

Solid State Adaptive Natural Density Partitioning (SSAdNDP) Manual

T.R. Galeev, B.D. Dunnington, J.R. Schmidt, A.I. Boldyrev

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1 Introduction

Solid State Adaptive Natural Density Partitioning (SSAdNDP) [1] is an extension of the AdNDP method [2] to periodic systems and as such was derived from a recently introduced periodic implementation [3] of the Natural Bond Orbital (NBO) analysis [4]. SSAdNDP allows the interpretation of chemical bonding in systems with translational symmetry in terms of classical lone pairs and two-center bonds, as well as multi-center delocalized bonding. The bonding pattern is expressed as a set of n -center – 2-electron (nc -2e) bonds. This manual only explains the usage of the program. A more detailed description of the algorithm may be found in the SSAdNDP paper [1].

The most recent version of this manual and the SSAdNDP program may be found (*coming soon*) online at: chem.usu.edu/~boldyrev/ssadndp.php

The Periodic NBO code is available from [the Schmidt group](http://the.Schmidt.group) at University of Wisconsin-Madison: schmidt.chem.wisc.edu/nbosoftware

The AdNDP code, method description and a manual can be found at: chem.usu.edu/~boldyrev/adndp.php

The NBO (Version 6.0) web-page is nbo6.chem.wisc.edu

Please cite the SSAdNDP (ref [1]), Periodic NBO (ref [3]), AdNDP (ref [2]) and NBO (see [4]) when publishing results obtained with SSAdNDP.

SSAdNDP program is a free software and comes with no guarantee. Please report bugs, any feedback or questions by e-mail: timur.galeev@aggiemail.usu.edu

2 Installation and Pre-SSAdNDP Steps

The package includes (somewhat modified) Projection, Periodic NBO, and Visualization codes written by Benjamin D. Dunnington and [Prof. JR Schmidt](#) [3]. The program does not perform full NBO analysis though (the Periodic NBO code is used to obtain the density matrix in Natural Atomic Orbital (NAO) basis; the bond search and further steps are then performed by SSAdNDP). The Periodic NBO program is [available](#) from the Schmidt group at University of Wisconsin-Madison.

The program is interfaced with the [Vienna Ab Initio Simulation Package \(VASP 4.6\)](#) [5] and requires a projection [3] of the plane-wave bands obtained from VASP to a Gaussian-type orbital basis set. See [Projection/READ.ME.txt](#) for details on installation and usage of the Projection code. [Intel Fortran Compiler](#) and [Intel Math Kernel Library](#) are required to compile the programs. Paths to the compiler and the libraries should be modified in the [Projection/makefile](#) and [SSAdNDP/Makefile.template](#) files. For the latter, the [mkmf](#) Perl script is used to obtain the makefile.

3 SSAdNDP General Search

Similar to AdNDP, SSAdNDP general search algorithm looks for all possible combinations of n atoms potentially contributing to an nc -2e bond. The user specifies what types of bonds the program should search for, usually starting with 1c-2e bonds (lone pairs) and proceeding to 2c-2e bonds, 3c-2e bonds, etc. A bond on a particular combination of n atoms is accepted if its occupation number (ON) exceeds the user-specified threshold (usually close to 2.00 |e|). After all combinations of n atoms have been tested, the electron density of the accepted bonds (if any) is depleted from the density matrix and the search continues for $(n+1)c$ -2e bonds. Thus, the number of accepted nc -2e bonds (predetermined by ON thresholds) will influence all further search results. Users new to the AdNDP/SSAdNDP approach are advised to familiarize themselves with the manual and examples accompanying the original [AdNDP](#) program. The general goal is to obtain a maximally localized and symmetry consistent bonding pattern with bond occupancies reasonably close to 2.00 |e|.

3.1 Running General Search

Assuming the programs have been installed properly and the projection has been performed successfully, the following will run the SSAdNDP analysis:

```
$/path-to-SSAdNDP/ssadndp.exe SSAdNDP.inp
```

The name of the input file determines the type of the analysis to be performed (SSAdNDP.inp for general search and SSAdNDP-UD.inp for the user-directed form) and cannot be altered. Two additional (optional) command-line arguments can be specified: a name for a 'check-point file' and either 'T' (True - update the file) or 'F' (False - do not update the file). 'T' is the default value and may be omitted. Thus, with

```
$/path-to-SSAdNDP/ssadndp.exe SSAdNDP.inp resid.dat
```

the program will attempt to read the current density matrix from **resid.dat** to use it for (further) bond search. If **resid.dat** is not present in the working directory, the program will calculate the density matrix from scratch. After SSAdNDP analysis, the updated density matrix will be written to the file.

The following can be used to read the density matrix from **resid.dat** without rewriting it.

```
$/path-to-SSAdNDP/ssadndp.exe SSAdNDP.inp resid.dat F
```

Use of check-point files may save time during analysis of large systems by storing the density matrix obtained at the intermediate steps (see Section 3.3 and is necessary whenever general search is followed by user-directed search (see Section 4).

An output file called **SSAdNDP.out** will be written during SSAdNDP run.

3.2 Input Files

The following is an example of the input file that can be used for analysis of a wavefunction obtained from a *spin non-polarized* (VASP card ISPIN=1) calculation. A copy of this file can be found in **Manual/sample_inputs_non-polarized/**.

```

GENERAL SEARCH INPUT FILE
Prepare files for visualization: T/F?
F
Number of different types of bonds in general search:
4
Number of centers, ON threshold, Distance threshold:
1 1.70 0
2 1.90 4.0
3 1.90 7.0
4 1.75 7.0

```

First, the user chooses (line 3) whether the files necessary for bond visualization (see Section 5) should be created during the search. For large systems writing those files may take a while, thus, the user may opt not to create them during trial searches. Next, the number of different types of bonds (varying in number of centers, n) in general search should be specified (line 5). Then, for every bond type, n , occupation number and distance thresholds are listed starting at line 7. Thus, in this example, the program will first search for lone pairs. All of the lone pairs with $ON > 1.70 |e|$ will be accepted and their electron density will be removed from the density matrix. The program will then look for 2c-2e bonds (with $ON > 1.90 |e|$) between any two atoms located within 4.0 Å of each other. The density corresponding to accepted 2c-2e bonds will be depleted and the search for 3c-2e bonds and then 4c-2e will be performed in a similar way.

For *spin polarized* systems (VASP card ISPIN=2) searches of different types of bonds (and/or thresholds) for different spins are generally required (in this case the ONs are expected be close to 1.00 $|e|$). This is reflected in the input file format. The following is an example and the corresponding sample file can be found in `Manual/sample_inputs_spin-polarized/`.

```

GENERAL SEARCH INPUT FILE
Prepare files for visualization: T/F?
F
Number of different types of bonds in general search (spin 1):
2
Number of centers, ON threshold, Distance threshold (spin 1):
1 0.8 0.
2 0.9 7.
Number of different types of bonds in general search (spin 2):
2
Number of centers, ON threshold, Distance threshold (spin 2):
1 0.8 0.
2 0.89 7.

```

3.3 Output and Check-point Files

The output file, `SSAdNDP.out`, is created in the working directory during SSAdNDP run. 'Initial density' is the sum of the diagonal elements of the current density

matrix. If the density matrix is calculated from scratch, the initial density should be equal to the total number of electrons per unit cell. Occupation numbers and atom numbers and their cell locations are written for every bond revealed. The cells are indexed relative to a 'central' cell (0, 0, 0). Thus, an atom indexed 2 (1, 0, -1) would therefore be the image of atom 2 of the central unit cell (0, 0, 0) obtained via translation by $(\vec{a} - \vec{c})$.

For large systems, calculation of the density matrix from scratch may be time consuming. Therefore, an SSAdNDP run with '0' in line 5 of the input file and a name of a non-existent file as the second command line argument:

```
$/path-to-SSAdNDP/ssadndp.exe SSAdNDP.inp chkfilename
```

can be performed in order to write the initial density matrix to a check-point file, which can later be used for trial SSAdNDP runs:

```
$/path-to-SSAdNDP/ssadndp.exe SSAdNDP.inp chkfilename F
```

Similarly, a check-point file may be saved at any step when the user is satisfied with some intermediate results (say, lone pairs and 2c bonds) before proceeding to further bond searches (say, trying different options for 3c, 4c, etc). In this case, the '**Initial density**' at the top of the SSAdNDP.out file of the new trial run should be equal to the '**Residual density**' written at the bottom of the output of the previously saved results.

4 SSAdNDP User-Directed Search

As the number of centers increases, the number of possible combinations quickly rises and general search becomes computationally intractable. The user-directed implementation of the SSAdNDP analysis allows a user to probe specific combinations of atomic centers for bonding. This may bias the resulting analysis as compared to a general search, but it allows the user to obtain chemically meaningful results on a particular fragment of interest. Also, often most of the density can be localized using general search, leaving only a few reasonable and symmetry-consistent multi-center fragments to probe manually.

Running the program with SSAdNDP-UD.inp input file will start the user-directed search.

```
$/path-to-SSAdNDP/ssadndp.exe SSAdNDP-UD.inp chkpoint_from_gen F
```

User-directed analysis is usually performed after general search, thus the residual matrix should be read from a check-point file.

The input file requires explicit specification of sets of atomic centers ('fragments') to probe for bonding. Thus, after indicating the total number of fragments (line 5), the user will enter the number of atoms in each fragment and list all the atoms and their locations respective to the 'central' cell. Finally, several potential bonds may be present on the same fragment, thus the number of bonds to be probed should be provided for every fragment. The formatting should be similar to the following example (Manual/sample.inputs_non-polarized/SSAdNDP-UD.inp):

```

USER-DIRECTED SEARCH INPUT FILE
Prepare files for visualization: T/F?
F
Number of fragments to search on:
2
Number of centers on fragment 1:
6
Atom numbers, cell a,b,c:
1, 0 0 0
2, 0 0 0
7, 0 -1 0
5, 0 -1 0
6, -1 0 0
4, -1 0 0
Number of bonds on fragment 1:
1
Number of centers on fragment 2:
7
Atom numbers, cell a,b,c:
1, 0 0 0
2, 0 0 0
3, 0 0 0
4, 0 0 0
5, 0 0 0
6, 0 0 0
7, 0 0 0
Number of bonds on fragment 2:
1

```

The ON will be computed for the first specified potential bond, the corresponding density will be depleted and then the program will proceed to the next bond (fragment). It is important to note that unlike NBO hybrids, AdNDP/SSAdNDP bonds are not rigorously orthogonal [2]. Although, this may lead to overestimation of bond ONs due to partial double use of some NAOs by neighbouring bonds, relaxing orthogonality ensures that for a given n , the results of general search are independent of the order in which the atom combinations are searched yielding symmetry-consistent set of bonds. Unlike general SSAdNDP search (where the density is depleted after all bonds for a given n are revealed), in the user-directed form, the density matrix is updated after every single bond's ON is found. Thus, for two adjacent symmetrically equivalent bonds, the resulting ONs will be different, if some bond overlap is present. In such case, the averaged occupation may be accepted as the bonds' ONs. On the other hand, for any two (or several) symmetrically equivalent neighbouring bonds, the degree of overlap (and ON overestimation) may be evaluated by comparing their ONs in consecutive user-directed SSAdNDP analysis.

For a spin-polarized wavefunction, the SSAdNDP-UD.inp has a different formatting allowing different inquiries for the two spins
(Manual/sample_inputs_spin-polarized/SSAdNDP-UD.inp):

```

USER-DIRECTED SEARCH INPUT FILE
Prepare files for visualization: T/F?
T
Number of fragments to search on (spin 1):
1
Number of centers on fragment 1:
6
Atom numbers, cell a,b,c:
1, 0 0 0
2, 0 0 0
3, 0 0 0
4, 0 0 0
5, 0 0 0
6, 0 0 0
Number of bonds on fragment 1:
3
Number of fragments to search on (spin 2):
1
Number of centers on fragment 1:
6
Atom numbers, cell a,b,c:
1, 0 0 0
2, 0 0 0
3, 0 0 0
4, 0 0 0
5, 0 0 0
6, 0 0 0
Number of bonds on fragment 1:
2

```

5 Visualization

If 'T' is entered in line 3 of `SSAdNDP.inp` or `SSAdNDP-UD.inp`, the program will create files called `vis_gs_nc-bonds.out` (separate file for every set of *nc*-2e bonds in general search) or `vis_ud_bonds.out` (one file for all bonds revealed by user-directed search). For spin-polarized calculations two sets (spin-1 and spin-2) of similar files will be created.

Visualization/visual.f90 code written by B.D. Dunnington can be used to transform these files to Gaussian cube format. The program can be compiled with [Intel Fortran Compiler](#):

```
$ ifort visual.f90 -o visual.exe
```

The program is executed with one of the `vis*.out` files as its first command line argument. In the following example, a cube file for each 3c-2e bond will be created.

```
$ ./path-to-Visualization/visual.exe vis_gs_3c-bonds.out
```


Optionally, three additional command line arguments - the numbers of grid points used for numerical integration (determining the resolution) in each cell direction - may be specified. The default values are all 50.

In general, the bonds may span over unit cells, therefore, by default, the bonds are represented in a supercell containing the 'central' and the neighbouring cells. A file called `lattice_vec.cube`, containing atomic coordinates, is also created by `visual.exe`. A visualization software, such as VESTA ([Visualization for Electronic and STructural Analysis](#)) [6], can be used to visualize the cube files. In VESTA, `lattice_vec.cube` should first be opened (uncheck 'Show sections', check 'Show isosurfaces') and then the bonds can be superimposed on the lattice as imported phases (`Edit` \Rightarrow `Edit Data` \Rightarrow `Phase ...` \Rightarrow `Import`). The supercell point (0.5, 0.5, 0.5) of the new layer should be placed at (0, 0, 0) of the Layer 0 (coinciding with the origin of `lattice_vec.cube`'s cell).

If none of the bonds spans over the central unit cell (a finite molecule in a large unit cell might be an example), additional command line argument 'F' can be used (the default value is 'T') in order to represent all of the bonds within the 'central' unit cell only:

```
$/path-to-Visualization/visual.exe vis_gs_3c-bonds.out 50 50 50 F
```

References

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