



Density functional theory study of nitrogen atoms and molecules interacting with Fe(1 1 1) surfaces



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ABSTRACT

We present Density functional theory (DFT) calculations for the investigation of the structural relaxation of Fe(1 1 1), as well as for the study of the interaction of nitrogen atoms and molecules with this surface. We perform spin polarized DFT calculations using VASP (Vienna Ab-initio Simulation Package) code. We use the supercell approach and up to 19 slab layers for the relaxation of the Fe(1 1 1) surface. We find a contraction of the first two interlayer distances with a relative value of $\Delta_{12} = -7.8\%$ and $\Delta_{23} = -21.7\%$ with respect to the bulk reference. The third interlayer distance is however expanded with a relative change of $\Delta_{34} = 9.7\%$. Early experimental studies of the surface relaxation using Low Energy Electron Diffraction (LEED) and Medium Energy Ion Scattering (MEIS) showed contradictory results, even on the relaxation general trend. Our current theoretical results support the LEED conclusions and are consistent qualitatively with other recent theoretical calculations. In addition, we study the interaction energy of nitrogen atoms and molecules on the Fe(1 1 1) surface. The nitrogen atoms are adsorbed in the hollow site of the unit cell, with an adsorption energy consistent with the one found in previous studies. In addition, we find the three molecularly adsorbed states that are observed experimentally. Two of them correspond to the adsorbed molecule oriented normal to the surface and a third one corresponds to the molecule adsorbed parallel to the surface. We conclude that our results are accurate enough to be used to build a full six-dimensional potential energy surface for the N_2 system.

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1. Introduction

Elementary reactive processes at surfaces are complex phenomena that can be highly dependent on minor details of the electronic interactions [1,2]. A clear illustration for this statement is the variation of the chemical activity with the particular face of a given metal surface. Metal surfaces made of identical atomic species but structurally altered in distinct terminations can give rise to completely different energy landscapes. The chemical activity can thus be enhanced or hindered depending on the particular crystal face under study.

The adsorption of nitrogen molecules on metal surfaces is no exception to this general statement and the particular crystal face on which the process takes place determines the final output. For instance, molecular beam experiments show that for N_2 on W

(100) the initial dissociation probability or sticking coefficient S is roughly $S \approx 1$, for relatively low surface temperatures and thermal energies of the beam [3,4]. The dissociation probability is, however, about two orders of magnitude smaller in W(110) for the same range of temperatures and energies [5]. The difference in reactivity between the two W faces is a dynamical effect driven by differences in the interaction energy at distances relatively far from the surface and not from the specific features of the surface sites in which the dissociating atoms are eventually adsorbed [6,7].

In Fe surfaces, it was already shown long ago that the dissociation probability S can vary by orders of magnitude depending on the crystal face [1,8,9]. Among many other reasons, the reactivity of N_2 on Fe surfaces is important because it plays a crucial role in the chemical industry. The dissociation of N_2 on iron-based compounds is commonly considered to be the rate limiting step in ammonia synthesis through the Haber–Bosch process. Common catalyzers make use of iron surfaces promoted with potassium cations [10,11].

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Under low pressures, the dissociation probability of N_2 is higher in the open surface Fe(111) and progressively decreases in Fe(100) and Fe(110). From the theoretical side, density functional theory (DFT) has been widely used to quantitatively study different features of the atomic and molecular adsorption processes of nitrogen in the three mentioned low-index faces [12–15]. In Fe(110), the dynamics of the adsorption processes has been theoretically calculated using a DFT-based potential energy surface (PES) [14]. The subtle effect of strain in the surface has been analyzed as well [16,17]. Surprisingly and to our knowledge, there are no full-dynamics studies for the adsorption dynamics of N_2 on the Fe(111) surface, in spite of this being the most reactive face. Molecular beam experiments showed that both the kinetic energy [18] and the vibrational energy [19] of the incident molecules are efficacious agents in promoting dissociation, the former being much more efficient than the latter. The adsorption probability S can increase by roughly five orders of magnitude changing the kinetic energy of the incident beam E_i from $E_i \approx 0.1$ eV to $E_i \approx 4.3$ eV. These numbers show well the relevance of dynamical effects in the dissociative adsorption of N_2 on Fe(111).

One of the difficulties when treating with the (111) face of Fe is that contradictory experimental and theoretical results have been obtained on the relaxation suffered by the first surface layers [20–25]. The disagreement, as will be shown later, can be not only quantitative but also qualitative. The absolute value of these differences is not particularly large, however, due to the small interlayer distance in the Fe(111) surface. We start this work with a theoretical study of the relaxation of the Fe(111) surface based on DFT calculations. With this analysis we intend, first, to offer new insight into the difficult puzzle of Fe(111) relaxation and, second, set the necessary basis for the subsequent study of the N atom and N_2 adsorption processes.

The second part of the article focuses on the interaction of N and N_2 with Fe(111). We will show the interaction energy for atoms and molecules placed at different symmetry points of the surface, as well as its dependence with the distance to the surface. The results presented here are a preliminary step previous to the building of a full potential energy surface, based on DFT calculations, on which a complete dynamical study of the adsorption process of nitrogen on Fe(111) can be performed.

2. Theoretical methods and computational details

We perform first-principles spin polarized DFT [26,27] calculations, as implemented in the Vienna Ab-initio Simulation Package (VASP) package [28–30]. VASP operates with a plane-wave basis set. In our calculations, the exchange correlation energy is obtained from the spin-polarized version of the Generalized Gradient Approximation (GGA) [31], with the Perdew–Wang (PW91) exchange–correlation functional. The PW91-GGA usually provides reasonable accuracy about structural information and binding energy [32]. The electron–ion core interactions are represented by Projector Augmented Wave (PAW) pseudopotentials [30]. A 400 eV cut-off energy is used for the expansion of the plane-waves basis set.

The Fe(111) surface is modeled by a periodic (2×2) unit cell as shown in Fig. 1. The surface layers are represented by a slab supercell approach, separated by a vacuum region of 15 Å, which is large enough to make the interaction between neighboring slabs negligible. The two-dimensional Brillouin zone integrations are performed through different samplings of k -points in Monkhorst–Pack grids [33]: we use ($21 \times 21 \times 21$) for the optimization of the bulk lattice constant, ($8 \times 8 \times 1$) for the surface slab relaxations, and ($6 \times 6 \times 1$) for the interaction of nitrogen atoms and molecules with the surface. The mentioned choices provide the adequate bal-

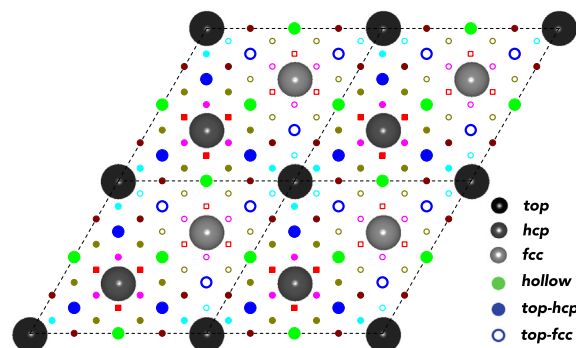


Fig. 1. Top view of the 2×2 unit cell of Fe(111).

ance between numerical accuracy and computing burden. Further computational details will be introduced in the subsequent sections.

3. Results and discussions

In this section we present results regarding: (i) the structural relaxation of the Fe(111) topmost layers, and (ii) the interaction energy for the N/Fe(111) and N_2 /Fe(111) systems.

3.1. Relaxation of the Fe(111) surface slab

The optimized bulk lattice constant is found to be 2.855 Å in this work, in good agreement with the experimental value of 2.867 Å [34]. The bulk modulus B_0 is calculated by a second-order polynomial fitting of the total energy curve versus the lattice parameter. The obtained value, $B_0 = 184$ GPa, is higher than the observed value, $B_0 = 168$ GPa [34], by about 10%, and similar to other theoretical results, $B_0 = 188$ GPa [35]. The Fe(111) surface is modeled using a slab of Fe layers with the thickness ranging between 7 and 19 layers. The atoms in the slab are allowed to move freely in the three directions of space (X , Y and Z) during the structural relaxation. Only the central layer in the slab is kept fixed during the relaxation. In our calculations, we observe that the Fe atoms only move in the Z -direction (perpendicular to the surface) whereas no movement in the XY -plan takes place. Hence, the Fe(111) surface exhibits only relaxation in the perpendicular direction and no surface reconstruction, as was already found before [36].

We define the relaxation of the inter-planar distance between surface layers as the variation of the surface interlayer distance relative to the bulk interlayer spacing: $\Delta_{ij} = (d_{ij} - d)/d \times 100$, where d_{ij} is the distance between the i th layer and the j th layer and $d = 0.82$ Å is the bulk interlayer spacing. In Fig. 2, the variations of the first three interlayer distances (Δ_{12} , Δ_{23} , and Δ_{34}) are represented as a function of the number of layers in the slab.

The left panel in Fig. 2 shows our calculations for the structural relaxation of different Fe(111) slabs, while the right panel summarizes previous studies including both experimental measurements and theoretical calculations. The relaxation values in the left panel of Fig. 2 show the convergence of our results with the number of layers in the slab. For a slab consisting of 19-layers, we obtain $\Delta_{12} = -7.8\%$ ($d_{12} = 0.74$ Å), $\Delta_{23} = -21.7\%$ ($d_{23} = 0.64$ Å) and $\Delta_{34} = 9.7\%$ ($d_{34} = 0.90$ Å), where the negative sign means a contraction inwards and the positive sign means an expansion outwards. The overall contraction of the first three interlayer spacing is of -17.43% . Looking at these numbers, one can say that the Fe(111) surface exhibits strong relaxation as compared with the other two low-index iron surfaces Fe(110) and Fe(100)

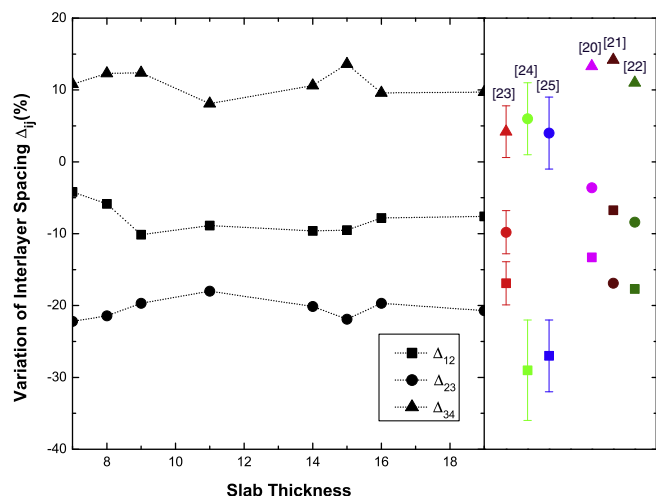


Fig. 2. Variation of interlayer spacing Δ_{ij} as a percentage of the bulk interlayer spacing for a Fe(111) surface with the number of layers in the slab and up to 19-layers. The results obtained in this work are in the left side of the graph. The right side summarizes the available experimental and theoretical studies on Fe(111). Numbers in brackets show the corresponding references [20–25].

[20,22,37]. This is not particularly surprising because Fe(111) is the most open iron surface among the three low-index surfaces and, according to Finnis–Heine [38] theory, the openness of the surface is related to the magnitude of the relaxation.

The right panel of Fig. 2 shows that different experimental techniques offer contradictory results with respect to the relaxation. Low Energy Electron Diffraction (LEED) measurements [23] show that the first two interlayer spacings are contracted and the third one expanded. However, Medium Energy Ion Scattering (MEIS) results [24] show that only the first layer contracts and the second layer expands. Similar discrepancies are found among previous theoretical calculations for the magnitudes of the topmost three slab layers relaxations [20–22]. Indeed, from Fig. 2 our results show a very good agreement with the theoretical work of Ref. [21]. In general, our results are in qualitative agreement with the LEED measurements as well as with the most recent theoretical calculations. Quantitative differences are however found.

3.2. Nitrogen adsorption energy on Fe(111)

The left panel of Fig. 2 shows that a relatively small number of slab layers is enough to represent the relaxation parameters of the Fe(111) surface. We have performed similar examinations of the system-size convergence for the interaction energy between nitrogen atoms and molecules and Fe(111) slabs. DFT calculations were carried out at 15 representative sites of the surface, as shown in Fig. 1. For both N/Fe(111) and N₂/Fe(111) we have used a (2 × 2) unit cell. For a nitrogen molecule approaching perpendicularly to the top site of the Fe(111) surface, we find that the adsorption energy of the nitrogen molecule does not depend on the number of layers in the slab, provided that the slab is thicker than 7 layers. Therefore, in the following, we model our Fe(111) surface by a slab consisting of 9-layers within the frozen surface approximation, in which no further relaxation due to the interaction with the nitrogen species is considered. It should be noted, however, that Refs. [8,39] reported that the (111) surface of Fe may exhibit reconstruction after interaction with abundant nitrogen, in the form of “surface nitrides”. Therefore, our calculations are representative only of the low-coverage regime of nitrogen on Fe(111).

3.2.1. Adsorption energy of nitrogen atoms on Fe(111)

We now turn our attention to the interaction of nitrogen atoms approaching a clean Fe(111) surface by means of DFT calculations. We have considered 15 representative XY-sites of the surface, as shown in Fig. 1. For a selection of these configurations we show in Fig. 3 the potential energy of N on Fe(111) as a function of the distance between the N atom and the Fe(111) surface for several representative sites at the surface. Fig. 3 shows that, among the 6 high symmetry sites of the surface, the most energetically favorable configuration for atomic adsorption is the hollow site, with the nitrogen atom adsorbed very close to the surface, at $Z \approx 0.5 \text{ \AA}$. The calculated adsorption energy is $E_{ads} \approx -5.82 \text{ eV}$. This value is in reasonable agreement within the energy (−6.6 eV to −5.7 eV) range obtained in previous theoretical calculations [12–15], as well as within the measured energy (−6.1 eV, −5.9 eV) range in experimental observations [8,9,40] for atomic nitrogen adsorbed on low-index Fe surfaces.

The theoretical study of the dynamics of N atoms on Fe(111) requires the knowledge of not only some representative configurations but of the full energy landscape. A three-dimensional (3D) Potential Energy Surface (PES) can be constructed from our 3D grid of ab initio energies by exploiting the symmetry properties of the surface and interpolating over the energy grid by means of the corugation reducing procedure (CRP) [41]. Briefly, CRP ensures a high quality 3D interpolation by considering the auxiliary function I^{3D} , defined as:

$$I^{3D}(R) = V^{3D}(R) - \sum_{i=1}^n V^{1D}(|R - R_i|)$$

where V^{1D} is a one-dimensional potential describing the interaction between the N atom at $R(X, Y, Z)$ and the i th Fe surface atom at $R_i(X_i, Y_i, Z_i)$. The one-dimensional potential V^{1D} is approximated by the DFT potential calculated for a nitrogen atom over a top site of the Fe(111) surface. $V^{3D}(R)$ is the actual DFT calculated potential.

In Fig. 4 we show a contour plot representing a two dimensional (2D) cut of the 3D-PES for the system N/Fe(111). The 2D cut corresponds to a distance of the N atom $Z = 0.5 \text{ \AA}$ above the surface. Fig. 4 shows regions of higher energy (weaker Coulomb attraction) due to the close interaction with the first and second layer atoms, illustrated by the blue color. The red color shows the preferred adsorption sites for the atomic nitrogen (hollow sites, with calculated adsorption energy $E_{ads} \approx -5.82 \text{ eV}$, as mentioned above). There are three equivalent hollow points in the same unit cell. In

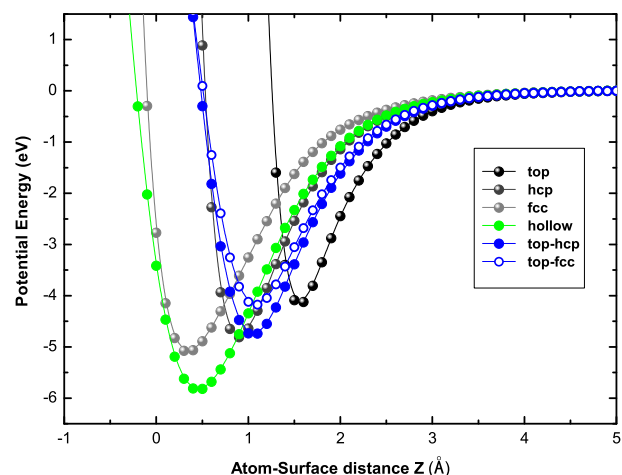


Fig. 3. Dependence of the ab initio potential energy for the system N/Fe(111) on the distance of the atom from the surface Z , for fixed X and Y .

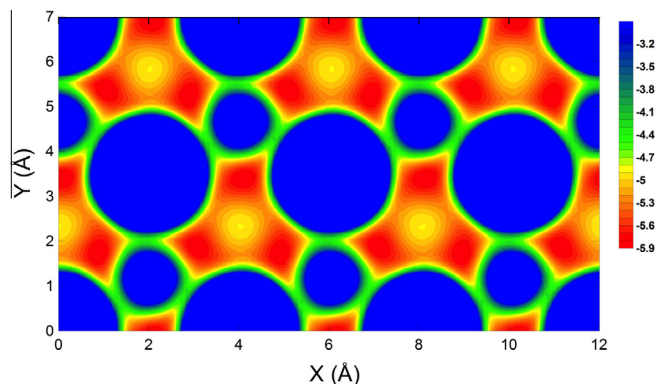


Fig. 4. Contour plot representing a 2D cut of the three-dimensional potential energy surface (3D-PES) for the system N/Fe(111) with fixed $Z = 0.5$ Å.

a simplified picture of the diffusion of N from one hollow site towards another adjacent one, there are two different energy paths that can be previewed. Which of them will have higher rate depends, among other features, on the different energy barriers, that were estimated to be 0.71 and 0.88 eV in Ref. [42].

3.2.2. Adsorption energy of nitrogen molecules on Fe(111)

Next, we show the results of the interaction of molecular nitrogen N_2 with a clean Fe(111) surface. All results shown here are obtained for nitrogen molecules at the equilibrium distance in the gas phase, namely $r_{eq} = 1.1125$ Å [14]. DFT calculations are performed for different molecular positions and orientations. The position of the molecule is defined by the coordinates of the molecular center of mass (X , Y , Z) and the orientation of the molecule is defined by the polar and azimuthal angles of the internuclear vector (θ and ϕ respectively).

Figure 5 illustrates the interaction energy of N_2 on Fe(111) as a function of the distance between the molecular center of mass and the surface Z . Most of the configurations in the plot correspond to the molecule oriented perpendicular to the surface ($\theta = 0^\circ$). The high-symmetry sites considered are those of Fig. 1. An additional configuration of the molecule is shown, with an orientation parallel to the surface ($\theta = 90^\circ$, $\phi = 0^\circ$). From Fig. 5 we can conclude that there are at least three possible molecular adsorption states. Two of them, on ‘top’ and ‘hcp’ positions, correspond to molecules

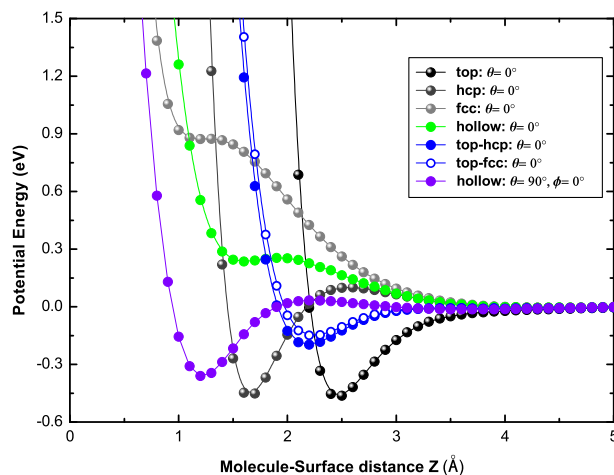


Fig. 5. Dependence of the ab initio potential energy for N_2 /Fe(111) on the distance of the molecular center of mass from the surface Z for fixed X , Y , θ and ϕ . In all the cases the internuclear distance is also fixed to the equilibrium bond length in the gas phase, $r_{eq} = 1.1125$ Å.

with orientation perpendicular to the surface. The third one, with a lower binding energy, corresponds to a molecule on ‘hollow’ site with its axis parallel to the surface.

For the molecule perpendicular on top of the first layer atoms (‘top’ site), the adsorption energy is $E_{ads} \approx 0.46$ eV and the distance to the surface is $Z \approx 2.5$ Å. This configuration remains a local minimum considering the full 6D-PES and corresponds to the experimentally observed γ -state [43,44]. The adsorption state perpendicular to the second layer atoms (‘hcp’ site) has a very similar adsorption energy $E_{ads} \approx 0.45$ eV, a distance to the surface of $Z \approx 1.7$ Å and it also persists as local minimum in the full 6D-PES. This is the so-called δ -state, an experimentally observed and distinctly different adsorption site [39], which seems to be populated only when the surface is already saturated with γ - N_2 and low surface temperature.

Our findings for the γ and δ adsorption states, normal to the surface, are also consistent with previous theoretical work in this system [42]. Reference [42], however, reports a slightly larger energy difference between the two states, the γ -state being about 0.14 eV deeper in energy than the δ -state. We find that both the γ and δ states have similar adsorption energies and the difference in the adsorption rate should be explained in terms of the dynamics of the process.

In addition to these adsorption states, there is experimental evidence of an additional adsorption state (α -state) with the molecule oriented parallel to the surface plane (π -bonded), which could be the precursor for dissociative adsorption [39,45]. Mortensen et al. reached the same conclusion in their theoretical work [42]. Our results in Fig. 5 also show an energy minimum for the molecule oriented parallel to the surface. However, the actual energy minimum is found for a value of the internuclear distance r larger than the gas-phase equilibrium distance r_{eq} . Our complete study of the α -state will be therefore performed in a future work.

4. Summary and conclusions

We have performed a large set of DFT calculations to understand and summarize different aspects of the Fe(111) surface as well as the nitrogen adsorption processes on it. We first study the relaxation of the topmost surface layers of Fe(111) as a function of the number of slab layers. The first two interlayer distances are shown to be shortened with respect to the bulk value (contraction), while the third one is shown to be enlarged (expansion). Our results show a qualitative agreement with LEED measurements as well as with other recent DFT studies, although some quantitative differences have been found.

Furthermore, we study the interaction of nitrogen atoms with a clean Fe(111) surface, and the results show that the only possible adsorption site is the hollow site. We numerically interpolate our DFT data using the CRP method and build a three-dimensional potential energy surface. DFT calculations on the interaction of molecular nitrogen with Fe(111) show three possible adsorption states, in agreement with available experimental information.

The calculations presented in this work can be also taken as a preliminary step to build the full six-dimensional potential energy surface of the N_2 /Fe(111) system. The study of the dynamics of the molecular and dissociative adsorption processes requires a complete description of the energy landscape as well as detailed analysis of the possible reaction paths and rates. Work along these lines is currently in progress.

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