

TIF320 – Assignment 2

Computational Materials and Molecules

Structure of Sodium Nanoclusters

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Task 2: What does the genetic algorithm do?

The genetic algorithm is an optimization method that can be applied to a wide range of problems and is based on the principles of natural selection. This is implemented by having several generations, where the best suited individuals from each generation procreate, and their offspring obtains a combination of attributes from their parents combined with some mutation. It is applied here to the problem of finding the ground state atomic structure of Na nanoclusters with 6, 7 and 8 atoms (Na_6 , Na_7 , Na_8).

First, 20 initial guesses of atom configurations are generated at random and relaxed using a custom-made Lennard-Jones calculator. The genetic algorithm (GA) uses these initial guesses, relaxes them using GPAW and sorts the candidates by their energy. The two candidates to procreate are chosen in this case by certain fitness criteria and a roulette selection method, and they pass on a combination of their genes to the offspring which is a new candidate. This candidate is given random mutations. These mutations are the “MirrorMutation”, which mirrors half of the cluster on a randomly oriented cutting plane and discards the other half, and the “RattleMutation”, which randomly displaces the atoms according to a standard deviation distribution. The mutated candidate is then relaxed using GPAW. This procedure is repeated a fixed number of times (80 times in our case).

The space of possible atom configurations is explored in this way to find the configuration that has the lowest energy, which will have multiple copies in the population, since, ideally, a configuration close to the ground state relaxes into the ground state.

Task 4: Why is relaxation insufficient to find the ground state?

After relaxing an initial guess of an atomic configuration, the found equilibrium state might be a local minimum of the energy and therefore, the GA is used to find the global minimum (ground state).

Task 5: Collect the results (of Task 1)

In fig. 1 the atomic configurations with the lowest energies found through the GA in Task 1 are shown. The corresponding energies are presented in atomic units. Atomic units are defined as the unit system where the physical constants the reduced Planck constant \hbar represents action, the elementary charge e the charge, the Bohr radius a_0 the length and the electron rest mass m_e , the mass, are set to unity. Whenever the units a.u. are used in this report, the atomic base units are implied. E.g. for energy, the unit is $1 E_h = 27.211 \text{ eV}$.

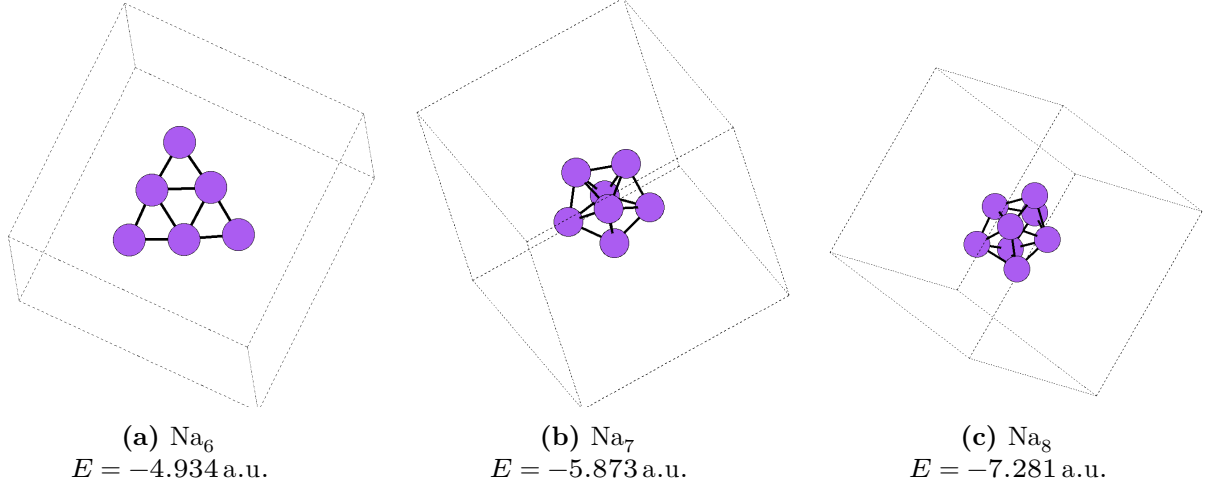


Figure 1: Ground state atomic structures found through the genetic algorithm of Na_6 , Na_7 and Na_8 . The corresponding energies are also given.

Task 6: Flat versus bulky

Nano clusters can form 2D structures because the excited atomic orbitals with a net angular momentum can form a symmetry that is mirrored on a plane. This symmetry can lead to lower energy bonds if the atoms arrange each other in a plane. When working with the Lennard-Jones potential, a spherically symmetric electronic potential is assumed which leads to structures that are 3D, since minimal interatomic distances lead to lower energies.

Task 7: First and second most stable structure

Since the GA samples a space around the ground state, it can also explore higher energy states. In fig. 2 the energies of all the candidates of the GA in Task 1 are shown. The candidates are sorted from the lowest (left) to the highest energy (right). To estimate the first higher energy state, additional to the ground state of the system, the second-lowest (significantly different) energy with more than a single candidate was selected. These energies are presented below

the figures. The energy differences from the ground state to the first higher energy state are therefore

$$\Delta E(\text{Na}_6) = 0.044 \text{ a.u.} \quad \Delta E(\text{Na}_7) = 0.144 \text{ a.u.} \quad \Delta E(\text{Na}_8) = 0.042 \text{ a.u.}$$

From Figure 2 we can assume that DFT reliably should find the clear distinct step between the ground state. This is due to the fact that the changes between atoms within the same state are quite small compared to the changes between two different states. For Na_6 the maximum difference within the ground state is 0.002 a.u. while the difference between the ground state and the first higher energy state is 0.041 a.u. which is a factor of 20 larger than the difference within the ground state. The same comparison for Na_7 is 0.001 a.u. compared to 0.143 a.u. which is a factor of 140 in difference. For Na_8 this is 0.005 a.u. compared to 0.034 a.u. which is a factor of 7 in difference. In other words, the differences are almost more than an order of magnitude for the cluster except for the Na_8 but a factor of 7 is still significant to be able to resolve the energy differences and so DFT is expected to have sufficient accuracy to distinguish the states. However, the LCAO + LDA method is usually less accurate than other options, but might in this case with the non-periodicity and localized nature provide more accurate results. Something the quantitative comparison between the states indicate.

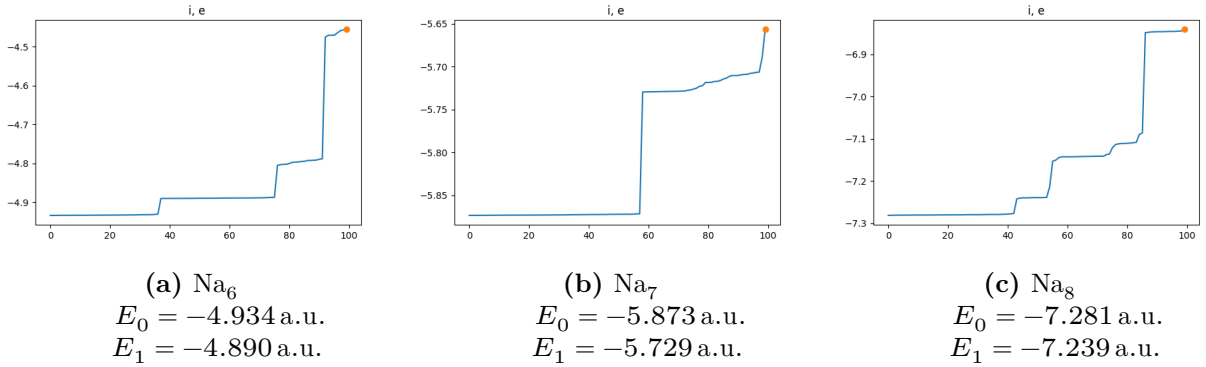


Figure 2: Energy of the candidates found through the GA in Task 1. The x-axis labels the candidates by position in the sorted list of candidates. The y-axis labels the energy in atomic units. The ground state energy E_0 is taken to be the lowest energy and the higher energy state energy E_1 is taken to be the second-lowest stable state (more than one candidate with this energy).

Task 8: A closer look at Na6

To see the effects on the accuracy of the different settings in the GPAW relaxation, the structures of Na_6 with the lowest and second-lowest energy are relaxed again using multiple different settings. The structures are taken from the course git repository and “christmas-tree” represents the structure found to be the ground state (see fig. 1) and “half-decahedron” is the found second-lowest energy state. The results are compiled in table 1. Each row represents a specific combination of settings applied to both structures. The first row are the default settings used in Task 1.

The “mode” setting determines in what ways the wave functions during the DFT calculations are approximated. It can be done using finite differences (“fd”, evaluated on a finite grid), using plane waves (“pw”, a linear combination of plane waves with the plane-wave cutoff set to $E_{\text{cut}} = 340$ eV) or using atomic orbitals (“lcao”, a linear combination of atomic orbitals specified as “dzp”).

The “xc” setting determines which exchange-correlation functional is to be used. The tried functionals are “LDA”, “PBE” and “RPBE”. “LDA” stands for local-density approximation and reduces the exchange-correlation to only depend on the electronic density n , i.e. the integral

$$E_{xc}[n] = \int n(\vec{r}) \varepsilon_{xc}(n(\vec{r})) d\vec{r} \quad (1)$$

where ε_{xc} is the exchange-correlation energy per particle of a homogeneous electron gas. “PBE” stands for Perdew, Burke, Ernzerhof, which is a GGA (generalized gradient approximation) exchange-correlation functional, and it extends LDA with the gradient of the electronic density. It is different from other GGA’s in that it is non-empirical and can be applied to a range of different problems without the need of fitting the functional to experimental data. “RPBE” is a slight revision of PBE which improves the chemisorption energies while still fulfilling the Lieb-Oxford criterion which provides a lower bound for the indirect part of the Coulomb energy.¹

The “h” setting determines how fine the real space is divided into a grid. I.e. it is the grid spacing in Å.

The “fmax” setting determines when the structure is considered to be relaxed and the iteration can be stopped. It is the maximum force that is allowed.

The results in table 1 show that only while “lcao” is used, the “christmas-tree” structure has a lower energy than the “half-decahedron” structure. It is however expected that “fd” gives accurate results with precise enough hyperparameters, since no particular basis has to be chosen there. This suggests that in reality, the “half-decahedron” is the proper ground state of Na_6 .

The plane waves mode is not particularly suitable for a localized problem like these nanoclusters and “lcao” seems to give different results than “fd”. Since the combination of “fd” and “PBE” is known to be reliable, this could be used for future calculations. However, it has to be noted that in table 1 “h” and “fmax” do not seem to have converged, and more precise parameters than $h=0.15$ and $fmax=0.05$ would have to be tried.

The Python script used to generate table 1 is appended at the end of this report.

¹B. Hammer, L. B. Hansen and J. K. Nørskov, Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals, Phys. Rev. B 59, 7413 (1999)

Table 1: Energies of the relaxed Na₆ structures using different settings in GPAW.

mode	Settings			Energies (a.u.)	
	xc	h (a.u.)	fmax (a.u.)	christmas-tree	half-decahedron
lcao	LDA	0.25	0.2	−4.9337	−4.8899
lcao	LDA	0.15	0.05	−4.9352	−4.8912
fd	LDA	0.25	0.2	−5.2561	−5.3213
pw	LDA	0.25	0.2	−5.2676	−5.3253
lcao	LDA	0.15	0.2	−4.9352	−4.8912
fd	PBE	0.25	0.2	−4.8188	−4.8584
fd	PBE	0.25	0.05	−4.8396	−4.8819
fd	PBE	0.15	0.2	−4.8213	−4.8606
fd	PBE	0.15	0.05	−4.8417	−4.8840
fd	RPBE	0.25	0.2	−4.4590	−4.5352

Task 9: Which calculation is the most accurate?

In the lecture, we learned that “fd” and “PBE” are the most reliable methods, therefore the last settings listed in table 1 should be trusted the most. In particular, the second to last setting should be the most accurate, since this is the setting with the fines “h” and “fmax”. It is however unclear whether the “RPBE” is more reliable than “PBE”, since it is the revised version of “PBE”.

When trying different “h” and “fmax” settings, the resulting relaxed clusters have different energies. Therefore, the used parameters are potentially not enough to have converged results. To get more accurate results, it is probably best to try more precise exchange-correlation functionals such as hybrid-GGA.

Other methods than DFT that lead to more reliable results but need more computation time are perturbation theory methods (e.g. Møller-Plesset) or configuration interaction methods (e.g. CISD or MCAS).

Task 10: Looking at the wave functions

Since Na has one valence electron and each band can be occupied by two electrons (opposite spin), only the lowest three bands in Na₆ and the lowest four bands in Na₇ and Na₈ are occupied (in the ground state). To extract the wave functions of the most stable structures found in the previous tasks, another GPAW relaxation using the second to last parameters in table 1 was performed and the resulting wave functions of the bands were saved to .cube files. The .cube files were then visualized using the program VESTA and the results are shown in fig. 3. For Na₆, the fourth band is not occupied.

Experimentally, it is known that Na₇ is not as stable as Na₈ (“the magic structure”). This can be explained when investigating the wave functions of the occupied bands. In fig. 3 it can be seen that the wave functions of Na₈ are more symmetric and in each show isosurface there are

two atoms. For Na_7 there is one atom in one of the isosurfaces and two atoms in the other one. Additionally, the symmetry plane of the wave functions of Na_8 have the four atoms in the plane, while for Na_7 the atoms are not placed on the symmetry plane as symmetric as for Na_8 . This electronic imbalance might lead to the instability of Na_7 . And the high symmetry of Na_8 might lead to its stability.

Furthermore, the electronic wave functions found here are similar to the atomic orbitals 1s and 2p. Each band can be filled with 2 electrons. However, for Na_7 there is only one electron in band 4. The fact that Na_7 cannot fully fill the first four bands leads to the instable behavior. Na_8 on the other hand, fully fills the shell (in the 2p analogy), as the 8 electrons fully occupy the first four bands. This leads to Na_8 being the “magic structure” as fully filled shells are the most stable.

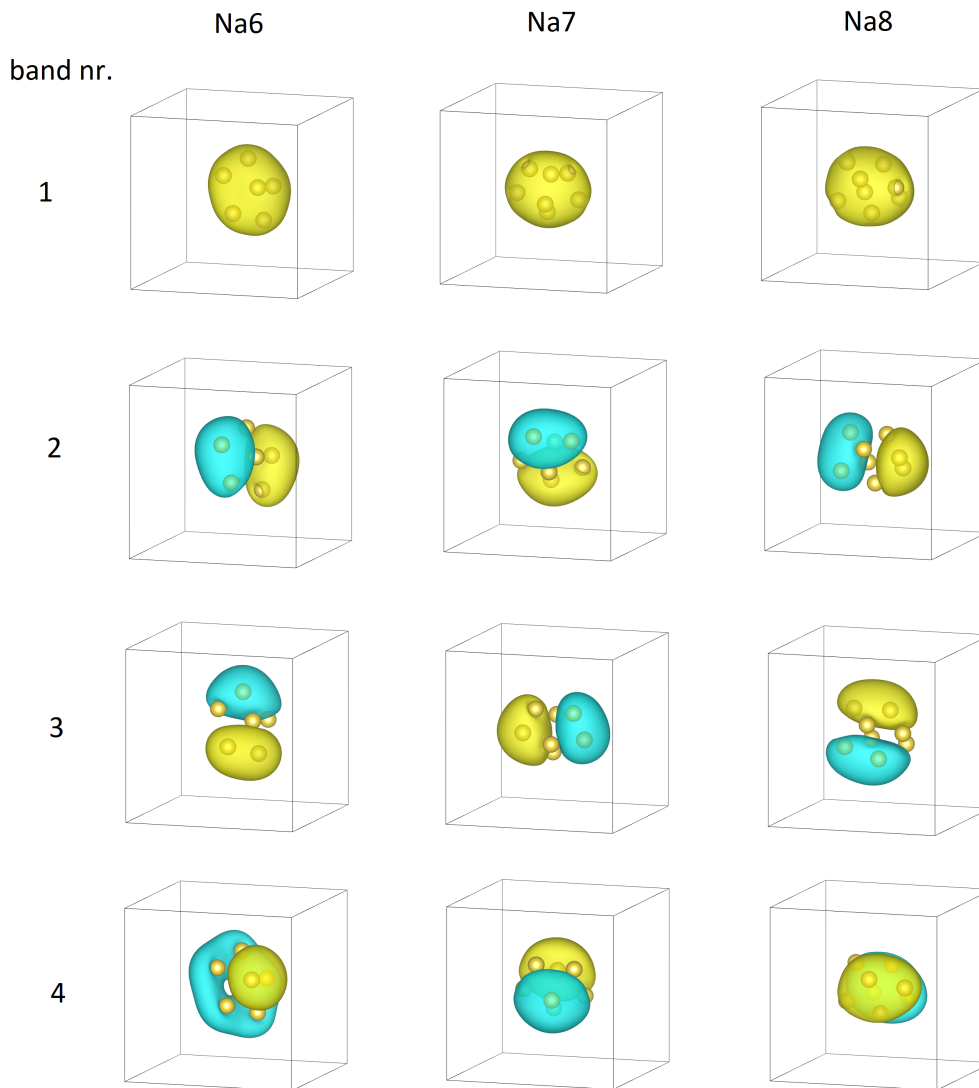


Figure 3: Wave functions of the lowest four energy bands for the most stable structures of Na_6 , Na_7 and Na_8 .

Appendix: Python script for task 8

```
1 from ase import Atoms
2 from gpaw import GPAW, FermiDirac
3 from ase.io import write, read
4 from ase.optimize import GPMIn
5 from pathlib import Path
6
7 Path("output/").mkdir(exist_ok=True)
8
9 Na6_low = read("christmas-tree.xyz")
10 Na6_high = read("half-decahedron.xyz")
11
12 fixed_params = {
13     "nbands": 10,
14     "occupations": FermiDirac(0.05),
15     "setups": {'Na': '1'},
16     "basis": "dzp"
17 }
18
19 params = [{
20     "mode": "lcao",
21     "xc": "LDA",
22     "h": 0.25,
23     "fmax": 0.2,
24 },
25 {
26     "mode": "lcao",
27     "xc": "LDA",
28     "h": 0.15,
29     "fmax": 0.05,
30 },
31 {
32     "mode": "fd",
33     "xc": "LDA",
34     "h": 0.25,
35     "fmax": 0.2,
36 },
37 {
38     "mode": "pw",
39     "xc": "LDA",
40     "h": 0.25,
41     "fmax": 0.2,
42 },
43 {
44     "mode": "lcao",
45     "xc": "LDA",
46     "h": 0.15,
47     "fmax": 0.2,
48 },
49 {
50     "mode": "fd",
51     "xc": "PBE",
52     "h": 0.25,
53     "fmax": 0.2,
54 },
```

```

55 {
56     "mode": "fd",
57     "xc": "PBE",
58     "h": 0.25,
59     "fmax": 0.05,
60 },
61 {
62     "mode": "fd",
63     "xc": "PBE",
64     "h": 0.15,
65     "fmax": 0.2,
66 },
67 {
68     "mode": "fd",
69     "xc": "PBE",
70     "h": 0.15,
71     "fmax": 0.05,
72 },
73 {
74     "mode": "fd",
75     "xc": "RPBE",
76     "h": 0.25,
77     "fmax": 0.2,
78 },]
79
80 for i in range(len(params)):
81     temp_params = params[i].copy()
82     fmax = temp_params.pop("fmax")
83
84     Na6_low_copy = Na6_low.copy()
85     Na6_high_copy = Na6_high.copy()
86
87     calc = GPAW(**temp_params, **fixed_params, txt=f'output/out_{i:03d}Na6_low.
txt')
88     Na6_low_copy.set_calculator(calc)
89     dyn = GPMin(Na6_low_copy, trajectory=f'output/{i:03d}Na6_low.traj', logfile
=f'output/{i:03d}Na6_low.log')
90     dyn.run(fmax=fmax, steps=100)
91
92     calc = GPAW(**temp_params, **fixed_params, txt=f'output/out_{i:03d}Na6_high
.txt')
93     Na6_high_copy.set_calculator(calc)
94     dyn = GPMin(Na6_high_copy, trajectory=f'output/{i:03d}Na6_high.traj',
logfile=f'output/{i:03d}Na6_high.log')
95     dyn.run(fmax=fmax, steps=100)
96
97     params[i]["Na6_low_energy"] = Na6_low_copy.get_potential_energy()
98     params[i]["Na6_high_energy"] = Na6_high_copy.get_potential_energy()
99
100 import pandas as pd
101 df = pd.DataFrame(params)
102 df.to_csv("output/results.csv")

```

Appendix: Python script for task 10


```
1 from ase import Atoms
2 from gpaw import GPAW, FermiDirac
3 from ase.io import write, read
4 from ase.optimize import GPMIn
5 from ase.units import Bohr
6 from pathlib import Path
7
8 Path("output/").mkdir(exist_ok=True)
9 Path("output/wavefunctions/").mkdir(exist_ok=True)
10
11 # GPAW parameters
12 params = {
13     "mode": "fd",
14     "xc": "PBE",
15     "h": 0.15,
16     "nbands": 10,
17     "occupations": FermiDirac(0.05),
18     "setups": {'Na': '1'},
19     "basis": "dzp"
20 }
21 fmax = 0.05
22
23 for i in [6,7,8]:
24     # Read the best clusters
25     atoms = read(f"Na{i}_best.xyz")
26
27     # Do a new GPAW calculations
28     calc = GPAW(**params, txt=f'output/out_Na{i}.txt')
29     atoms.set_calculator(calc)
30     dyn = GPMIn(atoms, trajectory=f'output/traj_Na{i}.traj', logfile=f'output/
log_Na{i}.log')
31     dyn.run(fmax=fmax, steps=100)
32     print(f"Na{i} energy = {atoms.get_potential_energy()}")
33
34     # loop over all wfs and write their cube files
35     nbands = calc.get_number_of_bands()
36     print(f"Na{i} number of bands: {nbands}")
37     for band in range(nbands):
38         wf = calc.get_pseudo_wave_function(band=band)
39         fname = f'output/wavefunctions/Na{i}_{band:03d}.cube'
40         print('writing wf', band, 'to file', fname)
41         write(fname, atoms, data=wf * Bohr**1.5)
```