NDOL v. 8.2

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Theoretical Introduction

It is widely recognized that predicting the energy and general characteristics of excitons is crucial for modeling how light interacts with nanoscopic systems. This is also important for addressing urgent human needs related to energy conservation[1–3] and understanding key biological processes.[4–9] These predictions help explain the actual state changes that occur and allow us to model substances and materials with specific properties. However, it's important to note that calculations of excited electronic states can only be done using quantum mechanics approaches, which is currently the only framework capable of explaining these phenomena.

Quantum methods that are used nowadays for calculations of electron transitions in molecules are either *semiempirical*[10–18], *time-dependent density functional theories (TD-DFT)*[19–21] *or ab initio SCF*[22–24], all departing from their respective Fockians.

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 Fockians 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 form 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 Fockians 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 results are based just on molecular states designed to provide appropriate density functionals. Nevertheless, 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 Fockian[18,25,26] 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 the Fockian matrix of each molecule only two experimental or independently deduced 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 confidence 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 later versions are NDOL8.

The NDOL Fockians and calculation formulas

The theoretical development of CNDOL has been already described elsewhere[18,25,26]. 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 shown. 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:

$$H_{\mu\mu} = -I_{\mu} + \left(P_A^l - Z_A^l\right)\gamma_{AA}^{ll} - \tfrac{1}{2}\, p_{\mu\mu}\gamma_{AA}^{ll} + P_A^k\gamma_{AA}^{lk} - \sum_{B\neq A}\left(Z_B^l\gamma_{AB}^{ll} + Z_B^k\gamma_{AB}^{lk}\right) \tag{1}$$

$$H_{\mu\mu} = -I_{\mu} + \left(P_A^l - Z_A^l\right)\gamma_{AA}^{ll} + \left(1 - \tfrac{1}{2}\, p_{\mu\mu}\right)\gamma_{AA}^{ll} + P_A^k\gamma_{AA}^{lk} - \sum_{B\neq A} Z_B\Gamma_{AB}^l \tag{2}$$

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

$$\begin{aligned} H_{\mu\mu} = &-\tfrac{1}{2}\left(I_{\mu} + A_{\mu}\right) + \left(P_A^l - Z_A^l\right)\gamma_{AA}^{ll} + \left(P_A^k - Z_A^k\right)\gamma_{AA}^{lk} - \tfrac{1}{2}\left(p_{\mu\mu} - 1\right)\gamma_{AA}^{ll} \\ &- \sum_{B\neq A}\left(Z_B^l\gamma_{AB}^l + Z_B^k\gamma_{AB}^k\right) \end{aligned} \tag{3}$$

$$\begin{aligned} H_{\mu\mu} = &-\tfrac{1}{2}\left(I_{\mu} + A_{\mu}\right) + \left(P_A^l - Z_A\right)\gamma_{AA}^{ll} + P_A^k\gamma_{AA}^{lk} - \tfrac{1}{2}\left(p_{\mu\mu} - 1\right)\gamma_{AA}^{ll} \\ &- \sum_{B\neq A} Z_B\Gamma_{AB}^l \end{aligned} \tag{4}$$

that were named as variants CNDOL/21 (eq. 3) and CNDOL/22 (eq. 4), respectively. In this work we will are 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 ($H_{\mu\mu}$)[a].

$$H_{\mu\mu} = U_{\mu\mu} - \sum_{B\neq A} V^l_{AB}$$

CNDO origin	$U_{\mu\mu}$	$-\sum_{B\neq A} V^l_{AB}$	
		$-\sum_{B\neq A}(Z^l_B\gamma^{ll}_{AB} + Z^k_B\gamma^{lk}_{AB})$ **S**plit core charge: **S**	$-\sum_{B\neq A}(Z_B\Gamma^l_{AB})$ **C**omplete core charge: **C**
CNDO/1	$-I_\mu + \gamma^{ll}_{AA} - Z^l_A\gamma^{ll}_{AA} - Z^k_A\gamma^{lk}_{AA}$ **S**plit core charge: **1S**	CNDOL/1SS (CNDOL/11)	CNDOL/1SC
	$-I_\mu + \gamma^{ll}_{AA} - Z_A\gamma^{ll}_{AA}$ **C**omplete core charge: **1C**	CNDOL/1CS	CNDOL/1CC (CNDOL/12)
CNDO/2	$-\frac{1}{2}(I_\mu + A_\mu) + \frac{1}{2}\gamma^{ll}_{AA} - Z^l_A\gamma^{ll}_{AA} - Z^k_A\gamma^{lk}_{AA}$ **S**plit core charge: **2S**	CNDOL/2SS (CNDOL/21)	CNDOL/2SC
	$-\frac{1}{2}(I_\mu + A_\mu) + \frac{1}{2}\gamma^{ll}_{AA} - Z_A\gamma^{ll}_{AA}$ **C**omplete core charge: **2C**	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; Γ^l_{AB} is the interaction integral between an electron with azimutal 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.

It must be remarked that Hamiltonians 1SS and 2SS give identical results as well as 1CC and 2CC when monocentric orbital γ's are evaluated as the difference between orbital ionization potentials and their corresponding electron affinities (see below). It is a pure algebraic artifact resulting from evaluation of terms.

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

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

where

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

I_μ and A_μ are the valence state ionization potential and electron affinity of the atomic orbital (AO) μ on atom A, respectively; $p_{\mu\nu}$ is the density matrix element between the AO's μ and ν 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, Γ_{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 μ and ν, $f(q_{\mu\nu})$ is the projection factor onto a vector joining the atoms where orbitals μ and ν 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:

$$\gamma_{AA}^{ll} = I_\mu - A_\mu \tag{7}$$

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

$$\gamma_{AB}^{lk} = \left({a_{AB}^{lk}}^2 + cR_{AB}a_{AB}^{lk} + {R_{AB}}^2 \right)^{-1/2} \tag{8}$$

where

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

The original Mataga – Nishimoto's formula uses $c = 2$ and the Ohno's formula uses $c = 0$. The limit of bicentric γ_{AB}^{lk} corresponds to the monocentric γ_{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:

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

$$F_{\mu\nu} = H_{\mu\nu} - \tfrac{1}{2}\, p_{\mu\nu}\gamma_{AB}^{lk} \tag{11}$$

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

$$\Psi^{CIS} = \sum_s a_s \Phi_s \tag{12}$$

$$(\mathbf{H} - \mathbf{EI})\mathbf{a} = 0 \tag{13}$$

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 $i \to k$ or $j \to l$, where k and l are empty MO's. Diagonal and off-diagonal of CIS matrix terms are:

$$
\begin{aligned}
{}^{1}H_{ss} &= \varepsilon_k^{SCF} - \varepsilon_i^{SCF} - \langle ik|ik\rangle + 2\langle ik|ki\rangle \\
{}^{3}H_{ss} &= \varepsilon_k^{SCF} - \varepsilon_i^{SCF} - \langle ik|ik\rangle \\
{}^{1}H_{st} &= 2\langle jk|li\rangle - \langle jk|il\rangle \\
{}^{3}H_{st} &= -\langle jk|il\rangle
\end{aligned}
\tag{14}
$$

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 $[c_{i\mu}]$:

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

where n_{si} is the occupation number of each i MO in the s state (being $n_{si} = 0,\ 1,\ 2$ 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 $[a_{sJ}]$:

$$
p_{\mu\nu}^{J} = \sum_{s=1}^{M} a_{sJ}^{2} p_{s,\mu\nu} \tag{16}
$$

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.

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

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

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_{μ}'s and A_{μ}'s for each atomic orbital.

NDOL8.0 program

Windows installation

File `NDOL8.X.X.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 entry called “Command prompt”.

Linux installation

Linux kernels 2.6 or newer can manage the executable file ndol8.X.X.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 NDOL8 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 NDOL

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. Allowed extensions are .xyz, .car and .zmt, as explained below.

<coordinate_file.extension> is the main input file containing the geometry of the polyatomic system to be calculated. Extension .opt is recommended.

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

Program:

ndolXXXXXX for Linux is:

ndol8.X.X.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:

Ndol8.X.X.exe => For Windows XP SP2 and SP3, Vista, 7, 8, 10 and 11 kernels operated in the corresponding DOS command shell line.

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 NDOL v.8.X.X 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 0.0000
 C 1.3375808 1 0.000000 0 0.000000 0 1 0 0 0.0000
 C 1.4703292 1 120.141823 1 0.000000 0 2 1 0 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 Ångstroms. 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 “Control of Molecular Symmetry”

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 ndol8.X.X 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.

A detailed numerical input for options is described in the ANNEX. The commands to be entered are described in the following. Bold letters indicate the exact keywords to be used.

The calculation mode:

FOCK-CN1 = CNDO/1
FOCK-CN2 = CNDO/2
FOCK-CNS = CNDO/S
FOCK-2SS = CNDOL/2SS
FOCK-2CC = CNDOL/2CC
FOCK-2CS = CNDOL/2CS
FOCK-2SC = CNDOL/2SC

NOCIS Inhibits calculations of electron excitations.

How configuration interaction is performed:

LIMCI-aN Configuration interaction is calculated with a*N terms, where N is the number of basis orbitals.
LIMCI-IP Configuration interaction is calculated as limited to the SCF states of lower energy than the HOMO absolute eigenvalue.
LIMCI-FC Full single configuration interaction is performed (FullCIS).

Calculation of excited state electron populations:

EXPOP n Excited state electron population and dipole moments are calculated for the n lowest energy CIS excitations. It also produces n *.xyz output files with data for Jmol software isosurfaces of the corresponding maps of electron charge distributions in ground and the n lowest excited states. Such .xyz files contain scripts for Jmol molecular graphics of all molecules in the system by open source software.

Parameterizing elements with non-default data:

NEWPARAM m “m” is the number chemical elements contained in the input data file desired to be newly parameterized. Modes FOCK-CNxare not allowed to use third row elements.

The default Slater orbital exponents for NDOL procedures are sourced from the work of Clementi and Raimondi[27] while the valence state ionization potentials and electron affinities are derived from Hinze and Jaffé[28]. The current option allows for the consideration of different parameters, including an adaptation for the "s" orbitals of nitrogen and oxygen, which were set as defaults in earlier versions of NDOL.

The input formalism requires the creation of a new file named 'atomic_parameters.opt' in the default directory, containing “m” lines. Each line must specify the atomic number of the element, denoted as the integer Z, followed by real numbers in PAR(K,8) that represent the parameters for that element. The format must adhere to FORTRAN specifications: I3 for the atomic number and 8F9.0 for the parameters. This format permits the entry of all values except for the atomic number (which must be an integer consistent with the I3 format), allowing explicit decimal points and as many decimal places as necessary. If no decimal point is included, it is interpreted as a real number with no decimal component. For example, a line might appear as follows:

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 “m”. 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).

FOCK-2CC, **2SS**, **2SC** and **2CS** modes 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 **FOCK-CN1, FOCK-CN2** and **FOCK-CNS**:

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 **FOCK-2SS, FOCK-2CC, FOCK-2CS** and **FOCK-2SC**:

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

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.

Selecting two electron integral formulas:

GAMMA n

n = 0 Calculated with the modified Ohno’s formula (1.0,1.0,1.0)[25]
n = 1 Calculated with the Ohno’s formula[29]
n = 2 Calculated with the Dewar-Sabelli-Klopman’s formula[30,31]
n = 3 Calculated with the Mataga-Nishimoto’s formula[32,33]
n = 4 Calculated with the modified Ohno’s formula (1.0,0.9,1.0)[25]
n = 5 Calculated with the Mataga-Nishimoto’s formula using reduced values, as:

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

where:

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

n = 6 Calculated with the Mataga-Nishimoto's formula modified according K. Nishimoto[34]. C1 value is taken as 1.0. Only for modes **FOCK-2SS, FOCK-2CC**, **FOCK-2CS** and **FOCK-2SC** .

Selecting desired excited state multiplicity output:

If **NOCIS** is not holding, both singlet and triplet manifold CIS output are calculated and printed. Nevertheless:

CIS1 Only singlet CIS states are calculated
CIS3 Only triplet CIS states are calculated

Considering molecular charge:

CHARGE m The total charge of polyatomic system is "m"

Describing the orbital origin and destiny of electron transitions in the output:

MOTRANS m The program output will detail the orbital origins and destinations of the "m" lowest energy CIS electron transitions, applicable to both singlet and triplet states based on the values of CIS1 or CIS2. The maximum value for "m" is 999. By default, with m set to 0 and missing **MOTRANS** keyword in the option file, the output will include information on the orbital origins and destinations of the lowest energy CIS electron transitions, anyway, but only up to 50 states with energies below 50000 cm^{-1} (200 nm) will be provided in the details.

Occupation of the basis atomic orbital:

MAXPOCCU Basis atomic orbital occupations are taken as following the "aufbau" principle. However, if **MAXPOCCU** keyword appears the atomic orbital occupation will be with maximum pairing. This option is only significant when modes are **FOCK-2SS** and **FOCK-2SC**

Selection of AO's exponents for the calculation of overlap integrals:

EXPSLAT is the default taken AO's exponents according Slater in Mulliken's paper[35]
EXPBURNS AO's exponents are taken according to Burns[36]
EXPCLEM AO's exponents are taken according Clementi and Raimondi[27]. This is the default for NDOL modes **FOCK-2SS**, **FOCK-2CC**, **FOCK-2CS** and **FOCK-2SC.**

Selection of one electron bicentric (resonance) integrals;

BETAMOD Resonance integrals are calculated according the modified Mulliken formula with c1=2.795396 y c2=3.458896.[37] If this keyword is missing, and by default, resonance integrals are calculated according the reported formulas for each **FOCK-** mode. In the case of NDOL modes they are calculated with the Wolfberg – Helmholz formula[38].

Allowed number of SCF iterations

MAXIT m Maximum number of allowed SCF iterations IS “m”. The default value is 2000.

Designing the SCF convergence accelerator

DAMP05 A damping factor of 0.5 is applied to the density matrix in each iteration to accelerate the convergence on the molecular orbital eigenvalues of the SCF procedure.

DAMPP a A damping factor “a” is applied to the density matrix in each iteration to accelerate the convergence on the molecular orbital eigenvalues of the SCF procedure. Recommended values are between 0.2 and 0.4.

DAMPF005 A damping factor of 0.05 is applied to the Fock matrix in each iteration to accelerate the convergence on the molecular orbital eigenvalues of the SCF procedure.

DAMPF a A damping factor “a” is applied to the Fock matrix in each iteration to accelerate the convergence on the molecular orbital eigenvalues of the SCF procedure. Recommended values are between 0.02 and 0.05

By default, the SCF convergence is performed on molecular orbital eigenvalues without any acceleration procedure.

SCF convergence threshold on molecular eigenvalues:

CONVLMT a A convergence criterium “a” is entered to refine or facilitate the SCF procedure.

The default convergence criterium on molecular eigenvalues is 0.00001 ev.

Controls of extra output data:

OUTR Outputs the interatomic distance matrix.
OUTGAM Outputs the two-electron integral value matrix.
OUTSCFXX Outputs an expanded SCF data information (120 spaces).
OUTCIC Outputs the CI coefficient matrix.
OUTCIC2 Outputs the quadratic CI coefficient matrix.
OUTSYMMO Outputs the symmetry matrix of molecular orbitals.

Initial guess of the SCF matrix:

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

CONST*CORE - (1/2)(MOLECULAR CHARGE)/N

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

SCF0S The first SCF diagonalization occurs with a density matrix built after diagonalizing the overlap integral matrix

SCF0SQ The first SCF diagonalization occurs with a density matrix built after diagonalizing the overlap integral matrix with diagonal terms calculated according:

CONST*CORE - (1/2)(MOLECULAR CHARGE)/N

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

SCF0AA a 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*a
FFF(I) = ((ln(I)/(ln(NAUX)))

SCF0AA3 Is the previous option where a = 3, as a preferred value.

Testing output:

TEST The only output produced are input data to test parameters.

Control for repulsion integral output file:

OUTFGAM 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))

Control of molecular symmetry for selected point groups:

SYMCS The molecular symmetry of the input molecular system is assigned to Cs point group

SYMC2 The molecular symmetry of the input molecular system is assigned to C2 point group

SYMC2V The molecular symmetry of the input molecular system is assigned to C2v point group

SYMD2H The molecular symmetry of the input molecular system 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 the above **SYMxxx** keywords are included 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.

FAST INPUT AND DEFAULT CALCULATION

NDOL 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/2CC Hamiltonian, including CIS of order n, where n is the total number of basis functions.

ANNEX

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:

000001014000000000001

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/1SS)
CNDOL/12 = 5 (CNDOL/1CC)
CNDOL/21 = 6 (CNDOL/2SS)
CNDOL/22 = [7] (CNDOL/2CC)

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/1CS)
CNDOL/11 with $U_{\mu\mu}$ of CNDOL/21 = 46 (CNDOL/2SS)
CNDOL/11 with $U_{\mu\mu}$ of CNDOL/22 = 47 (CNDOL/2CS)
CNDOL/12 with $U_{\mu\mu}$ of CNDOL/11 = 54 (CNDOL/1SC)
CNDOL/12 with $U_{\mu\mu}$ of CNDOL/21 = 56 (CNDOL/2SC)
CNDOL/12 with $U_{\mu\mu}$ of CNDOL/22 = 57 (CNDOL/2CC)
CNDOL/21 with $U_{\mu\mu}$ of CNDOL/11 = 64 (CNDOL/1SS)
CNDOL/21 with $U_{\mu\mu}$ of CNDOL/12 = 65 (CNDOL/1CS)
CNDOL/21 with $U_{\mu\mu}$ of CNDOL/22 = 67 (CNDOL/2CS)
CNDOL/22 with $U_{\mu\mu}$ of CNDOL/11 = 74 (CNDOL/1SC)
CNDOL/22 with $U_{\mu\mu}$ of CNDOL/12 = 75 (CNDOL/1CC)
CNDOL/22 with $U_{\mu\mu}$ of CNDOL/21 = 76 (CNDOL/2SC)

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

If default parameters are used options:

4= 6= 46=64
5= 7= 57=75
45=65=47=67
54=56=74=76.

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 of all molecules in the system by open source software. If IOPT(2).eq.1 it can only bring this output for the first excited state.
- 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.

Default Slater orbital exponents for NDOL procedures are taken from Clementi and Raimondi[8] and valence state ionization potentials and electron affinities from Hinze and Jaffé[9]. Different parameters must only be considered by the present option, including an adaption for N and O “s” orbitals that were defaults for previous versions of NDOL. 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)[7b]
= 1 Calculated with the Ohno’s formula[10]
= 2 Calculated with the Dewar-Sabelli-Klopman’s formula[11]
= 3 Calculated with the Mataga-Nishimoto’s formula[12]
= 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:

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

where:

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

= 6 Calculated with the Mataga-Nishimoto’s formula modified according K. Nishimoto[13]. 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^{-1} (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[14]
= 1 AO’s exponents according Burns[15]
= 2 AO’s exponents according Clementi and Raimondi[8]. 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 – Helmholz formula[16]
= 1 Resonance integrals are calculated according the modified Mulliken formula with c1=2.795396 y c2=3.458896[17]

IOPT(13): MUMBER 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 accellerate 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 Accellerated 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 EVENTUALLY, 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 potencial 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:

CONST*CORE - (1/2)(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:

CONST*CORE - (1/2)(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[18] 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 repulsión 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.

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