
DFT Calculations for Nitrogen Dissociation Using FLiNaK

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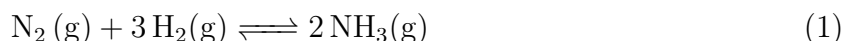
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1 Introduction

Ammonia is an essential chemical used in production of fertilizer, pharmaceuticals and polymers. It is estimated that 182 million metric tonnes of ammonia was produced in 2021 globally [1]. The most common way to produce ammonia is with the Haber-Bosch process, where high temperatures of around 350 to 450 degrees Celsius is used and a pressure of around 150 to 200 bars [1]. The Haber-Bosch process stands for around 1% of global energy consumption and emits around 1.3% of the global carbon dioxide emissions [1]. Therefore, there is an interest in finding alternative methods for ammonia production, of which the typical chemical reaction is [2]:



An important step in the production of ammonia is the breaking of the strong triple bond in an N_2 molecule. Metal surfaces are often used to facilitate the breaking of the bond by adsorbing the molecule.

Another way to dissociate the strong N_2 bond could be to use molten salts in combination with a metal surface. The advantage of using molten salts is their high thermal stability, chemical inertness and high heat conductivity [3]. As a result of these properties there is an interest in using molten salts for the purpose of dissociating N_2 . The high temperature stability is required to overcome the triple bond, which makes molten salts appealing to use. It is also chemical inert when the salt is at high purities and therefore would not corrode its surroundings. Another advantage comes from the possibility to dissociate the N_2 molecule at much lower pressure than in the Haber-Bosch process.

Using atomistic simulations, we plan to estimate the dissociation energy of nitrogen molecule in molten salts ((1:1:1) LiF-NaF-KF), with the goal of advancing ammonia production. We will compare the energetics for nitrogen on a metal surface in the salt environment, focusing on the splitting of the strong N_2 triple bond, which is a major bottleneck of ammonia production.

2 Computational Method

Density Functional Theory (DFT) is a technique used to study molecules, solids, surfaces and interfaces [4]. It is arguably the most used computational method in chemistry and physics, with estimates of over 30,000 new publications each year that use DFT [5]. Contrary to previous wave-function based methods, it uses the density n as the central variable to simulate material behaviour. This allows the calculation of complex systems efficiently and accurately.

Most DFT calculations, as well as those in this report, use the Kohn-Sham approach. In this approach, the real, interacting system is replaced with a non-interacting system that has the same density $n(\mathbf{r})$. To ensure that the electrons in this 'fake' system behave similar

to the 'real' electrons they are placed in an effective potential v_R :

$$v_R = v_H(\mathbf{r}) + v_{ion}(\mathbf{r}) + v_{xc}(\mathbf{r}) \quad (2)$$

with $v_H(\mathbf{r})$ the Hartree potential, the potential due to electrostatic repulsion between electrons, $v_{ion}(\mathbf{r})$ the potential due to interaction with the ions and $v_{xc}(\mathbf{r})$ the exchange-correlation potential. The latter one contains all the complicated interactions that are not included in the first two. Because the exact form of the exchange-correlation potential is unknown, much work in DFT has been done on finding a good approximation that is both accurate and computationally efficient.

The procedure of a DFT calculation is roughly as follows. It starts by making a rough estimate of the ground-state electron density $n(\vec{r})$ of the system. According to the first Hohenberg-Kohn theorem this electron density uniquely describes the ground state of a many-particle system. Using this density the effective potential from equation 2 is calculated and inserted into the Kohn-Sham equations:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_R\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \quad (3)$$

The single-particle wave functions $\phi_i(\mathbf{r})$ are then used to calculate a new density:

$$n(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2 \quad (4)$$

which can be fed back into the effective potential, iterating until it converges.

This project uses DFT implemented in python using the Atomic Simulation Environment package [6]. To examine the effect of the salt on nitrogen dissociation kinetics we split the calculations in two parts: first, we simulate N_2 in vacuum, then we 'put' it in an environment of FLiNaK.

2.1 Setup

In this report, we will examine nitrogen dissociation on nickel surfaces. Nickel is widely used for N_2 dissociation because its partially filled d-orbitals enable effective activation of the strong triple bond. Nickel provides an advantageous balance between adsorption strength and catalytic activity, while also being thermally stable, and relatively inexpensive. Therefore, it is well characterized as a catalyst for dissociating N_2 [7, 8]. To simulate the metal, we create a 4x4x3 Ni(111) Face-Centered Cubic (FCC) surface.

```
slab = fcc111('Ni', size=(4, 4, 3), vacuum=10.0)
```

The bottom two layers are then frozen in place. This is done to simulate the top layer and any adsorbed material sitting on a thicker solid metal. The top layer will then relax to a lower energy, while the bottom layers remain in their bulk crystal configuration. An additional

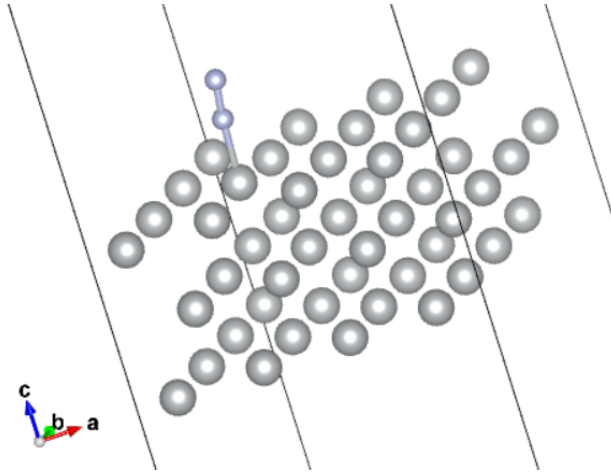


Figure 1: 4x4x3 (111) FCC Ni surface with N₂ molecule adsorbed on on-top position. Visualised using VESTA [9].

benefit of freezing the bottom two layers is the reduction of computing time. The program has to calculate the forces on each atom for each iteration. Atoms that do not move and contribute much to the final result will therefore extend the computing cost unnecessarily. For this reason we chose to only unfreeze the top layer, rather than the top two layers, as is often the case. Optimally we would have two frozen layers and more unfrozen layers, achieved by more layers in total.

```
ni_z_clean = [atom.position[2] for atom in full_system if atom.symbol == 'Ni']
unique_z_clean = np.unique(np.round(ni_z_clean, decimals=3))
frozen_layers_z_clean = unique_z_clean[:-2]
mask_clean = [(atom.symbol == 'Ni' and np.round(atom.position[2], decimals=3) in
               frozen_layers_z_clean) for atom in full_system]
full_system.set_constraint(FixAtoms(mask=mask_clean))
```

The DFT calculation were run with different configurations of adsorption sites for the N atoms and N₂ molecules. The preferred adsorption sites for N on Ni(111) is the hcp site, where it for N₂ is the top site [10]. Figure 2 shows these most stable adsorption sites. This was implemented by placing the N and N₂ slightly above the Ni(111) surface at the corresponding sites.

For example, to adsorb the N₂ molecule and the separate N atoms to the Ni surface, we use the `add_adorbate` function:

```
add_adorbate(slab_nn, 'N', height=h, position='hcp')
```

Where a Nitrogen atom 'N' is placed at a 'hcp' site a distance h above the Ni(111) surface `slab_nn`.

To compare the vacuum results with a molten salt environment, we insert a pre-written FLiNaK configuration by Jose Robles. The FLiNaK is placed at a height h above the metal

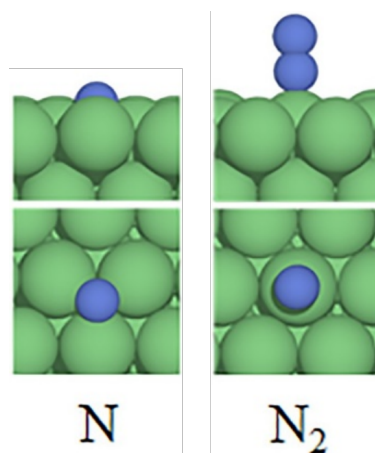


Figure 2: Side view and top view of the most stable adsorption structures for N and N₂ adsorbates on Ni(111). Adapted image from Ref. [10].

surface. This height should not be too low, since that will cause instabilities due to high repulsive forces. It should also not be too high, since that would require the calculation to take many calculational steps before converging.

The chosen calculator is the Grid-based Projector Augmented Wave (GPAW) code [11], which is natively integrated with the *ase* package. The tightly bound core electrons are treated using the PAW method, which replaces their sharply oscillating potentials with smoother, computationally efficient functions. The valence electronic wavefunctions are expanded using a plane-wave (PW) basis set. These wavefunctions are constructed by summing plane waves up to a specified kinetic energy cut-off, which defines the spatial resolution of the simulation. The method with which this energy cut-off is determined is further explained in section 2.2.1.

The chosen exchange-correlation functional is the Perdew-Burke-Ernzerhof (PBE) functional. This is an efficient and relatively accurate Generalized Gradient Approximation (GGA) functional. These types of functionals use the gradient of the density ∇n in addition to the density n itself. A major advantage of PBE is that it is non-empirical, meaning that it can be applied to a large range of systems with reasonable accuracy, even without empirical data [12].

Because of the 2D and periodic character of the setup, the k points are sampled in a $k \times k \times 1$ Monkhorst-Pack grid. The method of determining the best value for k is explained in section 2.2.2.

Electron smearing is used to help the convergence of the system. The reason it is done is because at zero temperature the occupied states for electrons contain a sharp edge with all occupied states filled below the fermi level and empty above the fermi energy. In the case of metals there are many states that are close to the fermi level so in the case of the self-consistency cycle the band can shift in energy from iteration to iteration. This means that the band can be occupied in one iteration and unoccupied in the next which gives a

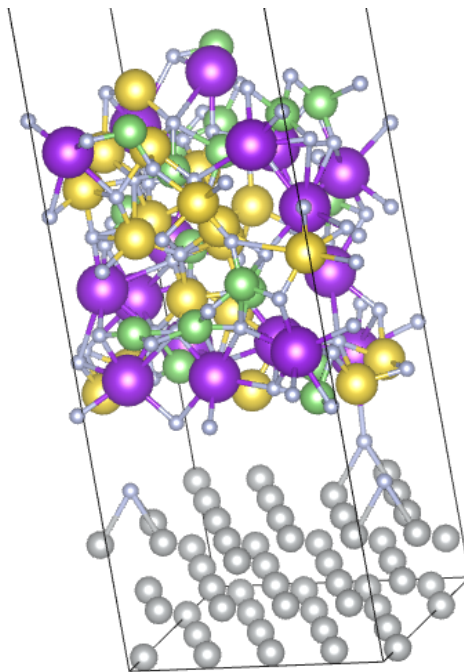


Figure 3: Illustration of a (111) FCC Ni surface with two adsorbed Ni atoms in a FLiNaK environment.

large difference in charge density between iterations. The large change in charge density can impede the convergence of the self-consistent solution.

By counteracting this, the electron is subjected to temperature smearing, which reduces abrupt occupation changes between iterations and makes Brillouin-zone integration easier. There are many different methods of applying a smearing and in this report a Fermi-Dirac method was used. The parameter σ was chosen to be 0.1 eV, which corresponds to about 900 °C.

This ultimately results in a GPAW setting of:

```
calc_clean = GPAW(mode=PW(PW_cutoff), xc='PBE', kpts=(k,k,1), random=True,
                  occupations=FermiDirac(smearing), txt=f'Ni_clean_225_4kpt.txt',
                  spinpol=False, nbands = nbands)
```

`random=True` is used to introduce some asymmetry, limiting the chance of ending up in a saddle point. During testing of the FLiNaK environment, we often encountered a convergence error that stated that there were not enough bands for occupied orbitals. To combat this, we set the number of bands to a fixed number and found that 1500 bands usually resulted in a successful calculation. Although this number is probably too high for most scenarios, it ensured that the code did not fail unexpectedly.

The Brodyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm was chosen as the optimizer. This method uses a quasi-Newtonian approach, which means that it approximates the Hes-

sian matrix of the loss function, continuously improving the approximation throughout the iterations. A convergence criterium of 0.05 was chosen.

Originally, the code was run with the setting `spinpol=True`, which takes the spin polarization into account in the calculations, but it showed to have severe impact on computation time. Simulating the simpler system of N₂ on Ni in vacuum timed out after running with 16 cores for a little more than 3 days. By changing `spinpol=False` some accuracy is lost, but the computation time is massively reduced. The same vacuum code now finished in around 16 hours.

2.2 Convergence

Before running the full DFT code we perform various convergence tests to determine suitable plane-wave cut-offs and k-point spacing. The reasoning for this is a compromise of accuracy for computational time. Adding a convergence criteria to the plane-wave cut-off and k-points gives a suitable stopping point for the DFT calculations, where no significant change in the difference in energies occurs by adding more plane-waves or k-points. This gives a less accurate results but reduces computational time dramatically.

2.2.1 Plane-wave cut-off

When performing DFT calculations the electrons can be described using a plane-wave. For a material with a lattice constant, Bloch's theorem can be used to describe them as:

$$\psi(r) = u(r)e^{ik \cdot r} \quad (5)$$

where $u(r)$ has the exact lattice periodicity, r is the position vector and k is the wave vector of the plane-wave. The problem is that for the exact wavefunction it requires infinitely many plane waves and therefore a cut off-energy is used. Each of the plane waves has a kinetic energy and therefore, a cut-off E_{cut} is set so all plane-waves with higher energies than the cut-off are not used for the wavefunction. With this said, the appropriate cut-off energy must be found to ensure that there are enough plane-waves for high accuracy when making the wavefunction, while keeping the computational time down. To solve this problem a convergence test is performed on the cut-off energy, where a convergence criteria is set so that if adding more plane-waves the change in energy will be insignificant and it would therefore not make sense to add more plane-waves.

To determine a suitable plane-wave cut-off energy we used a range from 300 eV to 650 eV with an increase of 50 eV per interval and a convergence criteria of 0.01eV and calculated the energy of each iteration. When the change was below the criteria, the code stopped.

2.2.2 K-point

Another important parameter is the k-points, which represent specific values of the electron wavevector k used to describe electron waves inside a periodic system. According to Bloch's

theorem, the electronic wavefunctions are characterized by wavevectors k in reciprocal space. Due to the periodicity of the crystal lattice, the k -values also become periodic in reciprocal space, meaning that only the first Brillouin zone needs to be sampled. The Brillouin zone represents the fundamental region of reciprocal space for a crystal lattice. In DFT calculations, a sufficient number of k -points must be used to accurately sample the Brillouin zone and calculate properties such as the electron density and total energy. The k -point convergence test used an interval of 1 to 10 k -points tested with an increase of 1 per interval, with a convergence criteria of 0.01 eV, the same as for the plane-wave cut-off.

3 Results

3.1 Convergence Tests

From the convergence test it was found that the cut-off energy for the plane waves were at 550 eV and 7 k -points for the mesh. The energy of the convergence test for the plane wave cut-off and k -points are shown in Figure 4. It should be mentioned that for the cut-off energy a mesh of the size of 12 k -points was used to ensure accuracy when finding the cut-off energy. After finding the cut-off energy it was used for the convergence test of the k -points.

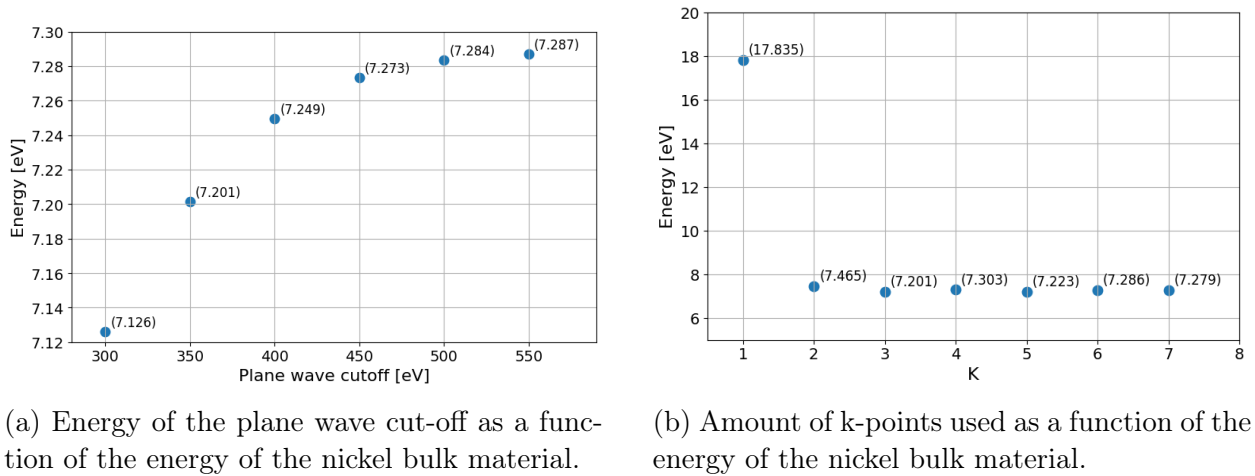


Figure 4: Convergence for plane-wave cut-off and k -points used with a criteria of 0.01 eV.

For the k -points, it is observed that using only a single k -point results in a significantly higher energy compared to the other calculations. This is likely because a single k -point corresponds only to sampling the Γ -point, which does not provide sufficient information about the entire Brillouin zone. As the number of k -points increases, the calculated energy becomes more consistent and converges toward a stable value. It was found that the system had converged at 7 k -points. However, performing DFT calculations with such a dense k -point mesh would be computationally expensive. Therefore, a lower k -point mesh of $4 \times 4 \times 1$ was chosen as a compromise between computational cost and accuracy. This mesh was used for the vacuum calculation, however, when FLiNaK was introduced to the system it was further reduced

to a $2 \times 2 \times 1$ mesh. The reduction was necessary and could be done because even for 2 k-points the energy had mostly converged with a difference of 0.186 eV from using 2 k-points, compared to the converged value of 7 k-points. Still, with the reduction of the mesh size it was expected that running the FLiNaK code would still take weeks to finish.

3.2 Vacuum

The resulting total energies of the vacuum system calculations are shown in table 1. The total energy of a system is found by the `get_potential_energy()` function, which includes the kinetic, electrostatic, and exchange-correlation energy [6]. These are computed with $4 \times 4 \times 1$ k-points. Using 24 cores this took up to 15 hours per calculation and 24 hours for a code calculating the total energy of N_2 and 2N on a single site. The 2N atoms were placed two unit cells away from each other.

System	Total Energy [eV]
Clean Ni	-325.32
Isolated N_2 molecule	-16.26
2N Adsorbed top	-336.97
2N Adsorbed hcp	-342.13
N_2 Adsorbed top	-342.06
N_2 Adsorbed hcp	-341.15

Table 1: Total Energies for DFT calculations of a Ni (111) surface in an environment of vacuum using $4 \times 4 \times 1$ k-point sampling.

We can then calculate the adsorption and surface dissociation energies. The adsorption energy of the nitrogen molecule can be calculated using:

$$E_{ads} = E_{N_2^*} - (E_{slab} + E_{N_2}) \quad (6)$$

The surface dissociation energy is the energy difference of the two adsorbed states, $N_2^* \rightarrow 2N^*$. This does not account for the large activation barrier still required to split the $N \equiv N$ bond of the already-adsorbed nitrogen molecule. In short, it is the difference between the total energy of the adsorbed N_2 system and the separate adsorbed N system:

$$E_{diss} = E_{2N^*} - E_{N_2^*} \quad (7)$$

With the total energies in Table 1 the adsorption energies and surface dissociation energies can be calculated with equations 6 and 7, yielding the results shown in Table 2.

System	Adsorption energy [eV]	Surface dissociation energy [eV]
N_2^* top, $2N^*$ top	-0.48	5.09
N_2^* hcp, $2N^*$ hcp	0.43	-0.98
N_2^* top, $2N^*$ hcp	-0.48	-0.07

Table 2: Total Energies for DFT calculations of a Ni (111) surface in an environment of vacuum using $4 \times 4 \times 1$ k-point sampling.

3.3 FLiNaK

Due to the added complexity of the FLiNaK salt in the simulation, computation times proved much longer than for the vacuum environment. For this reason, and because the results for $k = 2$ were not too dissimilar from higher k-points, we first ran the calculations for FLiNaK on a $2 \times 2 \times 1$ k-point grid. On 24 cores, these calculations took about 17 hours.

The FLiNaK salt was placed a height $h = 3 \text{ \AA}$ above the Ni surface. In the case of the adsorption of the N_2 molecule on the Ni surface, the molecule was placed in the center on the top or hcp site of the Ni(111) surface. The molecule was angled at 45° relative to the surface.

In the case of the separate adsorbed N atoms, the atoms were placed 2 unit cells away from each other on the hcp site of the Ni(111) surface.

System	Total Energy [eV]
Clean Ni	-663.96
Isolated N_2 molecule	-16.26
2N Adsorbed hcp	-674.3
N_2 Adsorbed hcp	-677.66
N_2 Adsorbed top	-677.91

Table 3: Total Energies for DFT calculations of a Ni (111) surface in a FLiNaK environment using $2 \times 2 \times 1$ k-point sampling.

The results of the DFT calculations are shown in table 3. These results are unreliable, however, since we never managed to converge the energies. Because of the size of the system, calculating a single step took upward of 17 hours on 24 cores, meaning that converging to below the criterium could take multiple weeks, assuming the same amount of steps was needed as in the vacuum system.

Nonetheless, if we assume the results from table 3 to be correct, we can calculate the adsorption and surface dissociation energies with equations 6 and 7. With the results from the DFT calculations the adsorption energy yields $E_{ads,N_2} = 2.55 \text{ eV}$ and the dissociation energy $E_{diss} = 3.35 \text{ eV}$. This would indicate that it is an endothermic reaction.

4 Discussion

From the results of the vacuum systems shown in Table 1 it is seen that in the case of N_2 the total energy of the system is lower when the molecule is adsorbed on a top adsorption site (-342.06 eV), compared to on a hcp site (-341.15 eV). This tells us that the top site is the more stable adsorption site for the N_2 molecule. For the 2N atoms we see the opposite to be true as the total energy of the hcp adsorbed 2N system (-342.13 eV) is lower than when adsorbed on the top site (-336.97 eV). The difference for N atoms is much larger than for the nitrogen molecule as the adsorption of N on the hcp site of Ni(111) is quite strong, which, as mentioned earlier in Figure 2, is in agreement with expectations from literature [10].

The adsorption and surface dissociation energies in Table 2 shows a big difference between the three different systems. In particular, for the surface dissociation energy where both the N_2 molecule and 2N atoms are placed on top sites the energy is both positive and a lot larger. This indicates that N_2 is a more energetically favoured state than 2N. This makes sense as we know that the nitrogen atoms strongly prefer the hcp sites.

When hcp is used as both adsorption sites the surface dissociation energy is the most negative, indicating that this is the system where dissociation is thermodynamically more favourable. However, as the adsorption energy is positive, adsorption is unfavoured and it would require 0.43 eV to adsorb a N_2 molecule on the hcp site. The most realistic case is the last one, where N_2 adsorbs at the top site and 2N atoms adsorb at the hcp site. In this case both the adsorption energy of N_2 and the surface dissociation energy are negative. This means that N_2 would adsorb on the Ni(111) top site, and if given enough energy to overcome the activation barrier of the $N\equiv N$ bond, would end in a more stable state with 2N adsorbed at hcp sites.

The adsorption energies of N_2 on top sites match the value reported in literature of -0.48 eV, but for the hcp sites they differ as reported values are -0.12 eV [10].

During the project, several problems arose regarding computation time. The system size proved a limiting factor, with our estimate of a full FLiNaK run, using $2\times 2\times 1$ k-point sampling, would take up to two weeks to compute. By the time we realized this there was not enough time to compute a full FLiNaK run using $2\times 2\times 1$ k-point sampling, let alone using $4\times 4\times 1$ or $7\times 7\times 1$ k-point sampling as the convergence test showed.

There are several factors that could possibly decrease the computation time. First of all, further optimising the height of the FLiNaK above the Ni surface could reduce the number of steps the FLiNaK needs to relax to near the Ni surface. By sampling a range of heights and relaxing the structure at that height for one step, one can determine the minimum force. This should correspond to the optimal height. This height can then be used to fully relax the system using the BFGS algorithm.

Another change that would drastically reduce the computation time would be (partly) freezing the FLiNaK salt. This would reduce the number of atoms for which the forces would

need to be calculated, but would make the result rather meaningless. The reason we examine liquid FLiNaK is to see if it can act as a stabilizer, but if it is frozen in place it cannot move around to stabilise the reaction products.

The total system consisted of 48 Ni atoms, 2 N atoms, 50 F atoms, 16 Li atoms, 17 Na atoms and 17 K atoms. Reducing the size of this system would reduce the computational cost, but would result in a less accurate result.

The current results for the FLiNaK environment are unreliable, however, if they were reliable we could draw some conclusions by looking at the difference between the vacuum and FLiNaK cases. If, for the sake of argument, we assume the results to be accurate, then the dissociation of nitrogen in FLiNaK is endothermic, which would make it unsuitable to use in ammonia production.

5 Conclusion

In this report, the potential of the use of FLiNaK in ammonia production was explored by using DFT calculations to assess the energetics of nitrogen dissociation on a nickel surface. Using the *Atomic Simulation Environment* we created a $4 \times 4 \times 3$ Ni(111) FCC surface, with the bottom two layers frozen. First, a N_2 molecule is adsorbed on the hcp and top sites. Then, two N atoms are adsorbed. Calculations are done using the Grid-based Projector Augmented Wave (GPAW) calculator in plane-wave (PW) mode. Perdew-Burke-Ernzerhof (PBE) is used as the exchange-correlation functional and electron smearing is done using Fermi-Dirac with $\sigma = 0.1$ eV. The Brodyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm was chosen as the optimization algorithm. Before running the full code, convergence tests were performed to determine suitable PW cut-offs and k-point spacing. A 550 eV PW cut-off was used and the test determined a $7 \times 7 \times 1$ k-point grid was best, however, due to computational limits $2 \times 2 \times 1$ and $4 \times 4 \times 1$ grids were used.

The calculations were done both for nitrogen adsorbed on Ni in vacuum and in a pre-built FLiNaK environment. In the vacuum environment, the system relaxed until $f_{max} \leq 0.05$. Calculations showed $E_{ads,N_2^*} = -0.48$ eV for the top site and $E_{ads,N_2^*} = 0.43$ for the hcp site. The surface dissociation energy for N_2^* and $2N^*$ both at top sites was 5.09 eV, indicating a endothermic reaction. N_2^* top and $2N^*$ at the hcp site had both negative E_{ads} and E_{diss} , making it, of those examined, the most likely configuration for nitrogen dissociation.

DFT calculations for the FLiNaK environment proved more difficult. Due to computational constraints, a $2 \times 2 \times 1$ k-point grid was used, but even then computing 1 step took over 15 hours. Ultimately, we were unable to properly converge the system. The unconverged results yielded $E_{ads,N_2^*} = 2.55$ eV and $E_{diss,N_2^* \rightarrow 2N^*} = 3.35$ eV. These results would show an endothermic reaction, but are highly unreliable due to the system not being properly relaxed.

6 Outlook

A direct next step in this project would be to run the full system containing FLiNaK to get more accurate adsorption and dissociation energies using $2\times 2\times 1$ and $4\times 4\times 1$ k-point sampling. We can then also calculate other quantities such the kinetic activation barrier. Other transition metals such as Ruthenium (Ru), Iron (Fe) or Molybdenum (Mo) can also be examined to compare against Ni.

More accurate results can be obtained by removing some of the approximations we used, for example by including spin-polarisation to better handle the single nitrogen atoms. This will come at a computational cost, since we found out during trial runs that spin-polarisation can increase the computation time by two or three times. A more hybrid approach can also be used, where the first steps are done without spin-polarisation and then the last steps are done with spin-polarisation, to relax to a more accurate energy.

The method presented in this report can be extended to different configurations of FLiNaK or even different kinds of molten salts, such as FLiBe. By examining different molten salts we can better predict a suitable candidate for use in ammonia production.

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