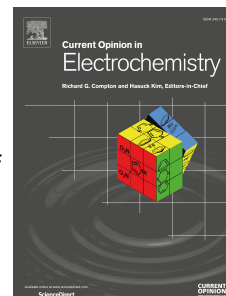# Journal Pre-proof

Nitrogen reduction reaction (NRR) modelling: A case that illustrates the challenges of DFT studies in electrocatalysis

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CURRENT OPINION IN ELECTROCHEMISTRY

Innovative Methods in Electrochemistry (2022)

Nitrogen reduction reaction (NRR) modelling: A case that illustrates the challenges of DFT studies in electrocatalysis

(Short title: DFT modelling of NRR processes)

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Abstract: Ammonia synthesis *via* nitrogen reduction reaction (NRR) is amongst the hottest topics in current applied catalysis field. Theoretical investigations usually cover the description of reaction mechanisms in support to the experimental findings but are also used to predict prior-to-synthesis behaviours. This brief review talks about the importance of the methodology, the reliability of the model, and the selectivity, as some of the most significant aspects to correctly develop a DFT-based project on NRR.

Keywords: nitrogen conversion • green ammonia • *in-silico* design • hydrogen evolution • nitrogen oxides

Introduction

Nitrogen reduction reaction (NRR) is the electrochemical process for ammonia (NH_3) production from N_2 and a proton source. Unlike the Haber–Bosch process,[1] the quintessential industrial procedure for large-scale ammonia synthesis, NRR is usually carried out at mild conditions of temperature and pressure and its ability to be integrated into a circuit where the energy supply comes from non-fossil sources makes NRR a process of great prospect from the environmental point-of-view.[2]

Since NH_3 is a chemical feedstock of primary relevance as the source of most fertilisers,[3] the development of electromaterials with capacity to catalyse NRR has experienced a boom in the last decade. In the present review, I cover some of the most important aspects for the DFT

modelling and *in-silico* design of NRR electrocatalysts: a brief guide highlighting the scope of the computational tools that we have as well as the most important challenges in the field.

Methodology: more than just a boring paragraph

Scientific reports on the modelling of heterogeneously catalysed NRR processes usually lack a detailed methodology section that makes difficult not only the reviewing process but also the reproducibility by readers, and reproducibility is a pillar of the scientific method.

Throughout these years as a reviewer of many articles in the DFT-NRR field, I have found surprisingly striking results in which verifying their reliability would have been as simple as going to the respective methodological section if it had been properly detailed. In other cases, I have been able to corroborate that these unusual results were simply due to explicit sources of error. A common case is the treatment of the free energy of gases with the same approximations applied to the case of adsorbate species, *i.e.*, ignoring the contributions of the translational and rotational modes than can be neglected in the case of adsorbates but not for gases. This leads to erroneous theoretical estimations being especially significant when evaluating the N_2 adsorption and NH_3 desorption steps, as well as the thermodynamics of the global reaction.

Each scientific problem has its own specificities, however and in general terms, we can expect that an adequate methodological description includes the aspects listed at Fig. 1 for the case of electrocatalysed heterogeneous reactions. In opinion of this author, the following references indicate works with adequate DFT methodological descriptions in the NRR field,[4–12] which does not exclude that there are many more not cited in this article for a simple question of space limitation. Other seminal works for the case of the oxygen evolution (OER)[13] and carbon dioxide reduction (CO2RR)[14] reactions can also serve as a source of orientation.
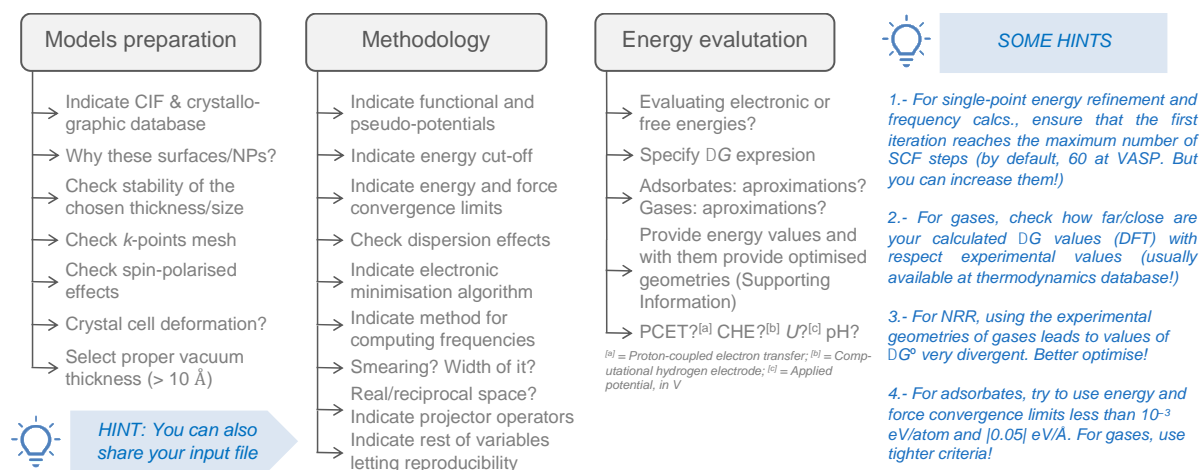
Figure 1. Brief guide indicating the main aspects to check/indicate during a NRR computational project for the case of solid-state codes with periodic boundary conditions. Note: VASP refers to the Vienna *Ab-Initio* Simulation Package,[15–18] probably the computational code of most use in the community.

Thermodynamics and kinetics: a complicated couple in DFT electrochemistry

In this section, I want to briefly comment about the need to describe minima and transition states (TS) in electrochemical reactions. Concerning the first, this aspect has been broadly studied in the frame of the proton-coupled electron transfer (PCET) approach[19] using the computational hydrogen electrode (CHE) as reference. Given that NRR is, like OER or CO_2RR, an electrochemical process consisting in the successive transfer of H^+/e^- pairs, this entails the proposition of elementary electrochemical reaction steps from which the one with the maximum (positive) relative free energy, ΔG, represents the theoretical estimation of the equilibrium reduction potential, ε, in virtue of the $\Delta G = -nF\varepsilon$ fundamental equation, where n and F refer to the number of electrons and the Faraday constant. This tells us that the evaluation of the binding energies of the reactants, products, and reaction intermediates gives fundamental information about what can be qualified as a "thermodynamics impediment" which must be reached for the reaction to occur. In other words, the evaluation of ΔG is a unique chemical descriptor that allows a quick and robust estimation of potential limiting steps on the basis that overpotentials and equilibrium reduction potentials are roughly similar in conditions of low current densities.

In virtue of the Tafel equation (Eqn. 1):

$$\eta = \pm A \times \log (i/i_0) \quad (1)$$

the overpotential, η, has a clear dependence with the current density, i. (A and i_0 refer to the Tafel slope and the exchange current density). In addition, the overpotential results from the contribution of several components, one of which is the activation overpotential, *i.e.*, the extra energy demanded by the system to reach a TS, *i.e.*, the kinetics associated with an activation barrier.

Whatever it is, answering to the question of which is the TS in a reaction in which reactants and products have a different number of electrons is a tricky task on which several methodologies and approaches have been developed.[20–22] The exhaustive and comparative analysis of them might be an interesting job being somewhat far within the scope of this review; however, it should be mentioned that none of these methodologies seems to be definitively conclusive or as easy to apply as the analysis of the binding free energies as chemical descriptors. In any case, the DFT community must be attentive to the advances on the modelling of kinetics in electrochemical reactions.

The model: you either have it or you don't

The employment of adequate methodologies for the modelling of catalytic processes, and in general for the study of any physicochemical phenomena, is a must. However, the development of accurate and robust methodologies is as important as the choice of the model. In 2019, we reported the capabilities of a novel material constituted by Ru-decorated 2H-MoS$_2$ for boosting N$_2$ reduction into NH$_3$ to the detriment of protons reduction into H$_2$.[23] From the physical characterisation data, specifically TEM and high-resolution HAADF-STEM imaging, we observed that the as-synthesised material consisted of Ru nanoparticles (NPs) with size < 2 nm being dispersed on the basal planes of 2H-MoS$_2$. Based on this information, we therefore built a structural model constituted by a hexagonal close packed (hcp) spherical Ru NP with a diameter of ~1.7 nm supported on a *ca.* 30 Å × 30 Å MoS$_2$ sheet (see Fig. 2). The ability to have predicted a theoretical reduction potential coinciding with the experimentally measured value was not only due to a suitable mechanistic hypothesis envisioning a synergistic interplay between the Ru NP as nitrogen binding site and the nearby S-vacancies as hydrogen provider centres, but also to the choice of a reliable model between what is experimentally observed and what is built at a theoretical level.

In numbers, this involved the construction of a model consisted in a composite structure constituted by 360 heavy atoms, which is certainly a fairly high number for its treatment at the

quantum mechanical level. In general, the optimisation of such a big structure or any other related models comprising the adsorption of the reaction intermediates require of very large and usually inaccessible amounts of computational resources only provided by high-performance computing centres. In this context, this theoretical work was carried out thanks to the resources offered by the KAUST Supercomputing Laboratory (KSL) using the Supercomputer Shaheen II. On average, each optimisation demanded approximately one day running in queue through parallelised calculations with 64 cores of 32 CPUs/core, *i.e.*, *ca.* 50,000 hours per calculation. In the eagerness of some theoretical research groups to provide mechanistic interpretations to catalytic phenomena, simpler but more computationally accessible models might be chosen, however, these results would unfortunately lead to imprecise conclusions or not being consistent with the experimental evidence. The model is everything, and the inability to replicate realistic models is simply erroneous and might contribute to relegate the theoretical research to a plane of little use.

The present review does not pretend to point out those studies with low viability of the chosen models, but rather it tries to highlight some of those studies that can serve as inspiration for a correct execution of a theoretical project applied to the catalytic N_2-into-NH_3 electrochemistry. As the NRR field has progressed, increasingly complex electrocatalysts have been designed, which inevitably entails the proposition of models that are also more complex in terms of their composition, structure, shape, and/or size.[24] Nowadays, the most important advances in the field are being observed in novel catalytic methodologies such as the lithium-mediated N_2-into-NH_3 conversion,[25–28] a process that combines a very reactive catalyst that breaks the N_2 molecule and, through electrolysis, converts the N adatoms into NH_3 as in the last steps of NRR. The catalyst is further regenerated with the application of an electrical potential.
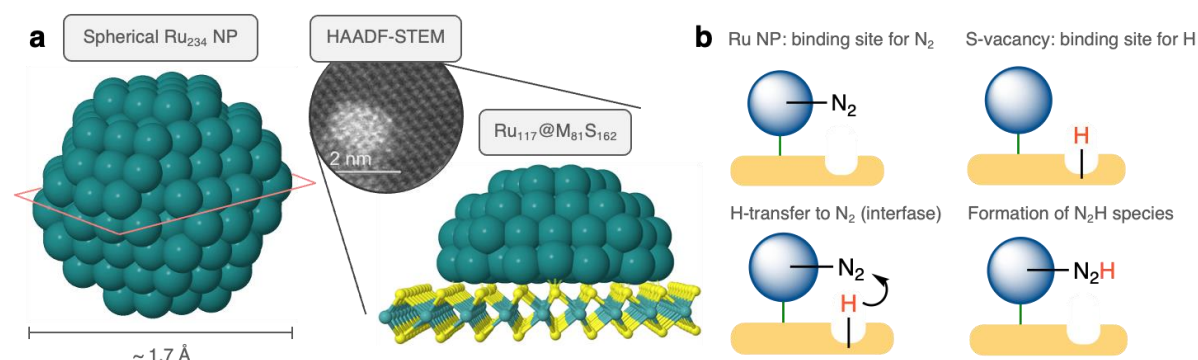
Figure 2. (a) Building of the model for the Ru@MoS$_2$ composite material based on HAADF-STEM imaging used as electrocatalyst for NRR. (b) Over this model, a series of S-vacancies are generated on the 2H-MoS$_2$ sheet with the reactivity occurring on both parts of the composite. One the one hand, those areas of the Ru NP close to the MoS$_2$ sheet act as N$_2$ binding site. On the other, the S-vacancy acts as binding site for H adatoms. The transfer of *H to the *N$_2$ occurs on the interfase of both moieties of the composite to finally produce the reduction of the N$_2$ into the N$_2$H intermediate species. The rest of the hydrogen transfer mechanistic steps occurs in a similar fashion. See more details at ref. [23], from which this figure has been adapted.

Selectivity lapsus

An essential aspect in the analysis of the NRR, predominantly in metal-catalysed reactions, is the competitiveness of protons[29,30] to be reduced into H adatoms (* + H$^+$ + e^- ⇌ *H) instead of the intermediate N$_2$H species (* + N$_2$ + H$^+$ + e^- ⇌ *N$_2$H) along the first elementary reduction steps of the hydrogen evolution reaction (HER) and NRR. (See the recent COIE article by Mukundan and co-workers).[31] While HER is usually a dominant process, the search of second-generation NRR electromaterials capable of supress the HER in favour of the N$_2$ conversion into NH$_3$ is probably one of the hottest and more challenging topics in current applied catalysis field. In the last years, a plethora of novel electrocatalysts have been reported in the literature with capabilities to reduce N$_2$ into NH$_3$ at low overpotentials, high rates, and high Faradaic efficiencies, however, recent experiments by Simonov and MacFarlane[32] trying to reproduce some of these most sound works have failed. In this sense, the lack of proper protocols for ammonia quantification[33–35] might be some of the reasons of studies reporting false positives.

On the other hand, and from the basis that DFT investigations are properly done on adequate models with adequate methodologies, the existence of strong divergences between experimental and theoretical results reveals either that the hypothesised reaction mechanism is not certain or that the experimental results may not be properly interpreted. This is the case of bismuth, being recently reported as an outstanding NRR electrocatalyst with catalytic performances at potentials between –0.6 and –0.8 V *vs.* RHE.[36–38] The theoretical results modelling NRR on bismuth nanoparticles in presence and absence of K$^+$ cations by Hao *et al*.[38] reveal overpotentials in excess of 2.8 V on this metal, values that are very far not only from their own experimental predictions but also from the margin of error that could exist in the DFT estimation.

In this regard, we, the DFT community, have failed to consider that NRR is not only in competition with HER. Nitrogen oxides (NO_x), which are hard-to-remove (in NRR experiments) and common pollutants of air as result of the industrial activity and the burning of fossil fuels by vehicles, are sources of nitrogen which present, for most metals, facile reduction processes towards NH_3.[39] In our very recent report,[40] our DFT investigations have shown that NO_x reduction reactions (NO_xRR) are not only more selective than NRR in metal electrocatalysis but, on the surface of most metals, NO and NO_2 are more predominantly reduced than protons into H_2 (see Fig. 3). This might circumstantially open new venues for the development of novel electromaterials capable of catalyse the NO_xRR but also cautions that future NRR DFT-based studies contemplate an in-depth analysis of the selectivity between NRR, HER, and NO_xRR for the sake of rationally explaining the adequacy of the predicted materials for the purposes that they are claimed.
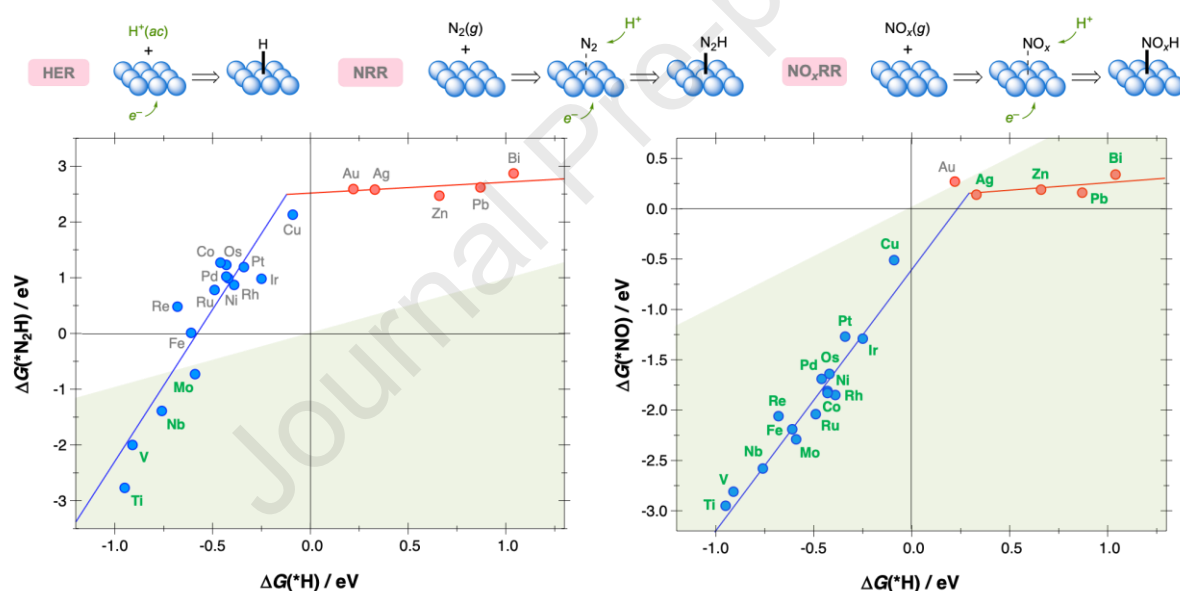
Figure 3. During the first hydrogenation step of the NRR and NO_xRR, N_2 and NO_x compete to be adsorbed on the metal surfaces to be subsequently reduced into the N_2H and NO_xH first-reduced intermediate species. In acidic media, these species compete also with protons to be reduced into H adatoms, *H (top). N_2 is weakly adsorbed and the formation of N_2H is less favoured than *H (bottom, left), rendering HER as a dominant process over NRR is most metals. On the contrary, NO is a highly nucleophilic species being strongly chemisorbed on the metal surfaces in most metals, even more than *H (bottom, right). This entails that NO occupies the reaction binding sites of the metals making more selective its further reduction into NOH than the reduction of H^+ into H adatoms. This behaviour has been also observed for NO_2, even more pronounced. See more details at ref. [40], from which this figure has been adapted. Note: ΔG refers to binding free energies with green shaded areas indicating than $\Delta G(*N_2H) < \Delta G(*H)$ and $\Delta G(*NO) < \Delta G(*H)$, respectively. Green labels highlight metals with where this is the case.

Conclusions

The modelling of heterogeneously catalysed NRR processes has experienced a boom in the last years at both, the description of reaction mechanisms rationalising the experimental findings, and hypothesising prior-to-synthesis behaviours on invented or suspected-to-function materials. A worryingly large number of these works lack of proper descriptions/applications of the theoretical protocols. Both, the methodology and the model are fundamental aspects for the theoretical analysis to be satisfactory, and satisfactory means, in this case, realistic and refined. In the modelling of NRR processes it is also important to check whether the proposed catalyst is selective towards NRR or if side/competitive reactions such HER or NO$_x$RR might be preferentially catalysed. Reports on outstanding NRR electrocatalysts are a plethora, but to date there is not any commercial NRR electrocatalyst derived from these works.

Acknowledgments

Declaration of interests

I declare no competing interests of any nature, financial, or personal.

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Papers of particular interest, published within the period of review (2019-2021), are highlighted as:

• Papers of special interest: refs. 2, 8, 23, 26, 27, 30, and 31.

Ref. 2: this progress report discusses recent developments and challenges in the field of electrocatalytic materials.

Ref. 8: in addition to the intrinsic value of this research, this complete work can serve as a methodological guide for electrochemical studies (thermodynamics and kinetics) in aqueous solution.

Ref. 23: this article describes a high active and selective NRR electrocatalyst, being one of the first reports to achieve a substantial suppression of the HER.

Ref. 26: this work reports the novel method of the so-called "cyclic stabilisation" of the lithium mediated NRR, probably the most promising technology for NRR to date.

Ref. 27: this is directly related with ref. 26, where most of these authors are also authors of this paper. Here, they discover that the presence of oxygen, far to hinder the reaction, improves the faradaic efficiency (and stability) of the lithium mediated NRR up to *ca*. 80%.

Ref. 30: this perspective analyses pros and cons of current methods of scaling relations between adsorption energy descriptors in identifying selective NRR electrocatalysts (*versus* HER).

•• Papers of outstanding interest: refs. 10, 28, 32, 33, 34, and 35.

Ref. 10: this theoretical work critically discusses the report of certain electromaterials as outstanding NRR electrocatalysts and provides theoretical evidence demonstrating the contrary.

Ref. 28: this paper reports a novel method for the lithium mediated NRR using a phosphonium salt as a proton shuttle instead of use sacrificial sources of protons. The commercial exploitation of this method is currently being studied by Jupiter Ionics Pty Ltd (www.jupiterionics.com).

Ref. 32: this work experimentally refutes the outstanding performance of many reported NRR electromaterials, establishing the probable cause of these false positives.

Refs. 33, 34, and 35: protocols that must be followed at experimental level to unambiguously determine the source of ammonia electroproduction.

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