User Manual

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License

AtomAccess

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We request that any results obtained through the use of *AtomAccess* are accompanied by the following reference:

A. J. McMillan, M. Sienkowska, P. Di Lorenzo, G. K. Gransbury, N. F. Chilton, M. Salamone, A. Ruffoni, M. Bietti and D. Leonori, Practical and Selective sp^3 C–H Bond Chlorination via Aminium Radicals. *Submitted*, **2020**.

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1. Introduction

AtomAccess is a ray-tracing program that assesses the steric hindrance at any atom in a molecule or molecular fragment. It reports the total percentage visible solid angle (%VSA) of the atom of interest and the %VSA of all individual clusters of accessible points. The %VSA of a cluster represents the fraction of the central atom surface that is accessible from a particular direction. Figure 1 illustrates the visible directions for a Dy atom in two different $[Dy(Cp^{R})_2]^+$ cations; the left cation has most visible points grouped in one large cluster, and the right cation has multiple small clusters of visible points.

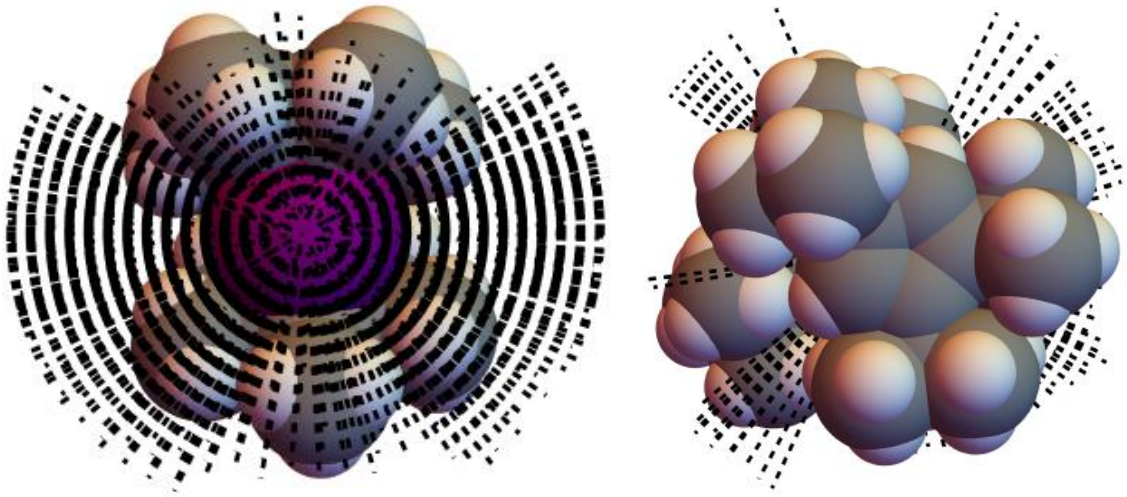

Figure 1. Two $[Dy(Cp^{R})_2]^+$ cations with black dashed lines to show visible angular points. Colour code: dysprosium (purple), carbon (grey), hydrogen (white). Calculation performed on $[Dy(Cp^*)_2]^+$ (left) and $[Dy(Cp^{ttt})_2]^+$ (right) fragments of crystal structures[1,2] using *AtomAccess* with a ZCW integration density of 9, non-bonded radii and csv option to generate a list of visible angular points, which were then visualised using Wolfram Mathematica 12.1.[3]

2. User Guide

AtomAccess is a Python script written for Python 3.[4] In this manual, < > brackets will be used to represent text that can be substituted with a name or value. *AtomAccess* is run in the command line as follows:

python AtomAccess.py <filename> *args

Where *args can include any of the optional arguments given in Table 1. This will generate a .out file containing the results. The input file must have the .xyz extension and follow standard xyz file conventions: the first line is the number of atoms, the second line is a comment line (ignored by *AtomAccess*) and the subsequent lines give the atomic symbol and x, y and z coordinates of each atom in Å. The atom of interest ("central atom") is assumed to be the first atom listed unless specified otherwise using the "--atom" option (Table 1).

Table 1. Optional arguments for *AtomAccess*

Optional arguments (*args)	**Description**
--help *or* -h	Print help documentation
--atom <N> *or* -a <N>	Specifies the atom of interest ("central atom") by the order in which it appears. Default: N = 1, first atom listed.
--density <N> *or* -d <N>	ZCW integration density, N is an integer, $0 \leq N \leq 15$. Table 2 shows the number of directions for each value of N. Default: N = 7. Testing indicates a minimum value of 7 should be used for reliable results and values above 11 tend not to improve accuracy. Keep this value constant when comparing structures.
--radialstep <N> *or* -r <N>	Radial step size in Å. Default N: 0.05. A value of 0.05 is generally sufficient. In some cases slightly more accurate results will be obtained with 0.02 or 0.01.
--clusterthreshold <N> *or* -t <N>	%VSA cluster threshold. Clusters of visible points below this size will be discarded and considered as blocked. Default N: 0, no clusters discarded.
--covalent	Override to use covalent radii
--nonbonded	Override to use non-bonded radii
--csv	Save csv file of visible polar coordinates (θ,φ). Only recommended for smaller ZCW integration densities.
--batch	Save a csv file with tabulated results. This can be used to collate results from multiple instances of *AtomAccess*. An input file <GroupID>.<UniqueID>.xyz will result in a line being added to the file <GroupID>_<clusterthreshold>_<radialstep>_<radiustype>.csv
--Cp	Report M-Cp_{cent} distances and Cp_{cent}-M-Cp_{cent} angle for $M(Cp^R)_2$ complexes.

AtomAccess uses a ZCW angular grid centred on the central atom to define the direction of each ray;[5] the remaining atoms will be referred to as peripheral atoms. The ZCW density can take values between 0 and 15 but does not scale linearly with the number of directions (Table 2).

Table 2. Number of directions in ZCW integration

Density	**Number of directions**
0	21
1	34
2	55
3	89
4	144
5	233
6	377
7	610
8	987
9	1597
10	2584
11	4181
12	6765
13	10946
14	17711
15	28657

AtomAccess uses the physics convention for spherical polar coordinates (radial distance *r*, polar angle θ, azimuthal angle φ), where (θ, φ) defines the direction of the ray and *r* defines the radial coordinate. Rays are traced out from the central atom in increments of the radial step until a threshold distance. The threshold distance is defined as 20 Å or the maximum distance between the central atom and any peripheral atom plus the largest radius of the peripheral atoms, whichever is lower. At each value of *r* the (*r*, θ, φ) point is checked as to whether it lies within the radius of any peripheral atom and if it does, this (θ, φ) direction is considered to be blocked. Visible rays are defined as being unblocked for all values of *r* up to and including the threshold distance.

The ZCW integration density and radial step can be specified with the "--density" and "--radialstep" options (Table 1). These should be kept constant when comparing different structures. A default density value of 7 and radial step of 0.05 Å have been chosen to give rapid results, these can be increased and decreased, respectively, to converge on more accurate results. Preliminary tests indicate integration densities > 11 and radial steps < 0.01 tend not to improve accuracy.

The radii of peripheral atoms are defined by their atomic covalent radii (suitable for organic molecules) or non-bonded radii (suitable for inorganic complexes), as taken from the RSC Periodic Table database of covalent (H-Og) and non-bonded (H-Lr) radii.[6] The default radius type for all peripheral atoms is chosen based on the identity of the central atom: covalent radii are used if the central atom is a non-metal or semi-metal (H, B, C, N, O, F, Si, P, S, Cl, Ge, As, Se, Br, Sb, Te, I, Po, At, Ts) and non-bonded radii are used if the central atom is a metal (all other elements). This can be overwritten by using the "--covalent" or "--nonbonded" options (Table 1).

Visible rays are grouped into clusters of adjacent rays, and the size of the cluster is calculated as the number of visible rays divided by the number of angular directions (Table 2) to give a %VSA for the cluster. The total %VSA is calculated as the sum of the %VSA for each cluster. The "--clusterthreshold" option (Table 1) allows all clusters below a certain %VSA to be discarded and not reported; this can be used to discard meaningless clusters that are too small to allow another atom to approach. The default is to report the size of all clusters and include all clusters in the total %VSA.

AtomAccess includes several options to enable further analysis. The "--csv" option (Table 1) can be used to generate a list of spherical polar coordinates (θ, φ) of all visible angular points. These can be used in other programs to visualise the accessible directions (Figure 1). The "--batch" option allows results from multiple different structures to be collated in a single csv output file (Table 1). The batch option requires the same *AtomAccess* settings to be used for all calculations and for the calculations to be performed in the same directory. The xyz input files must be also be labelled with the same group identifier, but can have different secondary identifiers, for example:

<GroupID>.<UniqueID_1>.xyz
<GroupID>.<UniqueID_2>.xyz
<GroupID>.<UniqueID_3>.xyz etc.

The unique identifier, total %VSA and %VSA for the largest cluster are reported in the resulting batch csv file.

3. References

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