dependent Density Functional Theory* is a very particular case, nowadays popular, where the key terms in the Hamiltonian are formulated *a posteriori* for selected experimental data. Formulas are so consistent that can give fair results in very general cases. However, interpretations could also be considered as non-theoretically consistent because the essence of DFT is just density functions and not molecular states. However, several popular works nowadays use TD-DFT “molecular orbitals” for performing interesting modeling of the nature of electronic transitions.

Computer resources required for processing both *ab initio* and TD-DFT calculations are expensive and increases exponentially with the size of the system, which still makes its use impossible for nanoscopic systems of importance even with the most powerful computers due to its size.

The NDOL Hamiltonian<sup>6</sup> means an *a priori* method of calculation, used and proven during several years, whose results are better or comparable to those of many existing semiempirical and ab initio methods. In order to build up of the Fock Hamiltonian matrix of each molecule only two experimental parameters are used for each atomic orbital. Those are the respective ionization potentials and electron affinities. Additionally, tabulated Slater exponents are used for the calculation of overlap integrals between atomic orbitals that are used as proportionality factors for one electron bicentric terms. It implies that no *a posteriori* parameters are included to fit the coincidence of the theoretical calculations with molecular experimental results of reference, which considerably increases the predictive trustworthiness of the method without affecting the computational efficiency of approximate methods. These Hamiltonians can be applied by means of programs NDOLxxxx (where xxxx is the year of production), developed by the Havana's laboratory in different versions since 1985 for personal computers.

### ***The NDOL Hamiltonian and calculation formulas***

The theoretical development of CNDOL has been already described elsewhere<sup>6-7</sup>. However, a detailed description of the four options for including *s* – *p* and eventually *d* basis orbital separation in both the CNDO/1 and CNDO/2 approaches is here displayed. A brief description is necessary for the sake of updating and consistency. If we split diagonal matrix elements from the original CNDO/1 diagonal one - electron Hamiltonian term, by taking into account the “*l*” azimuthally quantum number of atomic orbitals, two formulations appear:

$$H_{\mu} = -I_{\mu} + (P_A^l - Z_A^l)\gamma_A^l - \frac{1}{2}P_{A\mu} \gamma_A^l + P_A^k \gamma_A^l - \sum_{B \neq A}^k (Z_B^l \gamma_A^l + Z_B^k \gamma_A^l) \quad (1)$$

$$H_{\mu} = -I_{\mu} + (P_A^l - Z_A^l)\gamma_A^l + (1 - \frac{1}{2}P_{\mu})\gamma_A^l + P_A^k \gamma_A^l - \sum_{B \neq A}^k Z_B \Gamma_A^l \quad (2)$$

that are named as variants CNDOL/11 (eq. 1) and CNDOL/12 (eq. 2), and two other corresponding to the former CNDO/2:

$$H_{\mu} = -\frac{1}{2}(I_{\mu} + A_{\mu}) + (P_A^l - Z_A^l)\gamma_A^l + (P_A^k - Z_A^k)\gamma_A^l - \frac{1}{2}(P_{\mu} - 1)\gamma_A^l - \sum_{B \neq A} (Z_B^l \gamma_A^l + Z_B^k \gamma_A^k) \quad (3)$$

$$H_{\mu} = -\frac{1}{2}(I_{\mu} + A_{\mu}) + (P_A^l - Z_A^l)\gamma_A^l + P_A^k \gamma_A^l - \frac{1}{2}(P_{\mu} - 1)\gamma_A^l - \sum_{B \neq A} Z_B \Gamma_A^l \quad (4)$$

that are named as variants CNDOL/21 (eq. 3) and CNDOL/22 (eq. 4), respectively. In this work we will be using both CNDOL/2 matrix elements.

Combinations of terms are also possible, giving place to the so-called hybrid CNDOL Hamiltonians:

**Table 1.** Description and proposed nomenclature for the CNDOL diagonal one - electron matrix elements ( $H_{\mu\mu}$ )<sup>a</sup>.

$$H_{\mu\mu} = U_{\mu\mu} - \sum_{B \neq A} V_{AB}^l$$

CNDO origin	$U_{\mu\mu}$	$-\sum_{B \neq A} V_{AB}^l$	
		$-\sum_{B \neq A} (Z_B^l \gamma_{AB}^{ll} + Z_B^k \gamma_{AB}^{lk})$ <b>Split core charge: S</b>	$-\sum_{B \neq A} (Z_B \Gamma_{AB}^l)$ <b>Complete core charge: C</b>
CNDO/1	$-I_{\mu} + \gamma_{AA}^{ll} - Z_A^l \gamma_{AA}^{ll} - Z_A^k \gamma_{AA}^{lk}$ <b>Split core charge: 1S</b>	CNDOL/1SS (CNDOL/11)	CNDOL/1SC
	$-I_{\mu} + \gamma_{AA}^{ll} - Z_A \gamma_{AA}^{ll}$ <b>Complete core charge: 1C</b>	CNDOL/1CS	CNDOL/1CC (CNDOL/12)
CNDO/2	$-\frac{1}{2}(I_{\mu} + A_{\mu}) + \frac{1}{2}\gamma_{AA}^{ll} - Z_A^l \gamma_{AA}^{ll} - Z_A^k \gamma_{AA}^{lk}$ <b>Split core charge: 2S</b>	CNDOL/2SS (CNDOL/21)	CNDOL/2SC
	$-\frac{1}{2}(I_{\mu} + A_{\mu}) + \frac{1}{2}\gamma_{AA}^{ll} - Z_A \gamma_{AA}^{ll}$ <b>Complete core charge: 2C</b>	CNDOL/2CS	CNDOL/2CC (CNDOL/22)

a.  $I_m$  and  $A_m$  are the valence state ionization potential and electron affinity, respectively, of the  $m$  AO;  $Z$  is the effective nuclear charge of the atomic core;  $\Gamma_{AB}^l$  is the interaction integral between an electron with azimuthal quantum number  $l$  on atom A with the core of atom B. CNDOL/1SS, CNDOL/1CC, CNDOL/2SS and CNDOL/2CC correspond with the previous names CNDOL/11, CNDOL/12, CNDOL/21 and CNDOL/22 respectively.

The one-electron non diagonal term is common to all of them and can be expressed as:

$$H_{\mu} = \bar{v} - \frac{1}{2}(I_{\mu} + I_{\nu})f(r_{\mu}, l_{\mu}, l_{\nu}, q_{\mu}) \quad (5)$$

where

$$f(r_{\mu}, l_{\mu}, l_{\nu}, q_{\mu}) = S_{\mu} f'_{\nu}(q_{\mu}) \quad (6)$$

$I_\mu$  and  $A_\mu$  are the valence state ionization potential and electron affinity of the atomic orbital (AO)  $\mu$  on atom  $A$ , respectively;  $p_{\mu\nu}$  is the density matrix element between the AO's  $\mu$  and  $\nu$  on different atoms. It can be observed that differences with respect to the above mentioned CNDO methods arise when  $\gamma_{\mu\nu}$  are considered as the two electron integrals that are particular for any pair of AO's having distinct azimuthal quantum number  $l$  and  $k$  on atoms  $A$  and  $B$ , respectively;  $P_A^l$  is the sum of all AO's density matrix elements on atom  $A$  having the same azimuthal quantum number  $l$ ;  $Z_B$  is the effective nuclear charge (usually the number of valence electrons) of the B atomic core,  $\Gamma_{AB}^l$  is the interaction integral between an electron with azimuthal quantum number  $l$  in atom  $A$  and the core of atom  $B$ ;  $r_{\mu\nu}$  is the interatomic distance for a pair of atoms with AO  $\mu$  and  $\nu$ ,  $f(q_{\mu\nu})$  is the projection factor onto a vector joining the atoms where orbitals  $\mu$  and  $\nu$  are on;  $S_{\mu\nu}$  is the corresponding overlap integral calculated with current formulae for Slater orbitals.

Regarding functionals for two-electron integral terms, they could be calculated by several ways, including analytical formulas for Slater type orbitals. However, we follow the common use in the pioneer Pariser – Parr – Pople method (PPP) where Pariser's relation is mostly used for pair electron repulsions in a center A:

$$\gamma_{AA}^{ll} = I_\mu - A_\mu \quad (7)$$

The two center term will be considered as a *functional of electron repulsion* based on a combined form of traditional Mataga – Nishimoto – Ohno formulations:

$$\gamma_{AB}^{lk} = \left( a_A^{lk} \frac{1}{c} + \frac{R_{AB}^{lk}}{R_A^2 + R_B^2} \right)^{-1/2} \quad (8)$$

where

$$a_{AB}^{lk} = 2 \left( \gamma_{AA}^{ll} + \gamma_{BB}^{kk} \right)^{-1} \quad (9)$$

The original Mataga – Nishimoto's formula uses  $c = 2$  and the Ohno's formula uses  $c = 0$ . The limit of bicentric  $\gamma_{AB}^{lk}$  corresponds to the monocentric  $\gamma_{AA}^{ll}$  when  $R_{AB}$  tends to 0 and is null when  $R_{AB}$  tends to infinity. We are trying in this method a new version of this formula where  $c = 1$ , in order to overcome HF convergence problems arising when  $c = 2$  and non accurate results when  $c = 0$ . The formula with  $c = 1$  will be denoted as the modified Ohno's functional (OHM).

Then, the CNDOL Fock matrix elements remain:

$$F_{\mu\mu} = H_{\mu\mu} + \sum_{A \neq B} \left( P_B^l \gamma_{AB}^{ll} + P_B^k \gamma_{AB}^{lk} \right) \quad (10)$$

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} p_{\mu\nu} \gamma_{\nu A}^{lk} \quad (11)$$

Configuration interaction of single excited determinants (CIS) that gives  $E$  excitation energies is solved as,

$$\Psi^{CIS} = \sum_s a_s \Phi_s \quad (12)$$

$$(\mathbf{H} - E\mathbf{I})\mathbf{a} = 0 \quad (13)$$

where  $\mathbf{a}$  is the matrix of CIS coefficients and  $\mathbf{I}$  is the identity matrix. The elements of matrix  $\mathbf{H}$  are calculated from the SCF Hartree-Fock single excitation energies for any  $i \rightarrow k$  or  $j \rightarrow l$ , where  $k$  and  $l$  are empty MO's. Diagonal and off-diagonal of CIS matrix terms are:

$$\begin{aligned} {}^1H_{s\ s} &= \epsilon_k^{S\ C\ F} \epsilon_i^{S\ C\ F} \langle i\ k\ i\ k \rangle + 2\langle i\ k\ k\ i \rangle \\ {}^3H_{s\ s} &= \epsilon_k^{S\ C\ F} \epsilon_i^{S\ C\ F} \langle i\ k\ i\ k \rangle \\ {}^1H_{s\ t} &= 2\langle j\ k\ l\ i \rangle - \langle j\ k\ i\ l \rangle \\ {}^3H_{s\ t} &= -\langle j\ k\ i\ l \rangle \end{aligned} \quad (14)$$

unless  $i=j$  and  $k=l$ . In our procedure all possible SCF single transition energies  $H_{ss}$  are evaluated and ordered according to their values. The current program builds CIS matrix with the  $n$  lowest energy terms of singly excited determinants, where  $n$  is conventionally chosen as the total number of basis atomic orbitals, and then diagonalized.

Electron density of each  $s$  singly excited configuration comes from the corresponding SCF matrices  $[c_{i\mu}]$ :

$$p_{s,\mu\ \nu} = \sum_{i=1}^N n_{s,i} c_{i\mu} c_{i\nu} \quad (15)$$

where  $n_{s,i}$  is the occupation number of each  $i$  MO in the  $s$  state (being  $n_{s,i} = 0, 1, 2$  according the number of electrons in each MO) and  $c_{i\mu}$  are the MO coefficients. Each  $J$  state density element is then given by the squares of the corresponding coefficients of the CI coefficient matrix  $[a_{sJ}]$ :

$$p_{\mu\ \nu}^J = \sum_{s=1}^M a_s^2 p_{s,\mu\ \nu} \quad (16)$$

Similarly to this relation it is also possible to investigate the role of electron interaction integral values on each excitation energy after CIS. In the expressions above,  $a$ 's represent the corresponding CIS expansion coefficients and  $n$ 's mean molecular orbital occupations corresponding to the Slater determinant of the  $J$  electronic configuration. Therefore, the Coulomb and exchange (CE) energy contribution to each electron transition after the configuration interaction can be obtained by the expressions (17) and (18) for the singlet and triplet excited states, respectively.

$${}^1E_{\zeta}^{CE} = \sum_{\sigma=1}^N a_{\sigma\zeta}^2 (-J_{pr} + 2K_{pr})_{\sigma} \quad (17)$$

$${}^3E_{\zeta}^{CE} = \sum_{\sigma=1}^N a_{\sigma\zeta}^2 (-J_{pr})_{\sigma} \quad (18)$$

CE energy could be associated with the stabilization effect provided by the two electron integrals of each electron excitation with respect to the energy difference between eigenvalues of the involved MO's. Different kinds of electron transitions in one molecule and also their charge transfer (CT) character could also be estimated by this magnitude because it depends on the degree of charge interactions between the involved multielectronic wave functions.

It should be noticed that the many adjusted parameters, magic numbers and varied approximate functionals usually needed by semiempirical methods that reduce their theoretical consistency and reliability, are no longer necessary in CNDOL. In fact, the only input parameters needed, other than the molecular geometry of each polyatomic system, are Slater exponents to calculate overlap integrals for the one electron two center term (6), and the experimentally deduced  $I_{\mu}$ 's and  $A_{\mu}$ 's for each atomic orbital.

## ***NDOL2015 program***

### **Windows installation**

File ***NDOL2015.exe*** needs for installation to be copied in ***c:\windows*** or ***c:\winnt*** directory of the corresponding computer. It is not required other installation. The program can be then be called and loaded in the window of commands of any directory, under the Windows operating system. The window of commandos activates from the position "Start" in the screen, the menu "Accessories", and clicking an entry called "Command prompt".

### **Linux installation**

Linux kernels 2.6 or newer can manage the executable file *ndol2015.x*. It must have been copied to directory ***/usr/local/bin*** of the corresponding computer with root privileges. It is not required other installation. The program can be then be called and loaded by a text terminal on any directory or account.

### **Calculable systems**

This version of NDOL2015 can calculate all polyatomic systems with atoms from hydrogen to chlorine in the periodic table. This version cannot consider "d" atomic orbitals. However, also larger atomic numbers can be calculated if the parameters are especially provided and "d" orbitals are not participating in the calculation, i.e. Zn, Br, I, etc.



## INSTRUCTIONS FOR RUNNING NDOL2015

Input data for running NDOL programs is taken from the command line (either in the Linux or the DOS for Windows versions, as follows:

```
ndolXXXXXX <coordinate_file.extension> [<OPT>] [<SYM>]
```

ndolXXXXXX is the name of the program, which is used as a command in the corresponding computer operating system.

<coordinate\_file.extension> is the main input file containing the geometry of the polyatomic system to be calculated.

OPT and SYM are optional files. The order of appearance of file names in the command line is compulsory.

### PROGRAM:

ndolXXXXXX for Linux is:

ndol2015.x                   => For 2.6 Linux kernels and above.

Installed files are usually in a path searchable directory (i.e.: /usr/local/bin) and it is recommended to enter:

```
$ ls -l /usr/local/bin/ndol*
```

in order to realize which version is truly available in a given Linux computing system.

DOS for Windows versions are also available, where ndolXXXXXX is:

ndol2015.exe               => For Windows XP SP2 and SP3, Vista and 7 kernels operated in the corresponding DOS command shell line. Windows 8 has not yet been tested.

Appropriate installations for Windows systems must include these files in a directory accessible in the PATH environment variable. A common and harmless directory could be C:\WINDOWS.

Both Linux and Windows versions of NDOL2015 v. 7.0.1 allocate dynamically the required RAM memory according the size of the molecular system to be considered.

### MAIN INPUT FILE:

<coordinate\_file.extension> is the name and path of the input file where atomic coordinates are stored and the format is given by a fixed "extension" that MUST be one of .car, .out, .zmt, or .xyz;

".car" for Cartesian coordinate files in the style of the following example:

8

Acroleina opt. MP2|4-31G\*\*

```
1.212234 1.283900 0.000000 6
0.000000 0.719874 0.000000 6
-0.144416 -0.742647 0.000000 6
-1.220388 -1.324588 0.000000 8
1.349792 2.354178 0.000000 1
2.106201 0.674428 0.000000 1
-0.910775 1.302745 0.000000 1
0.810979 -1.301411 0.000000 1
```

The first line contains the number of atoms in the first four spaces. It must be an integer. The second and third lines are comment lines with free alphanumeric characters in 80 spaces. The rest of lines must contain atomic Cartesian coordinates (x,y,z) in Angstroms in the first three fields of 11 or 10 spaces (f11.0,f10.0,f10.0 in FORTRAN format codes) and the atomic number of the element in the last four spaces as an integer.

**".zmt"** for internal coordinate files in the MOPAC format, as in the example (see MOPAC manuals for details):

KEYWORDS GO HERE

Acrolein

optimized

```
C 0.0000000 0 0.000000 0 0.000000 0 0 0 0.0000
C 1.3375808 1 0.000000 0 0.000000 0 1 0 0.0000
C 1.4703292 1 120.141823 1 0.000000 0 2 1 0.0000
O 1.2166778 1 124.295032 1 180.000000 1 3 2 1 0.0000
H 1.0796518 1 122.121128 1 180.000000 1 1 2 3 0.0000
H 1.0825822 1 120.249828 1 0.000000 1 1 2 3 0.0000
H 1.0813598 1 122.523718 1 180.000000 1 2 1 3 0.0000
H 1.1063677 1 114.545861 1 0.000000 1 3 2 1 0.0000
0
```

**".out"** for main output files of MOPAC optimization jobs.

**".xyz"** for Xmol (Minnesota Supercomputer Center) simple Cartesian coordinate style format, as:

```
n #1st line MUST contain the number of atoms
one line label
H 1.0 1.0 1.0 #One line for each atom given in free format
```

where the lines corresponding to each atom contain the atomic symbol or number in the first place and the corresponding x, y and z coordinates in the following places in Angstroms. All are free formats.

#### OPTIONS FILE:

OPT is an option file and it is described below in the "OPTIONS FOR NDOL CALCULATIONS" section.

## SYMMETRY FILE:

SYM is the symmetry information file and the container information is described below in the "OPTIONS FOR NDOL CALCULATIONS" section, at item IOPT(24).

## OPTIONS FOR NDOL CALCULATIONS

Reading options of NDOL is performed from an OPT text (ASCII) file, which desired name and extension could appear in the command line after the molecular GEOMETRY file name when ndolXXXXXXXX program is called for execution. If no OPT file appears in the command line, a set of default options are used, as described in the following instructions.

DATA FORMAT: Options must be entered in the 25I3 FORTRAN format. It means that there are three contiguous spaces for each option field (or less if each option field is separated by commas). As an example, the line:

```
0000010140000000000001
```

Indicates that IOPT(1) = 0 (because the first three characters are 000), IOPT(2) = 1 (the following are 001), IOPT(3) = 14 (the following are 014), IOPT(4), IOPT(5) and IOPT(6) are all equal to 0, IOPT(7) = 1 and all resting IOPT(8) to IOPT(25) are also equal to 0. An alternative form for this options line is:

```
,1,14,,,,,1
```

where commas are used as indicators of finishing each three space field.

## OPTION VALUES:

IOPT(1): THE CALCULATION MODE:

```
CNDO/1 = 1
CNDO/2 = 2
CNDO/S = 3
CNDOL/11 = 4
CNDOL/12 = 5
CNDOL/21 = 6
CNDOL/22 = [7]
INDO/1 = 8
INDO/2 = 9
INDO/CI = 10
INDOL/11 = 11
INDOL/12 = 12
INDOL/21 = 13
INDOL/22 = 14
```

There are also combined Hamiltonians available, where the orbital kinetic energy and electron - nucleus attraction with the corresponding center ( $U_{\mu\mu}$ ) is calculated according one rule and the rest of the Hamiltonian according other:

```
CNDOL/11 with  $U_{\mu\mu}$  of CNDOL/12 = 45 (CNDOL/11/12)
CNDOL/11 with  $U_{\mu\mu}$  of CNDOL/21 = 46 (CNDOL/11/21)
```

CNDOL/11 with  $U_{\mu\mu}$  of CNDOL/22 = 47 (CNDOL/11/22)  
CNDOL/12 with  $U_{\mu\mu}$  of CNDOL/11 = 54 (CNDOL/12/11)  
CNDOL/12 with  $U_{\mu\mu}$  of CNDOL/21 = 56 (CNDOL/12/21)  
CNDOL/12 with  $U_{\mu\mu}$  of CNDOL/22 = 57 (CNDOL/12/22)  
CNDOL/21 with  $U_{\mu\mu}$  of CNDOL/11 = 64 (CNDOL/21/11)  
CNDOL/21 with  $U_{\mu\mu}$  of CNDOL/12 = 65 (CNDOL/21/12)  
CNDOL/21 with  $U_{\mu\mu}$  of CNDOL/22 = 67 (CNDOL/21/22)  
CNDOL/22 with  $U_{\mu\mu}$  of CNDOL/11 = 74 (CNDOL/22/11)  
CNDOL/22 with  $U_{\mu\mu}$  of CNDOL/12 = 75 (CNDOL/22/12)  
CNDOL/22 with  $U_{\mu\mu}$  of CNDOL/21 = 76 (CNDOL/22/21)

CNDOL/22 is the default mode (IOPT(1)=7).

A negative value of IOPT(1) inhibits calculations of electron excitations.

IOPT(2): HOW CONFIGURATION INTERACTION IS PERFORMED:

- = 0 Configuration interaction is calculated with up to the N lowest energy SCF states, where N is the number of basis orbitals.
- = 1 Configuration interaction is calculated as limited to the SCF states of lower energy than the HOMO absolute eigenvalue.
- = a Configuration interaction is calculated with a\*N terms, where N is the number of basis orbitals.

If IOPT (2) is less than 0 (with any value), a full single configuration interaction is performed (FullCIS).

IOPT(3): CALCULATION OF EXCITED STATE ELECTRON POPULATIONS:

- = 0 No excited state electron densities are calculated
- = M Excited state electron population and dipole moments are calculated for the M lowest energy CIS excitations.
- = 100+M indicates a large output, including files with printed orbital density matrices for the M lowest excited states.

NOTES:

- A negative value of IOPT(3) produces M \*.xyz output files with data for Jmol isosurfaces of the corresponding maps of electron charge distributions in ground and the M lowest excited states. Such .xyz files contain scripts for Jmol molecular graphics open source software.
- M cannot exceed 99.
- THIS OPTION WORKS "AS IS" ONLY SINCE VERSION 7.0.

IOPT(4): PARAMETERIZING ELEMENTS WITH NON-DEFAULT DATA:

- = number chemical elements desired to parameterize. Modes CNDO and INDO (IOPT(1) = 1, 2, 8 and 9) are not allowed to use third row elements.

Input formalism consists in adding to the line where options are entered, described above, as much as IOPT(4) new lines. Each one contains the information regarding the atomic number of the element to enter their parameters entered as the integer Z and PAR(K,8) real numbers containing the parameters for this element. The format I3,8F9.0 must be followed. It allows entering all but the atomic number (that must be an integer)

with explicit decimal dots and showing as much as necessary decimal fractions. If no dot is written, it is understood that it is a real number with no decimals. For example, the line:

```
0080001.23000002.8790000000015
```

means that  $Z = 8$ ,  $PAR(K,1)$  is 1.23,  $PAR(K,2)$  is 2.879 and  $PAR(K,3)$  is 15.0, being all  $PAR(K,4)$  to  $PAR(K,8)$  entered with a value of 0.0. The accounting variable  $K$  automatically takes values from 1 to a maximum of  $IOPT(4)$ . The above example line can also be written and understood by the program as:

```
8,1.23,2.87,15
```

or

```
8,1.23,2.87,15.
```

All energy values are entered as absolute values (no minus signs are required).

NDOL modes ( $IOPT(1) = 4 - 7, 11 - 14$ ) can include elements with  $Z > 18$  if their valence orbitals are not "d".

For all modes:

$PAR(K,1)$  = is the Slater exponent of "s" orbitals

$PAR(K,2)$  = is the Slater exponent of "p" orbitals

In the case of modes CNDO/1, /2 and /S, and INDO/1, /2 and /S ( $IOPT(1) = 1 - 3, 8 - 10$ ):

$PAR(K,3)$  = ionization potential of "s" electrons

$PAR(K,4)$  = ionization potential of "p" electrons

$PAR(K,5)$  = electron affinity of "s" electrons

$PAR(K,6)$  = electron affinity of "p" electrons

$PAR(K,7)$  = atomic resonance integral of element  $Z$

In the case of modes NDOL ( $IOPT(1) = 4 - 7, 11 - 14$ ):

$PAR(K,3)$  = ionization potential of "s" electrons

$PAR(K,4)$  = ionization potential of "p" electrons

$PAR(K,5)$  = electron affinity of "s" electrons

$PAR(K,6)$  = electron affinity of "p" electrons

In the case of modes INDOL ( $IOPT(1) = 11 - 14$ ):

$PAR(K,7)$  = INDO Slater Condon term for "s" electrons

$PAR(K,8)$  = INDO Slater Condon term for "p" electrons

If some parameter is missing, the program fills it with the included default for such element of the corresponding mode. The output file contains an initial table where all used mono-atomic data is displayed.

OBSERVE THAT IN THIS CASE SOME EXTRA LINES MUST FOLLOW THIS INDEX LINE IN THIS OPTION FILE, ACCORDING THE VALUE OF IOPT(4)

IOPT(5): SELECTING TWO ELECTRON INTEGRAL FORMULAS:

- = 0 Calculated with the modified Ohno's formula (1.0,1.0,1.0)<sup>7b</sup>
- = 1 Calculated with the Ohno's formula<sup>8</sup>
- = 2 Calculated with the Dewar-Sabelli-Klopman's formula<sup>9</sup>
- = 3 Calculated with the Mataga-Nishimoto's formula<sup>10</sup>
- = 4 Calculated with the modified Ohno's formula (1.0,0.9,1.0)
- = 5 Calculated with the Mataga-Nishimoto's formula using reduced values, as:

$$\gamma_{AB}^{lk} = \left[ \frac{(a_{AB}^{lk} + R_{AB})^2}{(a_{AB}^{lk} R_{AB})} \right]^{-1}$$

where:

$$a_{AB}^{lk} = \frac{2}{\gamma_{AA}^{ll} + \gamma_{BB}^{kk}}$$

- = 6 Calculated with the Mataga-Nishimoto's formula modified according K. Nishimoto<sup>11</sup>. C1 value is taken as 1.0. Only for IOPT(1) = 4 - 7, 11 - 14.

IOPT(6): SELECTING DESIRED EXCITED STATE MULTIPLICITY OUTPUT

- = 0 Both singlet and triplet CIS status are calculated.
- = 1 Only singlet CIS states are calculated
- = 2,3 Only triplet CIS states are calculated

IOPT(7): CONSIDERING MOLECULAR CHARGE

- = 0 The polyatomic system is neutral
- = q The charge of polyatomic system is "q"

IOPT(8): DESCRIBING THE ORBITAL ORIGIN AND DESTINY OF ELECTRON TRANSITIONS IN THE OUTPUT

- = 0 If IOPT(1) is not negative, the orbital origin and destiny of the lowest energy CIS electron transitions [both for singlets and triplets according the value of IOPT(6)] will be described in the program output. Only up to 50 states below 50000 cm<sup>-1</sup> (200 nm) will be detailed.
- = m If IOPT(1) is not negative, the orbital origin and destiny of the "m" lowest energy CIS electron transitions [both for singlets and triplets according the value of IOPT(6)] will be described in the program output. The maximum value of "m" is 999.

IOPT(9): BASIS ATOMIC ORBITAL OCCUPATION

- = 0 Basis atomic orbital occupations are taken as following the "aufbau" principle.

= 1 Atomic orbital occupation with maximum pairing.

This option is only significant when IOPT(1) = 4, 6, 11 and 13

#### IOPT(10): CORE REPULSION TERM CALCULATIONS

The present version calculates all several possible core - core repulsion terms included in the program and each one is detailed in the output.

#### IOPT(11): SELECTION OF AO'S EXPONENTS FOR CALCULATION OF OVERLAP INTEGRALS

- = 0 AO's exponents according Slater in Mulliken's paper<sup>12</sup>
- = 1 AO's exponents according Burns<sup>13</sup>
- = 2 AO's exponents according Clementi and Raimondi<sup>14</sup>. This is the default for NDOL procedures [IOPT(1) = 4 - 7, 11 - 14]

#### IOPT(12): SELECTION OF ONE ELECTRON BICENTRIC (RESONANCE) INTEGRALS

- = 0 Resonance integrals are calculated according the reported formulas for each IOPT(1) mode. In the case of NDOL modes it is calculated with the Wolfberg - Helmholtz formula<sup>15</sup>
- = 1 Resonance integrals are calculated according the modified Mulliken formula with  $c1=2.795396$  y  $c2=3.458896$ <sup>16</sup>

#### IOPT(13): NUMBER OF SCF ITERATIONS

- = NI Maximum number of allowed SCF iterations. The default value is 2000.

#### IOPT(14): SCF CONVERGENCE ACCELERATOR

- = 0 SCF convergence is performed on molecular orbital eigenvalues without any acceleration procedure.
- = 1 A damping factor of 0.5 is applied to project density matrix in each iteration to accelerate SCF convergence on molecular orbital eigenvalues.
- = 2 A damping factor is introduced in a subsequent line of this option file. It is entered as a real number in free format and will be applied to accelerate SCF convergence. Recommended values are between 0.2 and 0.4
- = 3 SCF convergence on eigenvalues with a damping factor of 0.05 towards Fock's matrix.
- = 4 Accelerated convergence with a damping factor on Fock's matrix supplied to the user. Such damping factor is introduced in a subsequent line of this option file. It is entered as a real number in free format. Recommended values are between 0.02 and 0.05
- < 0 Convergence is examined, in any previous option, on all occupied and non occupied orbitals. In the case where no damping factor is desired, iopt(14) must be smaller than -4.

OBSERVE THAT WHEN IOPT(14) IS 2, -2, 4 OR -4 AN EXTRA LINE CONTAINING THE VALUE OF THE DAMPING FACTOR IN FREE FORMAT MUST FOLLOW THE INDEX LINE OF THIS OPTION FILE [AND EVENTUAL-

LY, ALSO AND AFTER THE ATOM PARAMETER LINES INDICATED IN IOPT(4)].

IOPT(15): SCF CONVERGENCE THERESHOLD ON MOLECULAR EIGENVALUES

- = 0 The default convergence criterium on molecular eigenvalues is 0.00001 ev.
- = 1 A new convergente criterium is entered to refine or facilitate the SCF procedure in a subsequent line of this option file. It is entered as a real number in free format.

OBSERVE THAT WHEN IOPT(15) IS 1 AN EXTRA LINE CONTAINING THE VALUE OF THE NEW CONVERGENCE CRITERIUM FOR SCF ITERATIONS IN FREE FORMAT MUST FOLLOW THE INDEX LINE OF THIS OPTION FILE [AND EVENTUALLY, ALSO THE ATOM PARAMETER LINES INDICATED IN IOPT(4) AND/OR THE DAMPING FACTOR IN IOPT(14)].

IOPT(16): OPTIONS FOR INDO CORRECTIONS

- = 0 In cases of INDO and INDOL monocentric corrections F2 and G1 are taken from Pople, J. A.; Beveridge, D. L.; Dobosh, P. A., Approximate self-consistent molecular-orbital theory. V. Intermediate neglect of differential overlap. J. Chem. Phys. 1967, 47 (6), 2026-33.SE
- = 1 F2 and G1 are taken for Slater orbitals

IOPT(17): CONTROLS OUTPUT DATA

- = 0 The most compact possible compact output is given.
- = 1 Outputs the interatomic distance matrix.
- = 2 Outputs the two electron integral value matrix.
- = 3 Outputs an expanded SCF data information (120 spaces).
- = 4 Outputs the CI coefficient matrix.
- = 5 Outputs the quadratic CI coefficient matrix.
- = 6 Outputs the symmetry matrix of molecular orbitals.

Any combination of these numbers in the three available spaces will give the corresponding additional output values.

IOPT(18):

- = 0 No output file for potential surfaces is created
- = 1 A file for drawing potential surfaces is created with the extension .ptn.

IOPT(19): INITIAL GUESS SCF MATRIX

- = 0 The first SCF diagonalization occurs with a density matrix with null off diagonal terms and diagonal calculated according:

$$\text{CONST*CORE} - (1/2)(\text{MOLECULAR CHARGE})/N$$

where const = 0.125 for hydrogen and const = 0.5 for other atoms.

- = 1 The first SCF diagonalization occurs with a density matrix built after diagonalizing the overlap integral matrix
- = 2 The first SCF diagonalization occurs with a density matrix built after diagonalizing the overlap integral matrix with diagonal terms calculated according:

$$\text{CONST*CORE} - (1/2)(\text{MOLECULAR CHARGE})/N$$



where const = 0.125 for hydrogen and const = 0.5 for other atoms.

- = n The first SCF iteration is performed with a Fock's Hamiltonian built from a density matrix obtained after diagonalizing the one electron Hamiltonian and proceeding to a progressive increment of the electron interaction term in I=1,NAUX steps according to:

$$F(I) = H(MU,NU) + FFF(I)*G(MU,NU)$$

where:

H(MU,NU) is the MU,NU one electron matrix element

G(MU,NU) is the MU,NU two electron term

NAUX = 10\*IOPT(19)

FFF(I) = ((ln(I))/(ln(NAUX)))

n = 3 is a recommended value for this option.

IOPT(20): TEST OUTPUT

- = 0 Normal run  
= 1 The only output is input data to test parameters.

IOPT(21): INTERNAL CONTROL OF MOLECULAR GEOMETRY FORMAT

In the current version this parameter is automatically evaluated from the input file extension. IOPT(21) = 1 for .car files; IOPT(21) = 2 for .out files; IOPT(21) = 3 for .zmt files; IOPT(21) = 4 for .xyz files. See above for command line input options.

IOPT(22): MMH<sup>17</sup> INPUT/OUTPUT CONTROL

- = 0 No files for MMH input are produced  
= IOPT(5) An output file with energies calculated according IOPT(15) option is generated for MMH calculations. In this case, input geometry files can contain sequential geometries and the calculation finishes when the first empty line occurs or the end of input file is found.

NOTE: This option can not be used if the main input file is a MOPAC output file.

IOPT(23): CONTROL FOR REPULSION INTEGRAL OUTPUT FILE

- = 0 No output file with repulsion integrals is created.  
= 1 An output file called gammas.txt is produced with bicentric two electron integrals in columns as:

nat(i),nat(j),l+1(i),l+1(j),r(i,j),gamma(l+1(i),l+1(j))

IOPT(24): CONTROL OF MOLECULAR SYMMETRY

- = 0 Molecular symmetry is not accounted  
= 1 Molecular symmetry is assigned to Cs point group  
= 2 Molecular symmetry is assigned to C2 point group  
= 3 Molecular symmetry is assigned to C2v point group  
= 4 Molecular symmetry is assigned to D2h point group

Note: Input geometry is recommended to be in the plane XZ when molecular symmetry is wanted to be accounted. It is compulsory if the molecule is assigned to the C2v point group.

If IOPT(24) is not zero, a symmetry file SYM must be provided in the command line, as explained above. The name of this file is non fixed, although the extension .sym is recommended. This symmetry file must contain the following information:

Only if the molecule is assigned to the C2v point group:

First line:           Number of the atom that appears both in plane XY and XZ (Format I3).

All other symmetries, with the following lines:

One line:

NNXY = Number of atoms in the XY plane (Format I3)  
ICEN(I) = NNXY numbers of the atoms in the plane XY (Format NNXY\*I3)

One line:

NRXY = Number of atoms reflected by the XY plane (Format I3).  
ICEN1(I) = NRXY numbers of the atoms reflected by the XY plane, by pairs of them (Format NRXY\*I3)

One line:

NRYZ = Number of atoms reflected by the YZ plane (Format I3).  
ICEN2(I) = NRYZ numbers of the atoms reflected by the YZ plane, by pairs of them (Format NRYZ\*I3)

Important: Reading format is 25I3. Therefore, all lines reading more than 75 numbers must continue in the following line.

Example:

Porphin is assigned to the D2h point group. The SYM file for it, in one option, is:

```
002015016
036021026017019009020005025010030003029006034011037002036001033007035004031
012038008027013022014032018023024028
000
```

Where the initial line shows that there are 2 atoms in the XY plane, being them the number 15 and number 16. The following line indicates that 36 atoms are reflected by the XY plane, being them, by pairs, 21 and 26, 17 and 19, 9 and 20, etc. The following line is a continuation of the previous line to complete the 18 pairs (36 atoms). The last line says that there are no atoms reflected by the YZ plane.

IOPT(25): CONTROLS INTRAMOLECULAR DISPERSIVE ENERGY CALCULATION

The current version calculates intramolecular dispersive energy in any cases with a formula depending on  $1/R^{**6}$  between each pair of atoms. This formula was parameterized for simulating a correction of correlation energy similar to a full configuration interaction of double excited determinats.

IOPT(26)=0 original HINZE-JAFFE parameters are used .as are. for all atoms.

=1 NDOL parameters for s atomic orbitals of N and O are taken according default values of previous NDOL program versions.

NOTE: THIS OPTION WORKS "AS IS" ONLY SINCE VERSION 7.0.

#### **FAST INPUT AND DEFAULT CALCULATION**

NDOL2015 can be used with default option values in the case of neutral systems. In such case,

ndolXXXXXX coordinate\_file.extension

will provide a calculation with the CNDOL/22 Hamiltonian, including CIS of order n, where n is the total number of basis functions.

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