A Step-by-Step Lecture: Extracting NICS(1)zz from an ORCA 6.1.1 NMR Scan Log File

This lecture explains, in full scientific detail, how to locate and extract the **NICS(1)zz** value of a moving ghost probe from an ORCA 6.1.1 NMR scan output file. Every step is illustrated with the exact lines from the scan log you provided (the 51-point scan of 1,2,5-selenodiazole from r=0.0 Å to r=5.0 Å).

Step 1 — Understand the Overall Structure of the ORCA Log

An ORCA NMR-scan log is organized into a **prologue** followed by a sequence of **trajectory steps**. The prologue contains:

- The ORCA banner and version.
- The **INPUT FILE** echo (the exact contents of your `.inp` file).
- The basis-set and DFT setup information.
- A `SCAN-COORDS` header announcing that a scan calculation will be performed.

After the prologue, ORCA prints a sequence of blocks, one per scan point, each introduced by:

text

```
************************************************************
                        TRAJECTORY STEP   N
     ZSCAN  :   X.XXXXXXX
************************************************************
```

Within every trajectory step, ORCA performs a full SCF, a full CP-SCF response, and a full NMR shielding calculation. The **shielding tensor for every nucleus**, including every ghost atom, is printed as a 3×3 matrix inside that step.

Step 2 — Locate the Input Section to Identify the Ghost Atom

Scroll to the beginning of the log and search for the line:

text

```
================================================================================
                                       INPUT FILE
================================================================================
```

In your file, right after this header, you find the `%coords` block:

text

```
|  9> %coords
| 10>   CTyp xyz
| 11>   Charge 0
| 12>   Mult 1
| 13>   Units Angs
| 14>
| 15>   pardef
| 16>     zScan = 0.0, 5.0, 51;
| 17>   end
| 18>
| 19>   coords
| 20>     Se          0.04610159135910     -7.21843063093683      0.00044684570274
| 21>     N           1.64335339463610     -6.40267071353037      0.00054271753115
| 22>     C           2.54745181093044     -7.33240004772931     -0.00005593405127
| 23>     H           3.59608653377771     -7.06205058522509     -0.00017691792933
| 24>     C           2.07064586200286     -8.69240776982043     -0.00031204227707
| 25>     H           2.72058491327409     -9.55849497516503     -0.00060772943926
| 26>     N           0.78370212401969     -8.85318186759290      0.00047537046305
| 27>
| 28>     H:          1.41825095000000     -7.69981821000000      {zScan}
```

Two crucial observations follow.

1. The **eighth atom in the coordinate list is** `H:` — a ghost atom. Its z-coordinate is `{zScan}`, meaning it is the atom that is being moved by the scan.
2. The `pardef` block tells you that `zScan` takes 51 values from 0.0 Å to 5.0 Å, i.e. a step size of 0.1 Å.

Because ORCA numbers the nuclei in the output starting from **0**, this eighth atom (position 8 in the coordinate list) is reported as **Nucleus 7** in the output. Whenever you see a header `Nucleus 7H :` inside a trajectory step, that block of the shielding tensor belongs to your moving probe.

Step 3 — Locate the Trajectory Steps

Search the log for the first occurrence of:

text

```
                           TRAJECTORY STEP   1
          ZSCAN   :   0.00000000
```

This marks the beginning of the first scan point. In your file, `TRAJECTORY STEP N` runs from `1` to `51`, and the `ZSCAN` value printed on the next line is the distance in Ångströms from the ring centre. For example:

- `TRAJECTORY STEP 1` → `ZSCAN : 0.00000000` (ring centre, r=0.0 Å)
- `TRAJECTORY STEP 11` → `ZSCAN : 1.00000000` (r=1.0 Å)
- `TRAJECTORY STEP 21` → `ZSCAN : 2.00000000` (r=2.0 Å)
- `TRAJECTORY STEP 51` → `ZSCAN : 5.00000000` (r=5.0 Å)

The ZSCAN line, therefore, is your **abscissa** for the plot of NICS(1)zz versus distance.

Step 4 — Locate the Shielding-Tensor Block for the Ghost Atom

Inside each trajectory step, search for the section header:

text

```
-------------------
CHEMICAL SHIELDINGS (ppm)
-------------------
```

Immediately after this header, ORCA prints the shielding tensor for **every nucleus in the molecule, one block at a time**, in order of increasing nucleus index. Because your ghost atom is number 7 in the coordinate list, you must scan down past the blocks for Nuclei 0 through 6, and stop at:

text

```
 --------------
 Nucleus   7H :
 --------------
```

This is the only place in the entire log where the shielding information of the moving probe is printed.

Step 5 — Identify the Relevant Quantity Inside the Block

Inside the `Nucleus 7H` block, ORCA prints three tensors:

1. `Diamagnetic contribution to the shielding tensor (ppm)` — the diamagnetic (Lamb) part, σ^{dia}.
2. `Paramagnetic contribution to the shielding tensor (ppm)` — the paramagnetic part, σ^{para}.
3. `Total shielding tensor (ppm)` — the sum, $\sigma^{\mathrm{total}} = \sigma^{\mathrm{dia}} + \sigma^{\mathrm{para}}$.

For NICS you must **never** use the diamagnetic or paramagnetic parts separately, because NICS is defined from the full shielding tensor. The relevant quantity is therefore the **total shielding tensor**, which in your log looks like this (from `TRAJECTORY STEP 1`):

text

```
Total shielding tensor (ppm):
            15.342         -4.972         -0.002
            -4.968          2.914         -0.003
            -0.002         -0.001         16.176
```

The 3×3 matrix is laid out in rows:

$$\sigma^{\text{total}} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$$

The quantity of interest for the out-of-plane NICS is the **bottom-right element**, σ_{zz}. In the example above:

$$\sigma_{zz} = 16.176 \text{ ppm}.$$

Step 6 — Why σ_{zz} and Not Another Component?

The NICS is designed to measure the **ring current** that flows in the molecular plane. The magnetic field induced by this ring current is oriented **perpendicular to the ring plane**. If you choose your coordinate system such that the z-axis is the axis perpendicular to the ring plane (which is what your `%coords` block naturally provides, since all heavy atoms of the ring have essentially zero z-coordinate), then the component of the shielding tensor that reflects the ring current is precisely σzz. Using any other diagonal element (σxx or σyy) or any off-diagonal element would mix in contributions that are unrelated to the aromatic ring current.

The **out-of-plane component** σzz at a distance r above the ring centre is therefore the physically meaningful quantity.

Step 7 — Convert the Total Shielding Tensor into NICS(1)zz

The definition of the **Nucleus-Independent Chemical Shift** (NICS) is:

NICS=−σ

where σ is the total isotropic shielding. For the **zz** component:

$$\boxed{\mathrm{NICS}(1)_{zz} = -\sigma_{zz}}$$

The reason for the negative sign is a matter of **convention**, and it is dictated by the way the shielding tensor is defined in the nuclear Zeeman Hamiltonian used by ORCA. According to the ORCA 6.1.1 manual, the nuclear Zeeman Hamiltonian is written as

$$\hat{H}_I = -g_N \beta_N \, \mathbf{B} \, (1 - \sigma) \, \mathbf{I}$$

so a **positive** σ corresponds to a **shielding** (diamagnetic) effect and a **negative** σ corresponds to a **deshielding** (paramagnetic) effect. Aromatic ring currents produce a diamagnetic contribution at the ring centre and above it, so σ_{zz} is positive there. Since Schleyer and co-workers introduced NICS with the opposite sign convention — negative values meaning aromatic, positive values meaning antiaromatic — the value that must be reported is:

$$\mathrm{NICS}(1)_{zz} = -\sigma_{zz}.$$

ORCA does **not** apply this sign flip automatically, because the NMR module is written to produce the raw shielding tensor (a general-purpose magnetic property) and not a specialized aromaticity metric. The conversion to NICS is left to the user.

Applying the conversion to the example above:

NICS(1)zz(r=0.0 A˚)=−16.176 ppm.

Step 8 — Repeat for Every Trajectory Step

The same procedure must be repeated for every trajectory step from 1 to 51. The sequence is:

Trajectory step	`ZSCAN` value (Å)	σ_{zz} (ppm)	$\mathrm{NICS}(1)_{zz} = -\sigma_{zz}$ (ppm)
1	0.0	16.176	−16.176
2	0.1	...	...
3	0.2	...	...
...	...	...	...
51	5.0	2.060	−2.060

In your log, the complete set of σzz values for the moving probe appears in the `Nucleus 7H :` block of every `TRAJECTORY STEP`. After collecting all 51 pairs (ZSCAN,σzz), the resulting NICS(1)zz profile can be plotted against r, and the point with the **most negative** NICS(1)zz — i.e. the maximum of the shielding — identifies the distance at which the aromatic ring current is strongest. In your log, this occurs at r=0.90 Å, with NICS(1)zz=−31.6890 ppm.

Step 9 — Summary of the Extraction Recipe

1. **Open the log file** and locate the **INPUT FILE** section.
2. **Identify the ghost atom** whose coordinate is written as a scan parameter (or ends with a colon).
3. **Determine its printed nucleus index**: subtract 1 from its position in the coordinate list because ORCA numbers nuclei from 0 in the output.
4. **Scan down to the first** `TRAJECTORY STEP` and read the `ZSCAN` value.
5. **Locate the block** `Nucleus NH :` for that ghost atom.
6. **Read the bottom-right element** of the `Total shielding tensor (ppm)` 3×3 matrix: this is σzz.
7. **Negate it**: NICS(1)zz=−σzz.
8. **Repeat** for every trajectory step to obtain the full NICS(1)zz profile.
9. **Plot** NICS(1)zz versus r, and identify the distance at which the value is most negative.

Following this recipe yields a NICS(1)zz value that is scientifically meaningful, consistent with the established NICS convention, and fully compliant with the way ORCA 6.1.1 reports magnetic shielding tensors.

Why Does an ORCA NICS Scan Use 51 Points?

A step-by-step explanation of the scan grid in `zScan = 0.0, 5.0, 51;`

The key idea. The number 51 specifies the number of scan points sampled between 0.0 and 5.0 Å, including both endpoints. It therefore creates 50 equal intervals. In this case, each interval is 0.1 Å long.

1. Reading the ORCA scan instruction

The supplied ORCA 6.1.1 input echoed in the uploaded tutorial contains the following parameter definition:

```
zScan = 0.0, 5.0, 51;
```

The three entries have distinct meanings:

Entry	Meaning	Interpretation
`0.0`	Starting value, z_min	The first probe position is at z = 0.0 Å.
`5.0`	Ending value, z_max	The final probe position is at z = 5.0 Å.
`51`	Number of scan points, N	ORCA evaluates 51 discrete positions across the specified range, with the endpoints included.

In this particular input, the coordinate list contains a probe written as H: 1.41825095 -7.69981821 {zScan}. Its x and y coordinates remain fixed while the scan parameter supplies its z coordinate. Because the ring atoms lie essentially in the z = 0 plane, this moves the probe vertically above the ring centre and samples the magnetic shielding at different heights.

2. Why 51 points produce a 0.1 Å step

A common counting trap is to confuse the number of points with the number of intervals. If a grid includes the first and last positions, N points create N - 1 intervals between them. The uniform spacing is therefore calculated using N - 1, not N.

$$\Delta z = (z_{max} - z_{min}) / (N - 1)$$

Δz is the spacing between adjacent scan points; N is the total number of points.

For the scan in the supplied file, z_min = 0.0 Å, z_max = 5.0 Å, and N = 51. Substitution gives:

$$\Delta z = (5.0 - 0.0)\ \text{Å} / (51 - 1) = 5.0\ \text{Å} / 50 = 0.1\ \text{Å}$$

Thus the scan includes 51 probe positions but only 50 steps between consecutive positions. The full sequence is 0.0, 0.1, 0.2, 0.3, …, 4.8, 4.9, and 5.0 Å.

$$z_i = z_{min} + (i - 1)\Delta z, \quad i = 1, 2, \ldots, 51$$

Here i is the one-based trajectory-step number printed in the log.

3. Mapping scan points to ORCA trajectory steps

The uploaded tutorial reports 51 trajectory steps. Each trajectory step corresponds to one value of zScan, and the log prints that value on the ZSCAN line. For this grid, the relationship is z = 0.1 × (step number − 1) Å.

ORCA trajectory step	ZSCAN (Å)	Interpretation
1	0.0	Starting position
2	0.1	One interval above the starting position
11	1.0	The 1.0 Å point, conventionally used for NICS(1)zz
21	2.0	The 2.0 Å point
31	3.0	The 3.0 Å point
41	4.0	The 4.0 Å point
51	5.0	Final position

Computational consequence. According to the supplied tutorial, ORCA performs the SCF calculation, the CP-SCF response calculation, and the NMR shielding calculation at each trajectory step. Consequently, a 51-point scan provides 51 probe-position evaluations of the shielding tensor, rather than just one calculation at each endpoint.

4. Why choose 51 points? Is this number mandatory?

No. The value 51 is not a universal ORCA requirement. It is the number needed for a particular choice of range and resolution. Here, the user wants to scan a 5.0 Å interval in increments of 0.1 Å while retaining both endpoints. Solving for the number of points gives:

$$N = (z_{max} - z_{min}) / \Delta z + 1$$

$$N = (5.0\ \text{Å} - 0.0\ \text{Å}) / 0.1\ \text{Å} + 1 = 50 + 1 = 51$$

The added 1 accounts for the initial point at 0.0 Å. There are 50 increments of 0.1 Å between that point and the final point at 5.0 Å.

Desired spacing	Required points	Intervals
0.20 Å	26 points	25 intervals
0.10 Å	51 points	50 intervals
0.05 Å	101 points	100 intervals

A smaller spacing gives a denser profile and can resolve sharper changes more finely, but it also increases the number of scan evaluations and computational cost. The appropriate spacing is therefore a methodological choice; it is not determined by the range alone.

5. Important terminology: NICS(1)zz versus the full scan profile

The shielding component extracted in the supplied tutorial is the zz component of the total shielding tensor, denoted σ_zz. The corresponding NICS profile is obtained by changing its sign:

$$NICS_{zz}(z) = -\sigma_{zz}(z)$$

A terminology point is important when reporting the results. In the standard notation, NICS(1)zz specifically refers to the zz component evaluated at a probe position 1.0 Å above the ring plane. In this 0.0–5.0 Å scan, that position is trajectory step 11, where ZSCAN = 1.00000000 Å. The values at the other scan heights are points on the NICSzz(z) profile; they are not all, strictly speaking, NICS(1)zz values.

Application to the uploaded tutorial. The tutorial reports its most negative value at z = 0.90 Å (−31.6890 ppm). To keep the notation precise, this is best described as the minimum of the scanned NICSzz profile, NICSzz(0.90 Å) = −31.6890 ppm. The label NICS(1)zz should be reserved for the value at exactly 1.00 Å, unless a different convention is explicitly defined. The provided tutorial does not state the numerical NICSzz value at 1.00 Å in the excerpted result.

6. Common misinterpretations to avoid

- 51 is the total number of sampled points, not the number of intervals. The number of intervals is 51 − 1 = 50.
- 51 is not the spacing. The spacing is calculated from the range and the number of points; in this case it is 0.1 Å.
- 51 does not mean 51 Å and is not the number of atoms or nuclei in the system.
- The endpoints are included. If 50 points were requested over the same 0.0–5.0 Å range, the spacing would be 5.0/49 ≈ 0.10204 Å, not exactly 0.1 Å.

In one sentence: `zScan = 0.0, 5.0, 51;` tells ORCA to sample 51 equally spaced probe positions from 0.0 to 5.0 Å, including both endpoints, which yields 50 increments of exactly 0.1 Å each.

Basis of this explanation: the uploaded six-page tutorial, especially its echoed input parameter, ghost-probe coordinate, and trajectory-step examples. The notation note above clarifies the conventional meaning of NICS(1)zz.