

Natural Transition Orbital Calculations in the RASSI module of *OpenMolcas*

Introduction

This document is a manual for the natural transition orbital (NTO) calculation that is done in the RASSI module of *OpenMolcas*. It includes discussion of the theory of NTOs, an explanation of the code, and several input and output examples of the NTO calculations with the RASSI module.

Prior to adding the NTO calculation to the RASSI module, *OpenMolcas* already contained code for NTO calculations (and other analysis tools) in the WFA module

<https://molcas.gitlab.io/OpenMolcas/sphinx/users.guide/programs/wfa.html>

but the new implementation extends the capability in two key ways:

1. An external package, in particular *TheoDORE*,¹ is required for visualizing the NTOs calculated in the WHA module; however, NTOs calculated in the RASSI module can be visualized with *luscus*,

<https://sourceforge.net/projects/luscus/>

which is a more commonly used external package for *OpenMolcas* users than *TheoDORE*. The new implementation prints out the NTO files in the same format as how other orbital files, such as ScfOrb file and RasOrb file, are printed. So the output file can also be used for three-dimensional graphics with the GRID_IT module.

2. WHA cannot calculate NTOs for states with different symmetries, but the new implementation in RASSI can do this, as shown in Section 4 for this document.

To distinguish the NTO calculations in two modules, those performed in the RASSI module will be called RASSI-NTO, or simply NTO, and those performed in the WFA module will be called WFA-NTO. The comparison between RASSI-NTO and WFA-NTO is only made in Section 4, so all discussions in other sections of this module refer to the implementation in the RASSI module.

1. Theory

The definition of NTOs was originally proposed by Martin,² whose paper is cited by the manuals of *Gaussian 16*,³ *Q-Chem*⁴ and the WFA module in *OpenMolcas* (although, as discussed below, the implementations in these codes do not necessarily agree precisely with Martin's definitions).

Furthermore, Martin's NTOs are defined only for configuration interaction with single excitations (CIS) in Ref. 2; however the implementation of NTOs discussed here is for multiconfigurational (MC) wave functions generated in the *RASSCF* module, so in this section we explain the extension of NTOs to those multiconfigurational calculations. In addition, this section explains a mistake in Martin's paper. We will also show that we avoid the mistake in similar ways as other papers^{5,6} do.

1.1 Martin's definition

Here we use a CIS calculation with a restricted Hartree-Fock (RHF) wave function for the ground state to explain the theory in Martin's paper.

Suppose there are N_o occupied orbitals and N_v virtual orbitals in the ground state. An NTO calculation starts with the transition density matrix (TDM) from the ground state to state J . An element of a TDM is as follows:

$$D_{pq}^J = \sum_{\sigma} \langle J | a_{p\sigma}^{\dagger} a_{q\sigma} | 0 \rangle \quad (1)$$

where p and q are spatial orbitals with q ranging from 1 to N_o and p ranging from N_o+1 to N_{Bas} (which is equal to $N_o + N_v$); and σ is the spin.

Then two symmetric matrices are constructed from the TDM:

$$\mathbf{M}^J = (\mathbf{D}^J)^T \mathbf{D}^J \quad (2)$$

$$\mathbf{N}^J = \mathbf{D}^J (\mathbf{D}^J)^T \quad (3)$$

The eigenvector matrix (denoted \mathbf{U}^J) of \mathbf{M}^J multiplying the occupied canonical MO coefficient matrix (\mathbf{C}_o), which is a matrix of the coefficients of basis functions that form canonical MOs, gives the hole NTO coefficient matrix, \mathbf{C}_h^J , which is a matrix of the coefficients of basis functions that form NTOs. Similarly, the particle NTO coefficient matrix, \mathbf{C}_p^J , is a multiplication of the eigenvector matrix (\mathbf{V}^J) of \mathbf{N}^J and the virtual canonical MO coefficient matrix (\mathbf{C}_v). The formulas are as follows:

$$\mathbf{C}_h^J = \mathbf{U}^J \mathbf{C}_o \quad (4)$$

$$\mathbf{C}_p^J = \mathbf{V}^J \mathbf{C}_o \quad (5)$$

$$\mathbf{M}^J \mathbf{U}^J = \boldsymbol{\lambda}^J \mathbf{U}^J \quad (6)$$

$$\mathbf{N}^J \mathbf{V}^J = \boldsymbol{\kappa}^J \mathbf{V}^J \quad (7)$$

where $\boldsymbol{\lambda}^J$ and $\boldsymbol{\kappa}^J$ are eigenvalue matrices of \mathbf{M}^J and \mathbf{N}^J , respectively. If there are n nonzero eigenvalues of \mathbf{M}^J , one will also find n non-zero eigenvalues of \mathbf{N}^J . Each nonzero eigenvalue of \mathbf{N}^J equals one of the eigenvalues of \mathbf{M}^J . A particle NTO and a hole NTO that correspond to the same eigenvalue are called a particle-hole pair, and the square root of their eigenvalue is called an excitation amplitude, $\sqrt{\lambda_i}$ (or $\sqrt{\kappa_i}$), where i is the index of i th particle NTO, hole NTO or particle-hole pair, and λ_i (or κ_i) is a diagonal element of the matrix $\boldsymbol{\lambda}^J$ (or $\boldsymbol{\kappa}^J$) in the i th row.

Martin's paper says that the sum of the eigenvalues for particle NTOs or hole NTOs is 1 for CIS wave functions. This is a mistake made in Martin's paper. In the next section we show that it is not right and reformulate Equation (1) so that the sum is 1 for CIS wave functions.

1.2 NTOs of He atom

1.2.1 NTO using Martin's definition

According to Martin's definition, one may consider a He atom with three s -type basis functions. The ground state wave function and the CIS excited state wave function are

$$\Psi_1 = |\phi_1\alpha\phi_1\beta| \quad (8)$$

$$\Psi_2 = c_1 \frac{1}{\sqrt{2}} [|\phi_1\alpha\phi_2\beta| - |\phi_1\beta\phi_2\alpha|] + c_2 \frac{1}{\sqrt{2}} [|\phi_1\alpha\phi_3\beta| - |\phi_1\beta\phi_3\alpha|] \quad (9)$$

where $\{\phi_i\}$ is a set of orthonormal canonical MOs. Since both wave functions are normalized, we have $c_1^2 + c_2^2 = 1$.

The transition density matrix is

$$\mathbf{D}^1 = \begin{pmatrix} \sqrt{2}c_1 \\ \sqrt{2}c_2 \end{pmatrix} \quad (10)$$

And the two symmetric matrices are

$$\mathbf{M}^1 = (2) \quad (11)$$

$$\mathbf{N}^1 = \begin{pmatrix} 2c_1^2 & 2c_1c_2 \\ 2c_1c_2 & 2c_2^2 \end{pmatrix} \quad (12)$$

The eigenvalues are 2 and 0 for \mathbf{N}^1 and 2 for \mathbf{M}^1 .

This is clearly contradictory to Martin's claim that the sum is 1.

1.2.2 A modification of Martin's definition

However, if one calculates NTOs for α and β orbitals separately, one can obtain eigenvalues that sum to unity. Define

$$D_{pq,\sigma}^J = \langle J | a_{p\sigma}^\dagger a_{q\sigma} | 0 \rangle \quad (13)$$

Since we are calculating NTOs for singlet states, we may use the calculations for α spins as an example since the NTO calculation for β spin is the same as that for α spin.

$$\mathbf{D}_\alpha^1 = \begin{pmatrix} \frac{1}{\sqrt{2}}c_1 \\ \frac{1}{\sqrt{2}}c_2 \end{pmatrix} \quad (14)$$

$$\mathbf{M}_\alpha^1 = \begin{pmatrix} 1 \\ 2 \end{pmatrix} \quad (15)$$

$$\mathbf{N}_\alpha^1 = \begin{pmatrix} \frac{1}{2}c_1^2 & \frac{1}{2}c_1c_2 \\ \frac{1}{2}c_1c_2 & \frac{1}{2}c_2^2 \end{pmatrix} \quad (16)$$

The sum of eigenvalues of \mathbf{N}_α^1 is 0.5 for either particle NTOs or hole NTOs; therefore the sum of eigenvalues of both α and β is unity. The NTOs calculated for each spin are called spin NTOs. For singlet systems, one can find an α NTO that has the same spatial part as that of a β NTO; therefore the spatial part of that α NTO or that β NTO is called a spatial NTO, whose eigenvalue is defined here to be the sum of the eigenvalues of the α NTO and the β NTO.

The NTOs calculated from a CIS calculation are called CIS spin NTOs.

Ideas similar to that of spin NTOs are also found in other papers. The paper by Mayer, although it does not explicitly use the terminology of NTOs, calculates the spin NTOs for each spin separately.⁵ The paper by Plasser *et al.* also calculates the NTOs from a transition density matrix for spin orbitals.⁶

1.3 Extension of NTO theory

The idea behind an NTO calculation can be extended to complete active space self-consistent field (CASSCF), complete active space configuration interaction (CASCI), restricted active space self-consistent field (RASSCF), and restricted active space configuration interaction (RASCI) wave functions. The transition density matrix is still defined as equation (9), but p and q are the indices of active orbitals. This leads to a square TDM whose number of rows or columns is the number of active orbitals.

We use a RASCI calculation on He to explain how this method works, still with three s -type basis functions. In this RASCI calculation, one starts with RHF orbitals as initial orbitals, putting the occupied MO in the RAS1 space, no MO in the RAS2 space, and two MOs in the RAS3 space, and allowing at most one hole and one particle in the RAS1 and RAS3 spaces, respectively; then one calculates the first two states without optimizing orbitals. This calculation leads to two wave functions that are equal to equation (4) and (5), respectively. However, according to the new definition, the TDM and the other two matrices are as follows:

$$\mathbf{D}_\alpha^1 = \begin{pmatrix} 0 & 0 & 0 \\ \frac{1}{\sqrt{2}}c_1 & 0 & 0 \\ \frac{1}{\sqrt{2}}c_2 & 0 & 0 \end{pmatrix} \quad (17)$$

$$\mathbf{M}_\alpha^1 = \begin{pmatrix} \frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (18)$$

$$\mathbf{N}_\alpha^1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \frac{1}{2}c_1^2 & \frac{1}{2}c_1c_2 \\ 0 & \frac{1}{2}c_1c_2 & \frac{1}{2}c_2^2 \end{pmatrix} \quad (19)$$

The matrices in section 1.2.2 are submatrices of the corresponding ones in equations (13)-(15).

2. Method in the RASSI module of OpenMolcas

2.1 Methodological details

This RASSI-NTO calculation uses the method defined in section 1.3, namely the method that calculates active-space spin NTOs. It starts with a two-state transition density matrix, which is calculated by CASSCF, RASSCF, CASCI, or RASCI. These four kinds of calculation are performed in the RASSCF module. The RASSCF module prints out the CI coefficients of configuration state functions (CSFs) that are expressed in a state-averaged natural orbital (SA-NO) basis. The TDM is calculated from those CI coefficients; therefore the matrices calculated from the TDM, for example, \mathbf{M}_α^1 , are expressed in terms of SA-NOs, and their eigenvectors are applied to SA-NOs to generate NTOs.

The code that calculates active-space spin NTOs in the RASSI module is called NTOCalc, and it uses the methodology discussed in section 1.3. It calculates α spin NTOs without converting them to spatial NTOs if the wave functions are singlets.

If the active orbitals are put in different irreducible representations (irrep) when a symmetry is imposed to the wave function, the MO coefficients are stored in a no-symmetry form, as explained next. Suppose there are four irreps, having 1, 2, 3, and 4 basis functions, respectively, and there are two active orbitals, one in the second irrep and the other in the fourth irrep. Then the code first creates a new 2×6 (two rows for the two active orbitals, and six columns for the number of basis functions that are used for active orbitals) matrix to store the MO coefficients. The MO coefficients of the first active orbital will be put in the first and the second element in the first row of the new matrix, and the last four elements in the first row are zero. The MO coefficients of the second active orbital will be put in the last four elements in the second row, and the first two elements in the second row are zero. This new form of storing MO coefficients is what we call a no-symmetry form. The new matrix is the MO matrix that will be used to calculate NTOs, and the NTOs will be converted back to their original form to be printed out. For the previous example, the NTOs will be printed out as one orbital in the second irrep and the other the fourth irrep.

If two states have different symmetries, the TDM is calculated with a rotated biorthogonal MO basis.⁷ In this situation, the rotations are applied to the SA-NOs that are rotated once in the biorthogonalization process.

We now define excitation contribution (EC) for a particle-hole pair:

$$EC_{\text{NTO},i}^\sigma = \frac{\lambda_i^\sigma}{\sum_i \lambda_i^\sigma} \quad (20)$$

where λ_i^σ is eigenvalue of the i th particle-hole pair with spin σ , and i ranges from 1 to the number of active orbitals.

NTOCalc prints the excitation amplitude, eigenvalue, and excitation contribution of each pair of particle and hole NTOs. It also prints NTO files in the current working directory (where the rest of the output is printed) with a name in the form *Project.NTOrb.IState_JState.Spin.NTOType*. *Project* is the name of the project given by the variable \$Project, *IState* is an index assigned by the RASSI module for a state in the first JobIph file (see the explanation in Sections 3.1.2 and 3.2.2), and *JState* is an index assigned by the RASSI module for a state in the second JobIph file. *Spin* is either *a* for α or *b* for β , and *NTOType* is PART for particle NTOs and HOLE for hole NTOs. For example, a file named H2.NTOrb.1_2.a.PART has the information on α particle NTOs, between the first state and the second state assigned by the RASSI module. The excitation contributions are stored in places where the occupation numbers are stored for

other orbital files (for example, .ScfOrb, .RasOrb). NTO files can be used by the GRID_IT module to generate .lus files.

2.2 Input keywords

The input lines to activate an NTO calculation are as follows:

```
>>COPY $Scratch/$Project.JobIph $Scratch/JOB001
>>COPY $Scratch/$Project.JobIph $Scratch/JOB002
&RASSI
NTOC
NR OF JOBIPHS = 2 1 1
1; 2
```

The Emil commands are used to generate two JobIph files named JOB001 and JOB002.

&RASSI is the name of the module in which RASSI-NTO calculation can be performed.

NTOC is the keyword to activate the NTO calculation in the RASSI module. Without it the RASSI module will not do NTO calculations.

NR OF JOBIPHS is the keyword that specifies how many JobIph files to read, how many states in each JobIph file to use and which states in each JobIph file to use for the calculations performed in this module. The numbers 2 1 1 means there are two JobIph files, in the first file one state will be used and in the second file one state will be used. The number 1; 2 in the following line means in the first JobIph file the first state will be used, and in the second JobIph file the second state will be used. More information of this keyword can be found on the OpenMolcas manual.

3. Examples

3.1 An example for an NTO calculation from a RASCI calculation

3.1.1 Input File

```

&GATEWAY
Coord=C2H4.xyz
Basis=3-21G
Group=C1

&SEWARD

&SCF

&RASSCF
Lumorb
CIONLY
Spin=1
CIROOT= 2 2 1
INACTIVE=0
NACTEL= 16 1 1
RAS1=8
RAS2=0
RAS3=18

>>COPY $Scratch/$Project.Joblph $Scratch/JOB001
>>COPY $Scratch/$Project.Joblph $Scratch/JOB002

RASSI
NTOC
NR OF JOBIHPS = 2 1 1
1; 2

&Grid_it
All
FileOrb=$Scratch/C2H4.NTOrb.1_2.a.PART
>> COPY $CurrDir/C2H4.lus $CurrDir/2APart.lus

&Grid_it
All
FileOrb=$Scratch/ C2H4.NTOrb.1_2.a.HOLE
>> COPY $CurrDir/C2H4.lus $CurrDir/2AHole.lus

```

This is an input file that does a RASSI-NTO calculation for RASCI wave functions with RHF orbitals; the wave functions are the same as CIS wave functions for the first excited state. Modules GATEWAY to RASSCF generate RASCI wave functions, RASSI with the keyword NTOC calculates NTOs, and Grid_it modules produce output files that can be used to create pictures of the NTOs from the files, C2H4.NTOrb.1_2.a.PART and C2H4.NTOrb.1_2.a.HOLE.

3.1.2 Output

In the output file the information on natural transition orbitals is as follows:

```

State:      1  2
JobIph:    1  2
Root nr:   1  2
*****
*          NATURAL TRANSITION ORBITALS          *
*          BETWEEN STATE 1 AND STATE 2          *
*****
NTO CALCULATION ONLY DONE FOR ALPHA SPIN BECAUSE THE WAVE FUNCTION IS A SINGLET, SO
ALPHA NTOS ARE EQUAL TO BETA ONES

NATURAL TRANSITION ORBTIAL INFORMATION FOR ALPHA SPIN
-----

```

EXCITATION AMPLITUDE	EIGENVALUE	EXCITATION CONTRIBUTION(%)	HOLE NTO		PARTICLE NTO	
			SYMMETRY	INDEX	SYMMETRY	INDEX
0.68636	0.47109	94.22	a	26	a	26
0.12109	0.01466	2.93	a	25	a	25
0.07269	0.00528	1.06	a	24	a	24
0.06853	0.00470	0.94	a	23	a	23
0.05165	0.00267	0.53	a	22	a	22
0.04000	0.00160	0.32	a	21	a	21

```

-----
SUM OF EIGENVALUES 0.50000
-----
*****
*          END OF NATURAL TRANSITION ORBITALS          *
*          BETWEEN STATE 1 AND STATE 2          *
*****

```

The figures of the particle and hole NTOs are shown in the bottom row in Figure 1.

There are three lines before the NTO section, each line has 1 and 2. This part is called state information in this document. In the first line starting with State, 1 means the first state assigned by the RASSI module and 2 means the second state assigned by the module. In the second line starting with JobIph:, 1 indicates that the first module-assigned state comes from the first JobIph file, i.e. JOB001 in the scratch space, according to the input example in section 3.1.1; 2 indicates that the second module-assigned state comes from the second JobIph file, i.e. JOB002. The third line shows that the first module-assigned state is the first state in the first JobIph file, and the second module-assigned state is the second state in the second JobIph file. From this information we know that *JState* is 1 and that *Jstate* is 2 for the name of the NTO files produced for this state, which is the second state in the second JobIph file.

Before the table the output says that the NTO calculation is only done for α spin if the wave functions are singlets. Then it prints out the results for α spin NTOs.

The output prints out the excitaiton amplitudes, the eigenvalues and the excitation contribution of each pair of hole and particle NTOs whose eigenvalue is greater than 10^{-5} . Since only α -spin information is printed out, the sum of eigenvalues should be (and is) 0.5. This is different from *Q-Chem* or *Gaussian*,

whose output writes the eigenvalues of what we define as spatial NTOs. (See section 4 for more information.)

The program also prints the symmetry and the index of each hole NTO or particle NTO. The index of a particle NTO is its index only among the particle NTOs with the same spin, because a particle NTO and a hole NTO are calculated separately from two different matrices (and NTOs with different spins are calculated separately too). Therefore, for non-singlet systems, it is strongly encouraged to visualize the particle NTOs and hole NTOs for each spin.

The figures of the hole and particle NTOs from *Gaussian 16* are also shown in Figure 1. We can clearly see that with the same set of ground-state and excited-state wave functions, *Gaussian 16* and the RASSI-NTO code give the same set of NTOs.

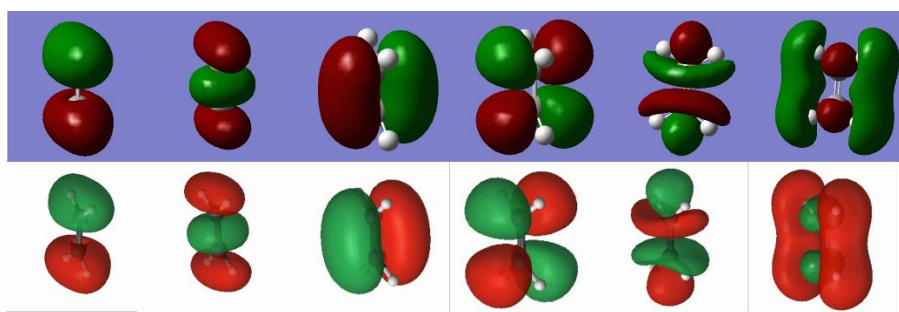


Figure 1. Hole NTOs and particle NTOs by *Gaussian 16* (top row) and OpenMolcas (bottom row). From the left to the right are three hole spin NTOs with the excitation amplitudes in an increasing order (0.07, 0.12, and 0.69) and three particle spin NTOs with the excitation amplitudes in a decreasing order (0.69, 0.12, and 0.07).

3.2 An example of an NTO calculation using wave functions with different symmetries

3.2.1 Input example

```

&GATEWAY
Coord=C2H4.xyz
Basis=3-21G
Group=Full
&SEWARD
&SCF
>> COPY $CurrDir/C2H4.ScfOrb $Scratch/INPROB
&RASSCF
LumOrb
Symmetry=1
Spin=1
INACTIVE=2 0 1 0 0 0 0 0
RAS2=2 2 2 1 1 0 1 0
NActele=10 0 0
CIRoot=1 1 1
>> COPY $Scratch/C2H4.Joblph $Scratch/JOB001
>> COPY $CurrDir/C2H4.ScfOrb $Scratch/INPROB
&RASSCF
LumOrb
Symmetry=3
Spin=1
INACTIVE=2 0 1 0 0 0 0 0
RAS2=2 2 2 1 1 0 1 0
NActele=10 0 0
CIRoot=1 1 1
>> COPY $Scratch/C2H4.Joblph $Scratch/JOB002
RASSI
NTOC
Nr of Joblphs=2 1 1
1;1
&Grid_it
All
FileOrb=$Scratch/C2H4.NTOrb.1_2.a.PART
>> COPY $CurrDir/C2H4.lus $CurrDir/2APart.lus
&Grid_it
All
FileOrb=$Scratch/C2H4.NTOrb.1_2.a.HOLE
>> COPY $CurrDir/C2H4.lus $CurrDir/2AHole.lus

```

Here, CASSCF wave functions with different symmetries are used in the RASSI module.

3.2.2 Output

Below is the part of the output that shows the state information and the eigenvalues and eigenvectors of NTOs.

State: 1 2
 Joblph: 1 2
 Root nr: 1 1

EXCITATION AMPLITUDE	EIGENVALUE	EXCITATION CONTRIBUTION(%)	HOLE NTO		PARTICLE NTO	
			SYMMETRY	INDEX	SYMMETRY	INDEX
0.66496	0.44218	94.13	b1u	1	b3g	1
0.12930	0.01672	3.56	b3g	1	b1u	1
0.08173	0.00668	1.42	ag	4	b2u	3
0.04858	0.00236	0.50	b2u	3	ag	4
0.03810	0.00145	0.31	b1g	1	b3u	2
0.01886	0.00036	0.08	ag	3	b2u	2
SUM OF EIGENVALUES 0.46974						

The particle and hole NTOs are shown in Figure 2.

The state information shows that the NTOs will be for the second module-assigned state, which is the first state in the second Joblph file. The NTO files are named C2H4.NTOrb.1_2.a.PART and C2H4.NTOrb.1_2.a.HOLE.

The CASSCF ground state has two important configurations, $(\pi)^2$ and $(\pi^*)^2$, respectively. This is a major difference of the wave functions in this section and the wave functions in Section 3.1, and it leads to an interesting result that both the π and the π^* orbitals can be important hole NTOs or particle NTOs.

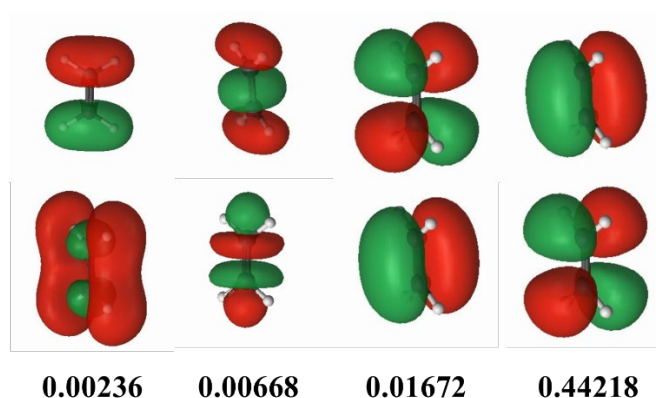


Figure 2. Hole NTOs (top row) and particle NTOs (bottom row) of C₂H₄ in D_{2h} symmetry. The numbers are the eigenvalues for each particle-hole pair.

In contrast to the previous example, the sum of eigenvalues is not 0.5, this is because the wave functions correspond to full configuration interaction within the active space, and excitations higher than singles do not contribute to the eigenvalues.

3.3 An example for an NTO calculation for non-singlets

3.3.1 Input example

```

&Gateway
Coord=C2H4.xyz
Group=C1
Basis=3-21G
&Seward
&SCF
UHF
Spin=2
Charge=1
&RASSCF
CIOnly
Charge=1
Spin=2
Inactive=0
RAS1=7
RAS2=1
RAS3=18
Nactele=15 1 1
CIRoot=2 2 1
THRS
1.0D-08 1.0D-04 1.0D-1
>> COPY $Scratch/$Project.JobIph $Scratch/JOB001
>> COPY $Scratch/$Project.JobIph $Scratch/JOB002
RASSI
NTOC
Nr of JOBIPHS = 2 1 1
1; 2
&Grid_it
All
FileOrb=$Scratch/ C2H4.NTOrb.1_2.a.PART
>> COPY $CurrDir/C2H4.lus $CurrDir/2APart.lus
&Grid_it
All
FileOrb=$Scratch/C2H4.NTOrb.1_2.a.HOLE
>> COPY $CurrDir/C2H4.lus $CurrDir/2AHole.lus
&Grid_it
All
FileOrb=$Scratch/C2H4.NTOrb.1_2.b.PART
>> COPY $CurrDir/C2H4.lus $CurrDir/2BPart.lus
&Grid_it
All
FileOrb=$Scratch/ C2H4.NTOrb.1_2.b.HOLE
>> COPY $CurrDir/C2H4.lus $CurrDir/2BHole.lus

```

This is an input file for the NTO calculation of a doublet system, $C_2H_4^+$.

3.3.2 Output

Below is the part of the output that shows the state information and the eigenvalues and eigenvectors of NTOs.

State: 1 2
 Joblph: 1 2
 Root nr: 1 2

EXCITATION AMPLITUDE	EIGENVALUE	EXCITATION CONTRIBUTION(%)	HOLE NTO		PARTICLE NTO	
			SYMMETRY	INDEX	SYMMETRY	INDEX
0.02928	0.00086	66.37	a	26	a	26
0.01517	0.00023	17.82	a	25	a	25
0.01369	0.00019	14.51	a	24	a	24
0.0041	0.00002	1.3	a	23	a	23
SUM OF EIGENVALUES 0.00129						

NATURAL TRANSITION ORBITAL INFORMATION FOR BETA SPIN

EXCITATION AMPLITUDE	EIGENVALUE	EXCITATION CONTRIBUTION(%)	HOLE NTO		PARTICLE NTO	
			SYMMETRY	INDEX	SYMMETRY	INDEX
0.97005	0.94099	97.75	a	26	a	26
0.14703	0.02162	2.25	a	25	a	25
SUM OF EIGENVALUES 0.96261						

Since the wave functions are not singlets, the information for two spins is printed out.

The NTOs of $C_2H_4^+$ in C_s symmetry is shown in Figure 3. The excited state corresponds to a β electron excited from the σ orbital, see the top left one in Figure 3(b), to the π orbital, see the bottom left one in Figure 3(b). The eigenvalues show that the first excited state is strongly dominated by β electron excitations.

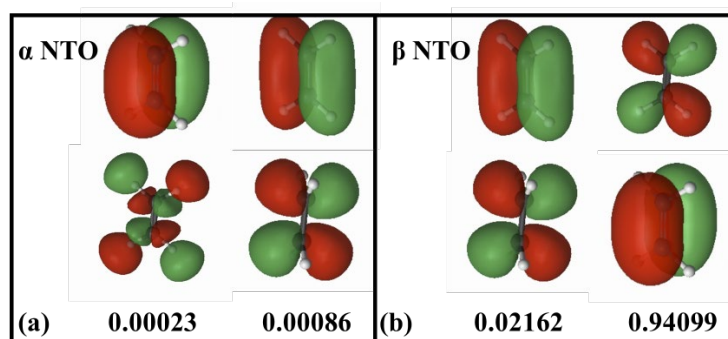


Figure 3. Hole NTOs (top) and particle NTOs (bottom) in α spin (a) and β spin (b) of $C_2H_4^+$ in C_s symmetry. The eigenvalues (from left to right) for each pair are 0.00023 and 0.00086 (α NTOs), respectively, and 0.02162 and 0.94099 (β NTOs), respectively.

4. A comparison among the NTO calculations using different programs

As mentioned previously, the WFA module also calculates NTO in *OpenMolcas*. Table 1 compares the printed eigenvalues of the NTO calculations in the RASSI module (corresponding the RASSI column), in the WFA module (called WFA-NTO in this section), by *Gaussian*, and by *Q-Chem*. Other codes do not distinguish between spatial NTOs and spin NTOs, so we first present the eigenvalues printed out in the output, and from this we deduce whether the eigenvalues are for spatial NTOs or spin NTOs.

All the calculations done in Table 1 use 3-21G basis set. Two systems are tested, C_2H_4 and $C_2H_4^*$, whose geometries are shown in Appendix A. The NTO calculations are performed for neutral and charged C_2H_4 and $C_2H_4^*$.

First, we compare the ratio of the eigenvalues from RASSI-NTO and WFA-NTO. The RASSI-NTO code calculates only α spin NTOs if the wave functions are singlets, and calculates both α and β NTOs in other cases. We find that the ratio is 2 for singlet systems, and 1 for the doublet system. We conclude that WFA-NTO prints out the eigenvalues of spatial NTOs when the wave functions are singlets and of spin NTOs when the wave functions are not singlets.

We also find that the ratio of *Gaussian* eigenvalues to the *Q-Chem* ones is 1 for singlets and 2 for the doublet. This suggests that Q-Chem prints out spatial NTOs when the wave functions are singlets, and spin NTOs when the wave functions are not.

The ratios of *Gaussian* eigenvalues to the RASSI-NTO eigenvalues are always two, and the output says “alpha occ. eigenvalues” even when the wave functions are singlets (see the examples in Appendix B on the output of *Gaussian*), we conclude that *Gaussian* always prints out spin NTOs and multiplies the eigenvalues by two before they are printed out.

Then we consider symmetries using the fifth NTO calculation in Table 1 as an example. In this case, the wave functions are in the D_{2h} point group, the ground state has A_g symmetry, and the first excited state has B_{2u} symmetry. As explained in section 2.1, the RASSI-NTO code uses an intermediate matrix to store the MO coefficients in a no-symmetry way, and it also uses the biorthonormalized MO basis when it gives results (eigenvalues and NTO coefficients) for NTOs of an excited state with a different symmetry from the ground state. On the contrary, the WFA-NTO code gives zeros for the eigenvalues, indicating that the code does not apply to cases where the excited state has a different symmetry from the ground state. This is an aspect where the RASSI-NTO is more general than the WFA-NTO.

Table 1. Eigenvalues of spin or spatial NTOs calculated by RASSI-NTO, WFA-NTO, and Gaussian

Molecule	Method	2S+1	Group	Excited State ^a	RASSI	WFA	Gaussian	Q-Chem	WFA/RASSI ^b
C ₂ H ₄	CIS or HF/RASCI (16;1;1,8,0,18) ^c	1	C ₁	1	0.47109	0.9422	0.94211		2
					0.01466	0.0293	0.0293		
					0.00528	0.0106	0.01061		
C ₂ H ₄	SA(2)- CASCF(2,2) ^d	1	C ₁	1	0.4999	0.9998			2
					0.0001	0.0002			
C ₂ H ₄	SA(2)- CASCF(2,2)	1	C ₁	2	0.00021	0.0004			2
					0.00021	0.0004			
C ₂ H ₄	SA(2)- CASSCF(10,8) 2,2,2,1,1,0,1,0 ^e	1	D _{2h}	2	0.03726	0.0745			2
					0.03675	0.0735			
					0.00013	0.0003			
C ₂ H ₄	CASSCF(10,8) 2,2,2,1,1,0,1,0	1	D _{2h}	1	0.44218	0			n.a.
					0.01672	0			
					0.00668	0			
C ₂ H ₄ *	CIS	1	C ₁	1	0.47282	0.9456	0.94558	0.9456	2
					0.01378	0.0276	0.02755		
					0.00497	0.0099	0.00997		
C ₂ H ₄ ⁺	HF/RASCI (15;1;1,7,1,18)	2	C ₁	1	0.0009/0.9410 ^f	0.00086/0.94099			1
					0.0002/0.0216	0.00023/0.02162			
					0.0002/0.0000	0.00019/0.00000			
C ₂ H ₄ ^{*+}	CIS	2	C ₁	1		0.00371/1.90584	/0.9530		n.a.
						0.00037/0.09001	/0.0450		
						0.00007/0			

^aThe ground state is dominated by the $(\pi)^2(\pi^*)^0$ configuration, and, except in the CIS calculation, the second most important configuration is $(\pi)^0(\pi^*)^2$. The first excited state is a state dominated by the $(\pi)^1(\pi^*)^1$ configuration. The second excited state is dominated by the $(\pi)^0(\pi^*)^2$ configuration, and, except in the CIS calculation, the second most important configuration is $(\pi)^2(\pi^*)^0$.

^bThis is the ratio of eigenvalues calculated by the WFA module and that by the RASSI module.

^cA RASCI calculation that uses HF orbitals is the same as a CIS calculation because there are 16 active electrons, 1 hole in RAS1, 1 particle in RAS3, 8 orbitals in RAS1, no orbitals in RAS2, and 18 orbitals in RAS3.

^dThis is a CASSCF calculation including two active electrons and two active orbitals, averaged over 2 states.

^eThe eight numbers are the numbers of active orbitals in a_g, b_{3u}, b_{2u}, b_{1g}, b_{1u}, b_{2g}, b_{3g} and a_u symmetries.

^fThe eigenvalues are shown as $\alpha_eigenvalue/\beta_eigenvalue$.

Appendix A. The geometries of C₂H₄ and C₂H₄*

Two geometries are used for calculations in Table 1. The first one is the geometry of ethylene, which has D_{2h} symmetry. The second one pulls the last H atom of ethylene 0.1 Ångstrom above the XY plane so that the molecule has no symmetry.

The input geometries are as follows, where the unit is Å.

C₂H₄

```
C 0.000000 0.660645 0.000000
H 0.918431 1.232652 0.000000
H -0.918383 1.232708 0.000000
C 0.000000 -0.660645 0.000000
H -0.918431 -1.232652 0.000000
H 0.918383 -1.232708 0.000000
```

C₂H₄*

```
C 0.000000 0.660645 0.000000
H 0.918431 1.232652 0.000000
H -0.918383 1.232708 0.000000
C 0.000000 -0.660645 0.000000
H -0.918431 -1.232652 0.000000
H 0.918383 -1.232708 0.100000
```

Appendix B. The eigenvalues printed out by *Gaussian* and *Q-Chem*

This section shows that *Gaussian* multiplies the eigenvalues of spin NTOs by 2 before they are printed out.

Below is a part of the output for the NTO eigenvalues of He with 3-21G basis set with *Gaussian*.

```
Alpha occ. eigenvalues -- 1.00000
Alpha virt. eigenvalues -- 1.00000
```

Starting with the α transition density matrix for He in the 3-21G basis set (using the definition in Section 1.2.2 because the NTO calculations presented here from *Gaussian* and *Q-Chem* are for CIS states)

$$\mathbf{D}_{\alpha}^{01} = \left(\frac{1}{\sqrt{2}} \right) \quad (16)$$

This gives

$$\mathbf{M}_{\alpha} = (0.5) \quad (17)$$

This means that the eigenvalue should be 0.5 for the α NTO, but *Gaussian* prints it out as 1.

Another proof is from the output of calculations for C₂H₄⁺ spin NTOs by *Gaussian* and by *Q-Chem*.

Below is a part of the output for C₂H₄⁺ NTO calculation with *Gaussian*:

```
Alpha occ. eigenvalues -- 0.00007 0.00037 0.00371
Alpha virt. eigenvalues -- 0.00371 0.00037 0.00007 0.00000 0.00000
...
Beta occ. eigenvalues -- 0.09001 1.90584
Beta virt. eigenvalues -- 1.90584 0.09001 0.00000 0.00000 0.00000
```


Below is the part of the output for $C_2H_4^+$ NTO calculation with *Q-Chem*:

e-/hole pair 1 beta : ampl = 0.9762 (95.3 %)

e-/hole pair 2 beta : ampl = 0.2121 (4.5 %)

The largest eigenvalue of the β spin NTOs is 0.976, and we have $1.90584/(0.9762)^2=2.00$. (Here note that *Q-Chem* reports the amplitudes.)

For the NTO calculation between the first excited state and the ground state of He_2^+ , *Gaussian* gives 1.97780 for the largest eigenvalue, and *Q-Chem* gives $(0.9944)^2$. The ratio is, again, 2.00.

In conclusion, when we compare the results of the NTO calculation that is done in the RASSI module with those that are performed in *Gaussian*, we should be aware that there is a ratio of 2 for the eigenvalues of spin NTOs.

References

- ¹ Plasser, F. TheoDORE: a package for theoretical density, orbital relaxation, and exciton analysis. URL: <http://theodore-qc.sourceforge.net/>.
- ² Martin, R. L. Natural transition orbitals. *J. Chem. Phys.* **2003**, *118*, 4775-4777.
- ³ Frisch, M. J.; *et al.* *Gaussian 16*, revision B.01; Gaussian, Inc.: Wallingford, CT, 2016.
- ⁴ Shao, Y. *et al.* Advances in molecular quantum chemistry contained in the Q-Chem 4 program package. *Mol. Phys.* **2014**, *113*, 184-215.
- ⁵ Mayer, I. Using singular value decomposition for a compact presentation and improved interpretation of the CIS wave functions. *Chem. Phys. Lett.* **2007**, *437*, 284-286.
- ⁶ Plasser, F.; Wormit, M.; Dreuw, A. New tools for the systematic analysis and visualization of electronic excitations. I. Formalism. *J. Chem. Phys.* **2014**, *141*, 024106.
- ⁷ Malmqvist, P.-Å.; Roos, B. O. The CASSCF state interaction method. *Chem. Phys. Lett.* **1989**, *155*, 189-194.