

Manual for the Friedel Oscillation eXtension (FOX) code

Tomasz Bednarek¹, James Pogrebetsky¹, Michał Tomza²,
Alexandra Siklitskaya^{*1}, and Adam Kubas^{†1}

¹Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224
Warsaw, Poland

²Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warsaw, Poland

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The manual provides a hands-on tutorial for the point-charge embedding scheme in order to improve the accuracy of the open-boundary quantum-chemical calculations on the small metallic clusters without increasing computational costs.

Contents

1	Software requirements	2
2	Source code availability	2
3	Guidelines for the proper setup	2
3.1	Optimal Pt cluster geometry	2
3.2	DFT functional and metallic cluster spin state	3
4	Relaxation of a CO molecule on Pt surface	3
5	Embedding procedure via the Friedel Oscillation eXtension	6
5.1	Structure of the FOX extension	6
5.2	Structure of files that store point charges	7
5.3	Structure of ORCA input with embedding charges	7
5.4	Specifying the CO adsorption site for charge generation	8
5.5	Embedding and calculation time	9
5.6	Choosing reference for adsorption energy calculations	9
6	Ready-to-go setup for running the embedding calculations	11
6.1	Recommended values of dipole moments	12

^{*}asiklit@ichf.edu.pl

[†]akubas@ichf.edu.pl

1 Software requirements

All quantum-chemical calculations have been tested using ORCA 5.0.2. [1] We recommend installing a visualization tool (e.g. Avogadro [2]) to view molecular geometries. Generation of the point-charge embedding is performed using the executable `generator.o`, which is currently compiled and tested for the x86_64 Ubuntu architecture. This executable requires the binary data file `model.bin`, containing the precomputed response of the Pt(111) surface on a dense real-space grid, evaluated using the theoretical framework described in our paper [3].

If an error such as `bash: ./generator.o: Permission denied` occurs, it can be resolved by granting executable permission with the command `chmod +x ./generator.o`.

On other operating systems, such as Windows or macOS, the executable can be run using a virtual machine (VM) with an Ubuntu system. On Windows, it is also possible to use the Windows Subsystem for Linux (WSL).

2 Source code availability

The full source code for this project is not publicly available in this repository. However, it can be provided upon reasonable request for academic or non-commercial purposes. If you are interested in accessing the code, please contact us at this email `fox@ichf.edu.pl`.

Please briefly describe your intended use or research interest in the project when reaching out.

3 Guidelines for the proper setup

3.1 Optimal Pt cluster geometry

Experimentally observed adsorption sites of CO molecules on the Pt(111) surface are **atop**, **bridge**, and **hollow** ones. Therefore, in order to theoretically calculate the adsorption energies of each of these positions, one should start by choosing an appropriate platinum cluster for modelling the metallic surface.

Cluster geometry should satisfy two basic requirements:

- (1) All three adsorption sites (*atop/bridge/hollow*) are present.
- (2) More than one atomic layer is necessary to represent the Pt surface electronic structure correctly.

The lattice symmetry breaking – arising from the presence of a surface – results in the occurrence of additional surface states (besides the bulk states already present in the crystal). These states exponentially decay from the top layer downwards, thus mostly localised within a few top layers. Moreover, the CO molecule that approaches the Pt(111) surface induces an electronic structure response within the metal bulk. A single 2D layer may have vastly different physical properties than 3D metal bulk, so it is essential to include a few atomic layers within the cluster.

The smallest cluster satisfying these conditions is a Pt₁₃ cluster (shown in **Fig. 1** on the right), which is similar to the lowest-energy Pt clusters available in the literature. [4] **Figure 1** also contains the content of `Pt13.xyz` file with Cartesian coordinates of each Pt atom that can be directly fed to the visualisation software.

Our embedding scheme is designed for the open-boundary-condition systems. This is more suitable for studying Friedl oscillations than the periodic approach because of the multi-cell interference resulting from the long-range character of oscillations (of the order of over a dozen Å). Henceforth, one can retrieve true

low-coverage CO adsorption energies. On top of that, this approach does not generate k -mesh-related errors, frequently apparent in periodic calculations.

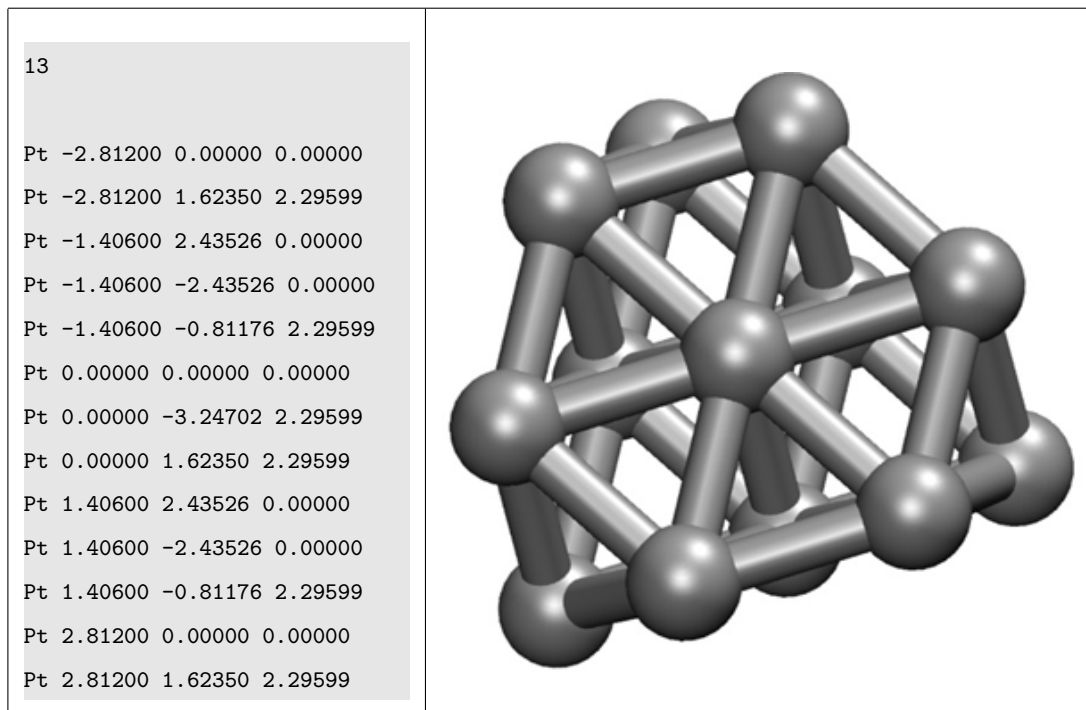


Figure 1: Pt13.xyz coordinate file and its visualization

3.2 DFT functional and metallic cluster spin state

We test our embedding scheme using the PBE functional ([5]). As shown in the main text, once the embedding is operative, it provides the correct **atop** site preference. Further testing has also been conducted with PBE0 ([6, 7]) hybrid functional, Hartree-Fock method, as well as with post-Hartree-Fock methods. All data presented in the current study were performed with multiplicity 1 in a restricted formalism.

4 Relaxation of a CO molecule on Pt surface

Only the CO molecule has been relaxed along the vertical axis using a constraint-optimisation algorithm present in ORCA software. The resultant four xyz geometries for all three adsorption sites (*atop/bridge/hollow*) are presented below (see Fig. 3):

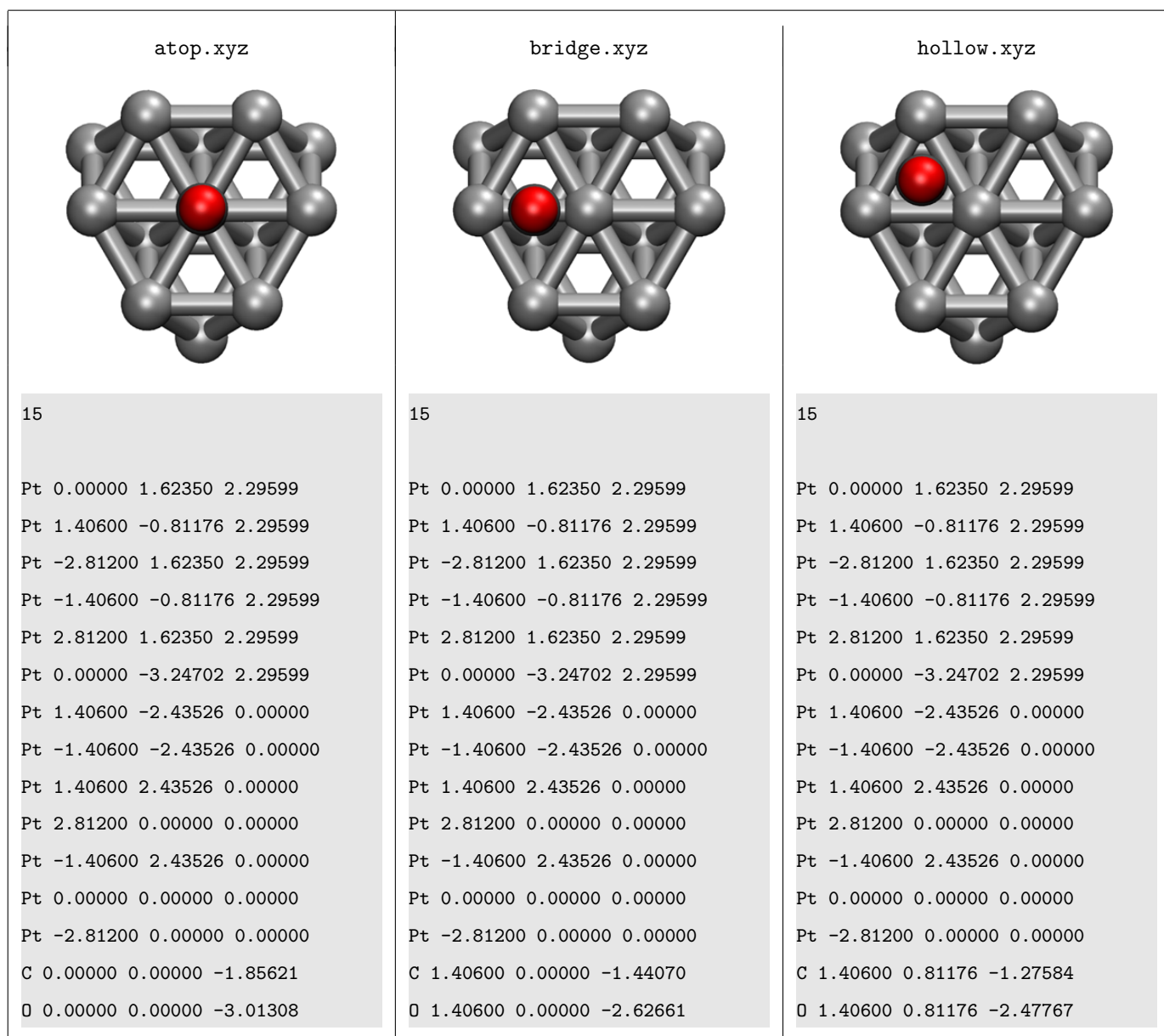


Figure 2: Structures of *atop/bridge/hollow* CO positions.

Since only the CO molecule is optimised, all the Pt atoms have to be fixed. At the same time, since CO should be placed at its adsorption position (atop, bridge, or hollow), only the z-coordinate of carbon and oxygen atoms has been optimised (owing to CO approaching the metallic surface along the z-direction). All the constraints are listed in the ORCA simple input file under the `%geom` menu. This leads to the following input files for the PBE method:

atop-opt.inp	bridge-opt.inp	hollow-opt.inp
<pre> ! PBE Def2-SVP Def2-ECP PAL16 opt %maxcore 5000 %scf MaxIter 1500 end %geom constraints {c 0 c} {c 1 c} {c 2 c} {c 3 c} {c 4 c} {c 5 c} {c 6 c} {c 7 c} {c 8 c} {c 9 c} {c 10 c} {c 11 c} {c 12 c} {a 11 13 14 c} {a 10 11 13 c} {a 12 11 13 c} {a 7 11 13 c} {a 6 11 13 c} {a 9 11 13 c} {a 8 11 13 c} end end *xyzfile 0 1 atop.xyz </pre>	<pre> ! PBE Def2-SVP Def2-ECP PAL16 opt %maxcore 5000 %scf MaxIter 1500 end %geom constraints {c 0 c} {c 1 c} {c 2 c} {c 3 c} {c 4 c} {c 5 c} {c 6 c} {c 7 c} {c 8 c} {c 9 c} {c 10 c} {c 11 c} {c 12 c} {c 15 c} {a 15 13 14 c} {a 11 15 13 c} {a 6 15 13 c} {a 8 15 13 c} {a 9 15 13 c} {a 11 15 14 c} {a 6 15 14 c} {a 8 15 14 c} {a 9 15 14 c} end end *xyzfile 0 1 bridge.xyz </pre>	<pre> ! PBE Def2-SVP Def2-ECP PAL16 opt %maxcore 5000 %scf MaxIter 1500 end %geom constraints {c 0 c} {c 1 c} {c 2 c} {c 3 c} {c 4 c} {c 5 c} {c 6 c} {c 7 c} {c 8 c} {c 9 c} {c 10 c} {c 11 c} {c 12 c} {c 15 c} {a 15 13 14 c} {a 11 15 13 c} {a 9 15 13 c} {a 8 15 13 c} {a 11 15 14 c} {a 9 15 14 c} {a 8 15 14 c} end end *xyzfile 0 1 hollow.xyz </pre>

Figure 3: ORCA optimization input files for the *atop/bridge/hollow-fcc* CO positions. Files *atop.xyz/bridge.xyz/hollow.xyz* correspond to the geometries in Figure 2.

The extra DA atom at the end of the file is a so-called **Dummy Atom**. It is necessary to set proper constraints

for the CO molecule. Please note that the structures are relaxed at the **def2-SVP** basis set in this example. Obtained structures can be subject to Hessian calculations to obtain further corrections, such as zero-point energy, etc.

5 Embedding procedure via the Friedel Oscillation eXtension

After the geometry optimisation, we follow with the embedding of the point charges. Those charges are generated using the **Friedel Oscillation eXtension (FOX)**, and they can easily enter quantum-chemical ORCA workflows directly via the input file.

5.1 Structure of the FOX extension

The extension consists of two files: one is the executable **generator.o**, and the other is the obligatory binary data file **Pt(111)-model.bin** with a description of the Pt bulk response. In the future, we plan to release binary data files for other metals as well. The usage commands of the extension are as follows:

```
./generator --help
(shows help and exits)

./generator [-i] <filename> -d <float> --o <int>
./generator [--input] <filename> --dipole <float> --order <int>
(runs the program with mandatory options)
```

The **-i** or **--input** flag is optional; the input filename can be provided directly as the first positional argument. This flag specifies the input file, which must be either in ORCA input format (***.inp**) or in XYZ format (***.xyz**). Only a single input file is supported per run, and only files with these two extensions are accepted.

The **-d** or **--dipole** flag specifies the effective *z*-component of the dipole moment of the adsorbed CO molecule, in units of eÅ. We recommend using values from Ref. [8]. A positive value corresponds to an effective positive charge on the carbon atom and a negative charge on the oxygen atom.

The **-o** or **--order** flag defines the order *n* (or diameter) of the embedding point charge arrangement. The corresponding physical diameter *d* of the embedding is calculated as: $d = (n - 1) \frac{a\sqrt{3}}{2}$, where $a = 2.812$ Å is the Pt-Pt bond length.

To generate embedded point charges for the atop adsorption site of CO on Pt(111) using the recommended dipole moment, and assuming the geometry is provided in the file **orca-atop.inp**, the following command can be used (for the maximum tested order of 15): **./generator.o orca-atop.inp --dipole 0.089 --order 15**.

The program outputs a file named **<filename>-<order>.pc** (where **<filename>** is the name of the input file w/o **.inp** or **.xyz** extension, and **<order>** is the embedding size) containing embedded point charges around the cluster and right away compatible with ORCA.

A scheme explaining the principle of functioning of the extension is shown in **Fig. 4**.

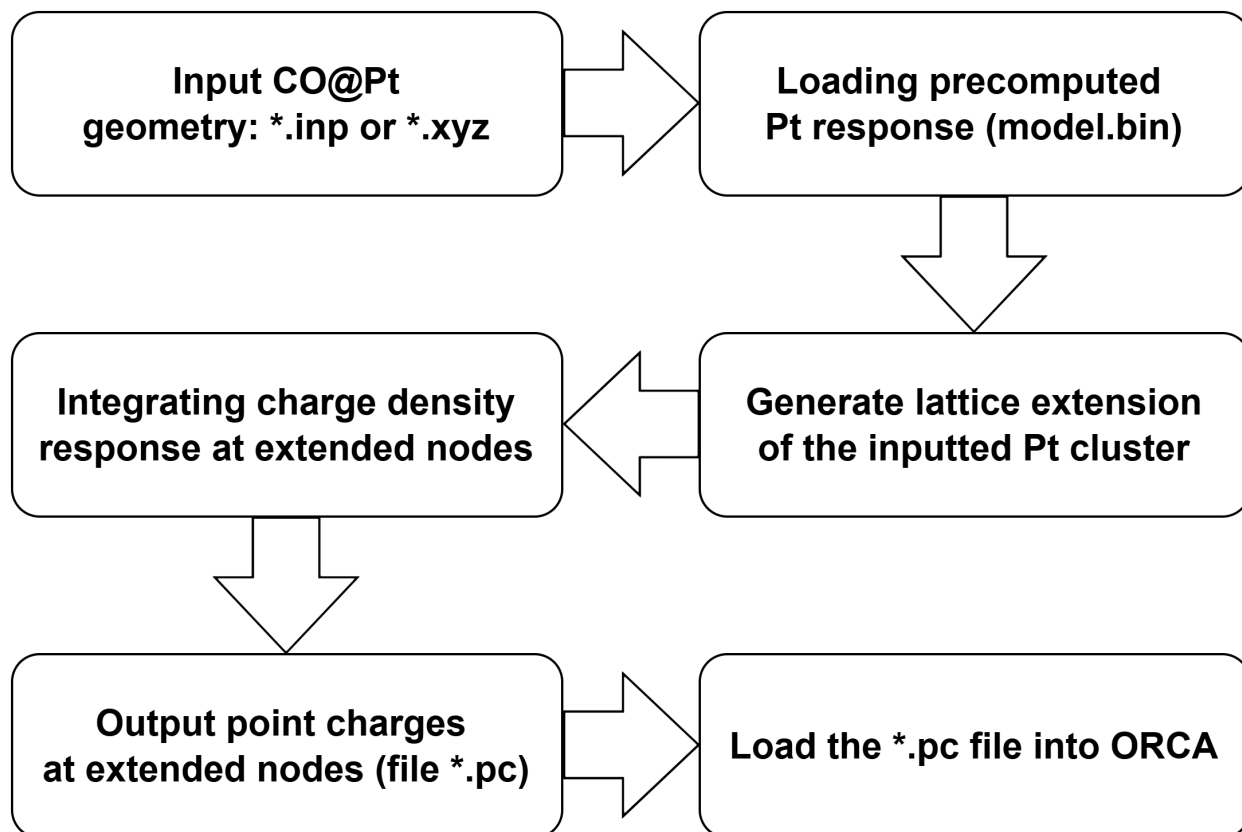


Figure 4: Block scheme of the logic behind the Friedel Oscillation eXtension FOX

5.2 Structure of files that store point charges

The structure of the *.pc file generated by FOX is very similar to the *.xyz files. Please take a look at the following example:

```

2                # number of point charges
-1 1.406 0.000 -1.400  # charge | X coordinate | Y coordinate | Z coordinate
+1 1.406 0.000 -2.528  # charge | X coordinate | Y coordinate | Z coordinate
  
```

In ORCA, one may include point charges in the same block as the atomic coordinates instead of providing an external *.pc file. However, the former approach also calculates interactions between the point charges. In our case, we do not wish to include these interactions; hence, we provide point charges externally. ORCA treats calculation with external point charges similarly to a QM/MM calculation, meaning that their presence should not significantly influence the calculation time.

5.3 Structure of ORCA input with embedding charges

The *.pc files contain the charges and xyz coordinates for the embedded charges. All of these correspond to the positions the actual Pt atoms would have in a bigger Pt cluster. In order to include the point charges in the calculation, a single line should be added to the file:

```
%pointcharges name-of-the-file.pc
```

where `name-of-the-file.pc` is the file containing point-charges positions and charge values. This brings the input to the following format (the example is for the atop position)

```
! PBE Def2-SVP Def2-ECP slowconv PAL16

%maxcore 5000
%scf
MaxIter 1500
end

%pointcharges "atop.pc" # declaration of file to read point charges

*xyzfile 0 1 optimized-CO-atop-PBE-Ms1.xyz
# 0 1 is the charge and spin multiplicity;
# optimized-CO-atop-PBE-Ms1.xyz is the xyz file with relaxed geometry for atop CO position

# Please note that the last line in this file has to be empty
```

Please note that to calculate the energy of other adsorption positions, one should use respective point-charges files – `atop.pc`, `bridge.pc` and `hollow.pc` – along with the correct `*.xyz` file. The `%scf` block sets the maximum number of SCF iterations to 1500. Although such a number is widely excessive, it is a good practice to set it higher for metallic systems. In case of convergence issues, one may play around with starting orbitals (e.g., using `hcore` guess).

5.4 Specifying the CO adsorption site for charge generation

The CO molecule may be kept at its atop position; however, one should be careful to use proper CO dipole moments for each position. For more details, please keep reading. Within the FOX approach, the position of the CO is taken into account in the embedding not only through the dipole moments but also through the shifting of the CO molecule to represent the different adsorption sites. Unfortunately, the latter introduces asymmetry into the charges, which can lead to unexpected adsorption energies at medium-sized embeddings (Fig. 5). However, we would like to note that CO may also be kept at its atop position without shifting, given that the proper dipole moment is applied. In fact, at big embedding sizes, the charges produced by the shifted CO result in only marginally different adsorption energies compared to the unshifted CO molecule. We do not recommend changing the CO position in the FOX code for the above reasons.

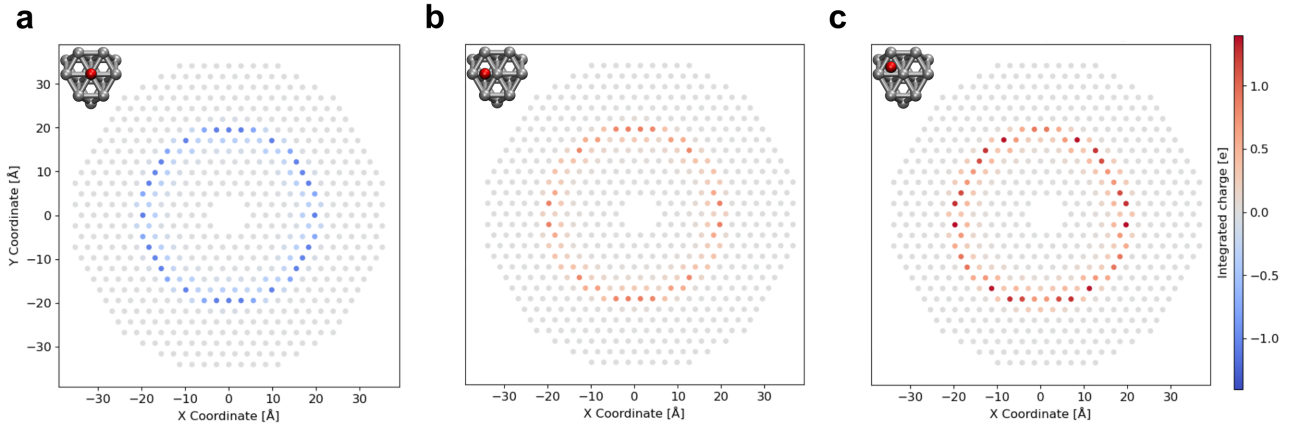


Figure 5: The top view of the geometry of the embedding charges for the (a) *atop*, (b) *bridge*, (c) *hollow-fcc*

5.5 Embedding and calculation time

Embedding does not have a significant impact on the calculation time. Unlike the polynomial time growth that comes with an increase in the system size, point charges are not treated as atoms and, therefore, do not have such an influence. However, the presence of embedding charges may influence the number of iterations needed for the SCF procedure to converge. As shown in Fig. 6, point charges only marginally affect the computation time.

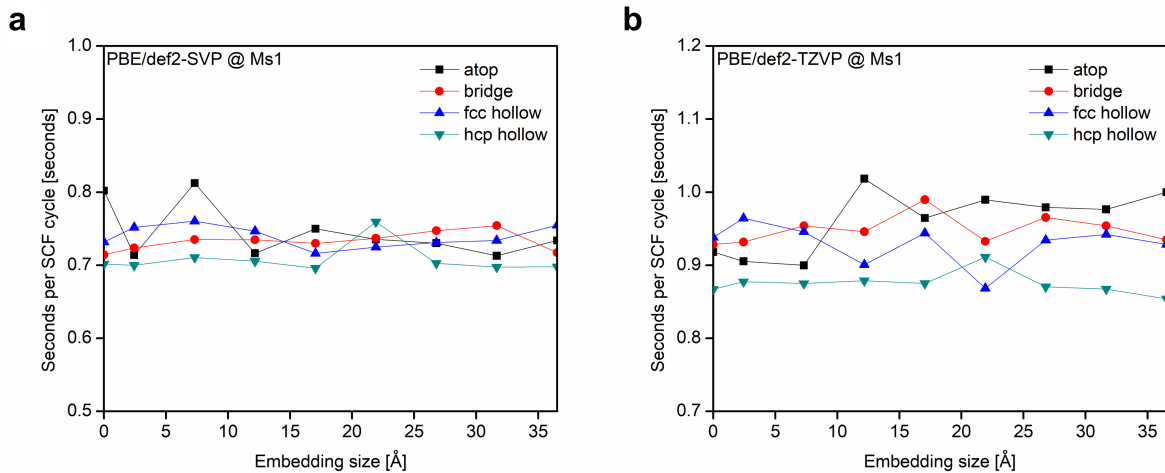


Figure 6: The dependence of time taken by a single SCF step on the embedding radius for the PBE functional and def2-SVP (A) as well as def2-TZVP (B) basis sets.

5.6 Choosing reference for adsorption energy calculations

CO molecule that approaches a metallic surface induces a response represented by a perturbed charge distribution. The latter is a direct result of the appearance of Friedel oscillations, which are calculated by our embedding model. To keep consistency between unbound and bound states, we have chosen the reference state as a CO molecule located 10 Å above the Pt surface (see Fig. 5), a distance at which no chemical interaction occurs. Point charges for such a case are stored in the `reference.pc` file (all close to zero).

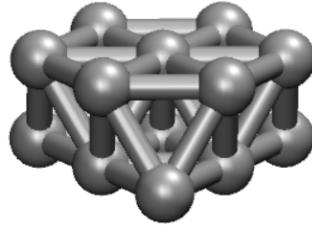


Figure 7: The geometry of the reference

CO adsorption energies are then calculated by the following formula

$$\Delta E_X = E_X^{abs} - E_{ref}^{abs}, \quad (1)$$

where E_X^{abs} refers to the absolute energy of the CO adsorbed at X position at the Pt surface, and E_{ref}^{abs} refers to the absolute energy of the CO adsorbed at 10 Å from the Pt surface.

Although the CO is fixed 10 Å away from the surface, the C-O bond length still should be optimised. In this case, the constraints are similar to the ones used for the *atop* position optimisation; however, the carbon atoms' coordinates must be frozen. For this reason, it is convenient to use the constraints similar to the ones used for the *atop* position, with the only difference being that the C atom is also fixed:

```
! PBE Def2-SVP Def2-ECP PAL16 opt
%maxcore 5000
%scf
MaxIter 1500
end

%geom
constraints
{c 0 c}
{c 1 c}
{c 2 c}
{c 3 c}
{c 4 c}
{c 5 c}
{c 6 c}
{c 7 c}
```

```

{c 8 c}
{c 9 c}
{c 10 c}
{c 11 c}
{c 12 c}
{c 13 c}
{a 11 13 14 c}
{a 10 11 13 c}
{a 12 11 13 c}
{a 7 11 13 c}
{a 6 11 13 c}
{a 9 11 13 c}
{a 8 11 13 c}
end
end
*xyz 0 1
Pt 0.00000 1.62350 2.29599
Pt 1.40600 -0.81176 2.29599
Pt -2.81200 1.62350 2.29599
Pt -1.40600 -0.81176 2.29599
Pt 2.81200 1.62350 2.29599
Pt 0.00000 -3.24702 2.29599
Pt 1.40600 -2.43526 0.00000
Pt -1.40600 -2.43526 0.00000
Pt 1.40600 2.43526 0.00000
Pt 2.81200 0.00000 0.00000
Pt -1.40600 2.43526 0.00000
Pt 0.00000 0.00000 0.00000
Pt -2.81200 0.00000 0.00000
C 0.00000 0.00000 -10.00000
O 0.00000 0.00000 -11.12800
*
```

6 Ready-to-go setup for running the embedding calculations

In the directory `example`, there are 4 ORCA input files placed: `orca-atop.inp`, `orca-bridge.inp`, `orca-hollow.inp` and `orca-reference.inp`. Let us follow the straightforward procedure to use the presented FOX extension.

1. Generation of the point-charge file via the command (for the atop adsorption position and the maximal embedding order) `./generate orca-atop.inp --dipole 0.089 --order 15`
2. The outputted point-charge file will be named `orca-atop-15.pc`, thus this name must be reflected in the `orca-atop.inp` file

3. Run your ORCA calculation as usual

6.1 Recommended values of dipole moments

According to the Ref. [8], the most optimal effective z -component dipole moments of CO at Pt(111) are:

- atop position: $\mu = 0.0890 \text{ e}\text{\AA}$,
- bridge position: $\mu = -0.0500 \text{ e}\text{\AA}$,
- hollow position: $\mu = -0.0790 \text{ e}\text{\AA}$,
- reference position: $\mu = 0.0254 \text{ e}\text{\AA}$.

They are referenced in Ref. [8] as the extrapolated (against the singlet-triplet CO energy gap) GGA dipole moments for the 1/4 ML coverage.

References

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