Machine Learning Potential for Material Science

Dissociative adsorption dynamics of N_2 on the Fe(111) surface based on a full-dimensional potential energy surface

***J. Li, J. Behler**, Universität Göttingen, Institut für Physikalische Chemie, Theoretische Chemie, Tammannstr. 6, 37077 Göttingen, Germany*

In Short

- Potential energy surfaces (PES) are prerequisites for large-scale simulations of molecules and materials, and we use machine learning for their representation.
- The dissociative adsorption of N_2 on the iron surface is the rate-limiting step in the Haber-Bosch ammonia synthesis. Fe(111) is the most active low-index iron surface.
- We apply our high-dimensional neural network method to develop the full-dimensional PES for this important process.
- Tens of thousands of dynamically relevant points will be sampled and calculated at the selected density functional theory level as implemented in the VASP code.
- Molecular dynamics will be performed to study the N_2/Fe(111) interaction.

Chemical reactions at gas-solid interfaces are of great significance due to their relevance in a broad range of fields, such as heterogeneous catalysis, corrosion, materials processing, aerosol chemistry, *etc*. The dissociative adsorption of N_2 on the iron surface is the rate-limiting reaction step in the Haber-Bosch ammonia synthesis, and has long been a topic of much interest in surface science.

In this proposal, we plan to investigate the dynamics theoretically in the dissociative adsorption of N_2 on the iron surface Fe(111), the most active low-index iron surface. However, this key reaction step has been simulated only recently based on a multi-dimensional potential energy surface (denoted as PES-2017 hereafter) by Nosir *et al*. in 2017[1]. It is mainly because that the involved calculation is prohibitively expensive, and the prerequisite of the dynamical simulation, namely, a reliable PES of the complex system, is difficult to develop. High-dimensional neural networks (HD-NN)[2,3], which have been applied successfully in constructing PESs for various molecules[4], gas-solid interfaces, and materials[5], are proposed to meet this challenge.

In the HD-NN approach, the total energy of the system is expressed as a sum of atomic contributions[2,6]. For each atom, a separate atomic NN is used to construct the functional relation between the chemical environment and the atomic energy contribution. The central component of all NN potentials are feed-forward NNs. **Figure 1** shows an example of our HD-NN.

Benchmark calculations have already been carried out for the selection of the Density Functional theory (DFT) method, and the Perdew-Burke-Ernzerhof (PBE) [7] flavor of DFT has finally been selected after comprehensive tests. Due to the magnetic nature of the Fe(111) surface, spin-polarized DFT calculations are performed. The fractional occupancies are determined through the broadening approach of Methfessel and Paxton with N = 1 and s = 0.1. A 3x3 unit cell is used to model the Fe(111) surface. The slab consists of six layers and the vacuum is set to 15 Å to avoid the interaction between neighbouring slabs. Consequently, there are 54 Fe atoms and 2 N atoms in the current slab model. As shown in **Figure 2**, the dipole arising from adsorbing N_2 only on one side is negligible. Indeed, our tests have shown that the inclusion of the dipole correction can result in artificial oscillations of the potential in some scans and is thus not used. The kinetic energy cutoff and the k-points grid haven been tested. The inclusion of the Tkatchenko and Scheffler (TS)[8] empirical correctionsfor dispersion energy results in a clear improvement of the PES and will be used. We finally choose to use the PBE+TS empirical corrections[8] with the *k*-points being 3x3x1 and the energy cutoff at 450 eV without dipole correction, as a compromise between efficiency and cost, as shown in **Figure 2**.

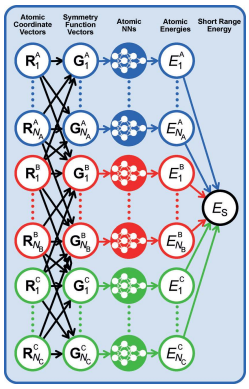

***Figure 1:** Scheme of the HD-NN method.*

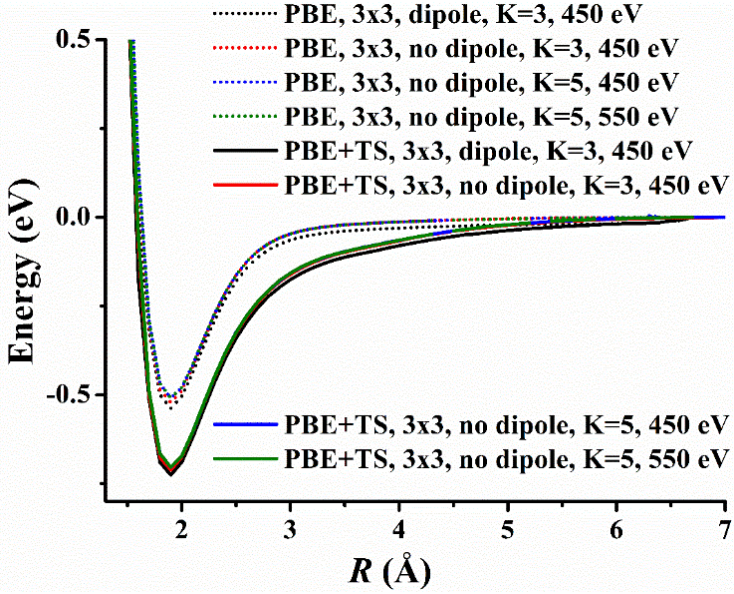

Figure 2: *Comparison of different settings in the DFT calculations along the distance between the center of mass of the N_2 and the top-layer surface iron. N_2 is fixed at its equilibrium bond length for this test.*

Unlike the previous PES-2017[9], we plan to build a full-dimensional PES without freezing the iron atoms of the slab, namely, the coordinates of all atoms, including the N_2 molecule and the iron atoms of the slab, are mobile. Therefore, more points will be needed to accurately describe various regions of the PES. In total, 180 kNPL are required for 60 000 DFT energy calculations.

Once the PES is available, the reaction dynamics will be investigated mainly by running a large number of trajectories for reasonable statistics. In particular, the sticking probabilities will be calculated and compared to available experimental results[10]. The details of the reaction dynamics and mechanisms will be analyzed.

WWW

https://www.researchgate.net/profile/Jun_Li51

More Information

[1] Nosir, M. A.; Martin-Gondre, L.; Bocan, G. A.; Díez Muiño, R., *Phys. Chem. Chem. Phys.* **19**, 24626 (2017). doi:10.1039/C7CP03701E

[2] Behler, J.; Parrinello, M., *Phys. Rev. Lett.* **98**, 146401 (2007). doi:10.1103/PhysRevLett.98.146401

[3] Behler, J., *Angew. Chem. Int. Ed.* **56**, 12828 (2017). doi:10.1002/anie.201703114

[4] Li, J.; Song, K.; Behler, J., *Phys. Chem. Chem. Phys.* **21**, 9672 (2019). doi:10.1039/C8CP06919K

[5] Quaranta, V.; Hellström, M.; Behler, J., *J. Phys. Chem. Lett.* **8**, 1476 (2017). doi:10.1021/acs.jpclett.7b00358

[6] Behler,J., *J. Chem. Phys.* **145**, 170901 (2016). doi:10.1063/1.4966192

[7] Perdew, J. P.; Burke, K.; Ernzerhof, M., *Phys. Rev. Lett.* **77**, 3865 (1996). doi:10.1103/PhysRevLett.77.3865

[8] Tkatchenko, A.; Scheffler, M., *Phys. Rev. Lett.* **102**, 073005 (2009). doi:10.1103/PhysRevLett.102.073005

[9] Nosir, M. A.; Martin-Gondre, L.; Bocan, G. A.; Díez Muiño, R., *Phys. Chem. Chem. Phys.* **19**, 7370 (2017). doi:10.1039/C6CP07174K

[10] Rettner, C. T.; Stein, H., *Phys. Rev. Lett.* **59**, 2768 (1987). doi:10.1103/PhysRevLett.59.2768

Funding

Alexander von Humboldt Foundation (Humboldt Fellowship for Experienced Researchers for JL).