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The role of exchange-correlation functionals in the potential energy surface and dynamics of N₂ dissociation on W surfaces

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We study the dissociative adsorption of N₂ on W(100) and W(110) by means of density functional theory and classical dynamics. Working with a full six-dimensional adiabatic potential energy surface (PES), we find that the theoretical results of the dynamical problem strongly depend on the choice of approximate exchange-correlation functional for the determination of the PES. We consider the Perdew-Wang-91 [Perdew *et al.*, Phys. Rev. B **46**, 6671 (1992)] and Perdew-Burke-Ernzerhof (RPBE) [Hammer *et al.*, Phys. Rev. B **59**, 7413 (1999)] functionals and carry out a systematic comparison between the dynamics determined by the respective PESs. Even though it has been shown in earlier works that the RPBE may provide better values for the chemisorption energies, our study brings evidence that it gives rise to a PES with excessive repulsion far from the surface. © 2008 American Institute of Physics.

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I. INTRODUCTION

The dynamics of molecules impinging on metal surfaces has deserved much attention in recent years given its relevance to many technological applications.^{1–4} In this context, the dissociative adsorption of diatomic molecules constitutes an attractive field of research, being a key step in many catalytic processes. In particular, N₂/W provides a most appealing combination to study these phenomena. On the one hand, dissociation of N₂ (on Fe surfaces) is the rate-limiting step in ammonia synthesis, a most important reaction in the chemical industry.¹ On the other hand, tungsten presents large crystallographic anisotropies as regards adsorption yields and sticking coefficients.^{5,6} Given these facts, it is not surprising that there should be a large body of experimental data available for N₂ on different W surfaces.^{7–13}

From the theoretical point of view, a molecular dynamics problem is often addressed under the frozen surface and adiabaticity hypothesis, which neglect molecular energy loss mechanisms such as phonon and electron excitations. Evidence of nonadiabatic effects has recently been provided by Wodtke and co-workers,^{14,15} through the observation of electron emission due to relaxation of highly excited vibrational states of NO molecules impinging over low-work function metal surfaces. Nevertheless, adiabaticity has proven to be a most reasonable approximation to describe dissociation and scattering of diatomic molecules such as H₂ and N₂ on various metal surfaces.^{16–21}

Within this framework, the problem can be split into two parts. First the potential energy surface (PES) is obtained. In a second step, the PES is used in either classical or quantum

dynamics. To obtain a realistic description of the molecular evolution, it is often essential to work with the full six-dimensional (6D) PES.²¹ For example, in the case of N₂/W(100), a static analysis of nonactivated paths leading to dissociation has shown that the molecules always follow a complex 6D track.²² In addition, a 6D dynamics is particularly relevant at low impact energies when dissociative adsorption mediated by dynamic trapping is an important mechanism. The building of the PES is performed in two steps; first a 6D grid of energies is computed and, subsequently, an interpolation is performed over that grid for all possible orientations and positions of the molecule. To this end, accurate interpolation procedures have been developed.^{23–25}

At this point, any discrepancy between theory and experiment might lead one to challenge the frozen surface or adiabaticity hypothesis. However, there are other possible sources of inaccuracy in the theory. We focus here on the exchange-correlation (XC) functional, which is introduced in any calculation based on density functional theory (DFT) in an approximate fashion. The generalized gradient approximation (GGA), in which the XC energies are a function of both the electron density and its gradient at the evaluation point, is the state of the art in massive *ab initio* calculations. However, there are different GGAs available and a systematic analysis of how much the theoretical predictions for a dynamical problem are affected by the choice of XC functional is still lacking.

The Perdew-Wang-91 (PW91) (Ref. 26) and the Perdew-Burke-Ernzerhof (RPBE),²⁷ both GGA XC functionals, have been widely used for various systems. Developed as an improvement over PW91, the RPBE XC functional provides better agreement with experimental measurements of quanti-

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ties such as the chemisorption energies for several systems.²⁷ Note, however, that this implies testing the PES in just a small region of the 6D PES around the local minimum where chemisorption takes place. The sensitivity of dynamical processes, which involve a much larger volume, is yet to be tested. Vincent *et al.*²⁸ showed that results for the dissociation probability of H₂ on Ru(0001) depend on the XC functional choice. Though they suggested that RPBE predictions were likely to be better than PW91 ones, the lack of experimental information to compare with prevented them from confirming that point. Honkala *et al.*²⁹ have shown that the barrier for N₂ dissociation on Ru low-symmetry sites decreases when changing from RPBE to PW91.

In the present contribution a thorough and systematic comparison will be carried out between the theoretical predictions for the dissociative adsorption of N₂ on W(100) and W(110), when using the PW91 and RPBE PESs. Volpillac and Salin²² and Alducin *et al.*^{30,31} have presented respective dynamical studies for these systems using PW91, and have found reasonable agreement with experimental data. Now, we intend to check how different RPBE results are from PW91 ones, to analyze whether the differences between both dynamics are qualitative or quantitative, and to test RPBE as a possible improvement over PW91 in a molecular dynamics problem.

The paper is organized as follows. In Sec. II, the technical details of the PES calculation are presented together with a comparison between static features of the RPBE and PW91 PESs for both systems under consideration. In Sec. III, the dissociative sticking probability is shown, also for both tungsten surfaces, as a function of the impact energy. RPBE results for different incident angles are compared with PW91 predictions and experimental data. In Sec. IV, a detailed analysis is performed of the evolution along reaction trajectories for the N₂/W(110) system. Conclusions are supplied in Sec. V.

II. PES

The full 6D adiabatic PESs of the N₂/W(100) and the N₂/W(110) systems have been determined by Volpillac and Salin²² and Alducin *et al.*,^{30,31} respectively, using the GGA PW91 functional. The general procedure to construct the 6D PES is identical in both references. Energies are calculated over a 6D grid by means of the DFT-based “Vienna *ab initio* simulation program” (VASP) (Refs. 32–35) using a (2×2) periodic five-layer slab. The supercell vector along the Z axis was set to 26.990 Å for the W(100) surface and to 27.328 Å for the W(110) one. Once the energies have been computed, an interpolation is performed between grid nodes using the corrugation reducing procedure²³ to obtain the PES for any value of the molecular center of charge $\mathbf{R}=(X,Y,Z)$ and of the spherical coordinates of the internuclear vector (r,θ,φ) (Fig. 1). For N₂/W(100), the energy grid comprised a total of 3264 points, associated with 17 configurations of the N₂ molecule over the surface. A configuration is defined by fixing (X,Y,θ,φ). In the same way, 5610 points were calculated for N₂/W(110), associated with 30 configurations. A larger number of configurations was required in the latter

FIG. 1. (Color online) Definition of the coordinate system and surface geometries. Surface W atoms are in green and the N₂ nuclei in red. The color circles in each surface unit cell indicate the sites of the various configurations used to construct the PES.

because of the less symmetrical character of the W(110) surface. We show in Fig. 1 the sites (defined by a value of X and Y) for which *ab initio* energies have been determined.

In the present work, we have performed exactly the same calculations (same number of configurations, identical grid of *ab initio* points and same values for VASP parameters) replacing the PW91 functional by the RPBE one in both systems. Following Hammer *et al.*,²⁷ the ion cores have been described using PW91 ultrasoft (US) pseudopotentials. The calculated RPBE bulk interatomic distances a and slab relaxations are very close to the PW91 ones. For instance, in W(110) we find, with RPBE, $a=3.175$ Å ($a=3.173$ Å with PW91), a distance of $0.680a$ (as with PW91) between the first and second layers, and of $0.712a$ ($0.708a$ with PW91) between the second and third layers.

It is of interest to evaluate how the PES is affected by a change in the XC functional. The dissociation dynamics of low energy N₂ on W under the PW91 PESs has been found to be extremely sensitive to details of the PES far from the surface ($Z>3$ Å) (Ref. 31) and, accordingly, we concentrate on the latter region. In the top panel of Fig. 2 we plot one-dimensional cuts of the PESs as a function of distance to the surface, Z , for various configurations, with the intermolecular distance set to its equilibrium value in vacuum, $r_{\text{eq}}=1.113$ Å. Results are displayed for the RPBE and PW91 PES's (full and dashed lines, respectively) and for both W faces. The zero of potential energy corresponds to Z infinite (in practice, half the distance between two slabs in the supercell). The RPBE and PW91 curves are qualitatively similar but the RPBE energies are systematically larger than the corresponding PW91 ones. For both systems, the top-vertical configuration presents a potential well at $Z\sim 2.6$ Å. In the PW91 PES, this well can be accessed from large Z without overcoming a potential barrier. This is no longer the case for the RPBE PES as we find barriers of ~ 80 and ~ 14 meV,

FIG. 2. (Color online) Top panels: Dependence of the *ab initio* RPBE (full lines) and PW91 (dashed lines) potential energy on the distance Z between the molecule center of mass and the surface. The molecular internuclear distance is $r=r_{eq}$. Bottom panels: Dependence on Z of the difference between RPBE and PW91 energies. Panels on the left (right) show the results for N₂/W(110) [N₂/W(100)]. The configurations displayed are top: $\theta=0^\circ$ (black); top: $\theta=90^\circ$, $\varphi=0^\circ$ (red); W(100) bridge: $\theta=90^\circ$, $\varphi=0^\circ$ (dark green); W(110) bridge: $\theta=45^\circ$, $\varphi=54^\circ$ (violet); W(110) [W(100)] hollow: $\theta=90^\circ$, $\varphi=54^\circ$ [45°] (blue).

respectively, for the (110) and (100) surfaces. Note that the depth of the potential well is also modified. Its values are displayed in Table I, together with experimental energies for molecular adsorption. When comparing them, one should keep in mind that our calculations are for a frozen surface and, therefore, surface atom relaxation is not accounted for. Still, the less attractive character of the RPBE wells suggests a better accordance with the experimental data. In fact, this last feature is not specific of N₂/W but has been observed for other systems as well.²⁷

In order to facilitate the comparison between both calculations and explicitly show the more repulsive character of the RPBE PES, we have plotted the difference between the RPBE and PW91 energies in the lower panel of Fig. 2. It is remarkable that the general behavior of these energy differences is the same for the two systems under study. Down to distances $Z \sim 2$ Å the differences are roughly configuration independent and monotonously increasing with decreasing distance to the surface. For $Z < 2$ Å, the variation with configuration gets larger.

TABLE I. Depth of the potential well when using PW91 and RPBE, within the surface frozen approximation. Zero-point energy corrections are not included in the calculations. Also, experimental chemisorption energies.

System	PW91 (eV)	RPBE (eV)	Experiments (eV)
N ₂ /W(100)	1.048	0.821	0.399 ^a 0.455 ^a
N ₂ /W(110)	0.665	0.389	0.260 ^b 0.450 ^c

^aReference. 36.

^bReference. 37.

^cReference. 38.

FIG. 3. (Color online) Dissociation probability as a function of impact energy for the N₂/W(100) system under normal incidence. Theory: Red line, PW91 results (Ref. 22); thick blue line, RPBE results. Experiments: Triangles down, data at 1000 K; squares, data at 800 K; circles, data at 300 K; triangles up, data at 100 K (Refs. 8–11 and 13).

III. DISSOCIATIVE STICKING PROBABILITY

In this section results for the dissociative sticking probability using the RPBE PES will be presented and compared with those previously obtained by means of the PW91 one in Refs. 22, 30, and 31. The N₂/W(100) system under normal incidence using the PW91 PES was studied by Volpilhac and Salin.²² As depicted in Fig. 3, they found qualitative agreement between theory and experiment, though calculations for a frozen surface cannot account for the strong sensitivity to surface temperature observed in the measurements at low impact energies.^{8–11,13} In agreement to experimental findings for low temperature, the theoretical dissociation probability tends to 0 as the impact energy tends to 0, a frequent behavior when dynamic trapping plays an important role. In the low energy range, its variation with increasing energy is very sensitive to small changes in the PES. For N₂/W(110), Alducin *et al.* also found nonactivated paths to dissociation, in contradiction to traditional claims for this system. In spite of this, the behavior of the dissociation probability at low energies is strikingly different from that of N₂/W(100). As displayed in Fig. 4, the probability goes to zero when the impact energy goes to zero, in qualitative accordance to experiments at 800 K, for both normal and off-normal incidence.^{7,11} The latter result proves that the nonactivated character of a system does not necessarily entail a finite dissociation probability for vanishing energies. Indeed, the mere existence of a nonactivated path is a static property of the PES, and the dynamical constraints can be such that this path has a very low probability of being followed at low energies.

Calculations beyond the frozen surface approximation are clearly desirable for a more meaningful comparison between theory and experiment, particularly in the (100) case. However, there is at present no well established accurate scheme to achieve this goal. Therefore, before facing such a challenging program, one should fully explore the sources of

FIG. 4. (Color online) Dissociation probability as a function of impact energy for the $N_2/W(110)$ system. Normal and 60° incidence. Theory: Red line, PW91 results (Refs. 30 and 31); thick blue line, RPBE results. Experiments: White squares, data at 800 K from Ref. 7; black squares, data at 800 K from Ref. 11.

systematic inaccuracies that are likely to affect both the frozen and unfrozen surface calculations. The choice of XC functional is an important feature of DFT calculations that has not been addressed in a systematic way for the dynamics of molecules interacting with surfaces. In Figs. 3 and 4 the RPBE dissociation probabilities of $N_2/W(100)$ and $N_2/W(110)$ are plotted together with both the PW91 results and the experimental values. The RPBE probabilities significantly differ from the PW91 ones.

For the (100) surface, when the energy goes to zero, the PW91 probability goes to 1 while the RPBE probability goes to zero. This is to be expected given the presence, in RPBE, of a minimum barrier of 14 meV, which restricts the access to the top-vertical well. Note that such a barrier is altogether absent in PW91. The RPBE probability increases slowly above 14 meV, which shows that the phase volume allowing to approach the surface at low energies is much smaller than in the PW91 calculations, as an effect of the more repulsive character of the RPBE PES. A maximum of 0.44 is reached around 300 meV. Above this energy, PW91 and RPBE behave in a similar way, differing in around 30%. As regards the comparison with experiment, the most striking discrepancy is in the low energy region in which the RPBE results do not reproduce the increase of the experimental probability when the energy tends to zero. On the contrary, for high impact energies, where experimental results tend to be independent of surface temperature, RPBE provides a better agreement than PW91.

For the (110) surface, the PW91 and RPBE results are also found to differ strongly. For normal incidence, the RPBE probability remains very small up to ~ 700 meV. For larger energies, it first increases rather abruptly and then be-

haves as PW91, with a difference in absolute value of about 30%. The comparison with experiment seems to favor RPBE results, contrary to what has been observed for the (100) surface in the low energy range. Considering the 60° incidence case (with respect to the Z axis), RPBE predicts almost no sticking until an incident energy of 1.5 eV is reached, in flagrant disagreement with both experimental and PW91 results.

From the information depicted in Figs. 3 and 4 and the previous discussion, one cannot state that RPBE represents a systematic improvement over PW91 in its description of the present dynamical problem. Therefore, we must analyze the dynamics in the hope that we can assess more precisely under which conditions one or the other functional is more adequate.

IV. COMPARISON OF PW91 AND RPBE DYNAMICS FOR $N_2/W(110)$

In this section we take the $N_2/W(110)$ system as a working example and study the evolution of impinging molecules under the RPBE and PW91 PESs. From the quantitative comparison of these dynamics we discuss the relative accuracy of both PESs.

A. 60° incidence

The very low dissociation probability obtained with the RPBE PES for 60° incidence (with respect to the Z axis) is a surprising result that deserves further analysis. In this subsection, we will consider the case of 5000 trajectories with an impact energy of 0.9 eV. The perpendicular energy is then $E_\perp = 0.225$ eV.

The PW91 dynamics of impinging molecules is followed in Fig. 5 by plotting their center of mass position over the surface unit cell when first reaching the distance Z in the range of $3.4 > Z > 3.1$ Å (top panels). We give in the same figure the associated distribution in polar angles θ of the internuclear axis (bottom panels). It may be noted that only 5% of the molecules reflect before reaching $Z = 3.1$ Å, and that the distribution of molecular orientations is only slightly modified in this large distance region. The dissociation probability is 10% under the present conditions (Fig. 4).

The situation is completely different in the RPBE case, shown in Fig. 6 for the same Z range. Only 62% of the molecules reach $Z = 3.3$ Å. At this distance, the θ -distribution is highly localized around $\theta = 90^\circ$ (molecular axis parallel to the surface). Then a drastic change takes place in the interval between 3.3 and 3.2 Å as only 0.4% of the molecules reach the latter distance. This is again due to the more repulsive character of the RPBE PES, compared to the PW91 one. For example, we consider the hollow configuration for $\theta = 90^\circ$, $\varphi = 54^\circ$, $Z = 3.2$ Å, and $r = r_{eq}$ (blue curves in Fig. 2). The potential energies are ~ 0.17 eV for PW91 and ~ 0.27 eV for RPBE. This means that molecules in this configuration, with the mentioned perpendicular impact energy, cannot approach the surface closer than this distance under the RPBE PES. In other words, in the RPBE calculations, the unrealistic

FIG. 5. (Color online) Evolution of N₂ on the W(110) surface in calculations performed with the PW91 PES for 5000 trajectories. The incidence conditions are $E_i=0.9$ eV and $\Theta_i=60^\circ$. Top panels: Position on the unit cell of the molecule center of mass when first reaching a distance Z to the surface. Bottom panels: Associated normalized distribution in polar angles of the N₂ internuclear axis. N_Z gives the fraction of molecules reaching Z . The dissociative sticking probability is $\sim 10\%$.

quenching of dissociation under 60° incidence is due to the more repulsive character of the RPBE PES, for $Z > 3$ Å, with respect to the PW91 one.

B. Normal incidence

The PW91 calculations^{30,31} have shown that the low energy dynamics under normal incidence is characterized by

dynamic trapping of the molecules in the vicinity of the potential well at $Z \sim 2.6$ Å. The discrepancy between experimental and PW91 dissociation probabilities in this energy range was attributed to an overestimation of the dynamic trapping efficiency as a dissociation mechanism.³⁰ It was concluded that the origin of such a discrepancy did not lie on the access to the potential well but rather on the balance

FIG. 6. (Color online) Same as Fig. 5 for calculations performed with the RPBE PES. Only 1 out of the 5000 trajectories ends in dissociation. Note that the panels for $Z=3.2$ Å and $Z=3.1$ Å do not give statistically meaningful information in view of the small number of events.

FIG. 7. (Color online) Same as Fig. 5 for calculations performed with the RPBE PES for 60 000 trajectories and for incidence conditions: $E_i=0.25$ eV and $\Theta_i=0^\circ$. The dissociative sticking probability is $\sim 0.1\%$.

between reflection and dissociation for those molecules that have been trapped in the well. RPBE calculations show a better agreement with experiment in this low energy regime, and one could wonder whether this agreement is due to a qualitative or quantitative difference between both descriptions. In other words, does dynamic trapping still exist under RPBE?

In Fig. 7 the RPBE dynamics is depicted for 60 000 trajectories with incidence energy $E_i=0.25$ eV. Dynamic trapping is indeed at work here. The incident molecules go through an ordering stage favoring clearly a top-vertical configuration at $Z=2.5$ Å. They bounce a few times in the vicinity of this well and eventually find a path toward either reflection or dissociation. We have verified that the average number of rebounds experienced by these molecules is larger in RPBE than in PW91 dynamics. This means that, under the former, it is more difficult to escape the top-vertical well.

To shed some light on the smallness of the RPBE dissociation probabilities at low impact energies, we show in Fig. 8 the dynamics followed by 5000 molecules under the PW91 PES. The incidence conditions are the same as the ones in Fig. 7, and therefore a quantitative comparison between both dynamics can be performed. The dynamic trapping scenario is not as restrictive in the PW91 case as in the RPBE one. Under PW91 dynamics, 65% of the incident molecules reach $Z=2.5$ Å, whereas in the RPBE case only 12% are able to reach this distance. The difficulty, under RPBE, to reach distances to the surface below 3 Å is a direct consequence of the more repulsive character of the PES for $Z>3$ Å, as discussed in the previous subsection.

Still in Fig. 8, we find that the probabilities to dissociate once the molecules reach $Z=2.5$ Å are 18% in PW91 and

only 1% in RPBE. *Ab initio* calculations of the minimum reaction path of N_2 chemisorbed on W(110) show that, whereas in the PW91 the dissociation barrier is 0.467 eV lower than the barrier to reflection, the difference is only 0.145 eV (Ref. 39) in the RPBE case. The latter result is in better agreement with the experiments of Refs. 40 and 41 that suggest similar energy barriers toward reflection and dissociation.

Summing up, although dynamic trapping persists in RPBE dynamics, its effectiveness as a dissociation mechanism is greatly diminished when compared with the PW91 case. There are two reasons for this: (i) The access to the top vertical well is hindered, given the too repulsive character of the RPBE PES in the long distance range; (ii) the RPBE probability to escape the well toward dissociation is smaller, which is in part driven by a smaller difference (consistent with experimental findings) between the barriers toward dissociation and reflection.

A detailed analysis for the W(100) case leads to conclusions that are consistent with the previous ones for W(110): The drastic reduction of the dissociation probability at low energies (Fig. 3) in RPBE calculations is due to an excessive increase in repulsion (with respect to the PW91 PES) at large distances from the surface.

V. CONCLUSIONS

State of the art theoretical studies of the dynamics of molecules impinging on metal surfaces are based on DFT calculations where the XC functional is approximated by a GGA functional. By contrast to the computation of chemisorption energies, whose accuracy is determined by only a

FIG. 8. (Color online) Same as Fig. 7 for calculations performed with the PW91 PES for 5000 trajectories. The dissociative sticking probability is 12%.

small region of the 6D PES, dynamical processes involve PES properties over a much larger volume. For the latter reason, inaccuracies arising in dynamical processes from the use of approximate XC functionals have not been well documented until now. This might lead to overestimate the role of the frozen surface and adiabaticity hypothesis if the latter would be considered *a priori* as the only explanation for the discrepancy between theory and experiment.

In the present work, we have shown that the calculated reactivity for N₂ molecules impinging on either W(100) or W(110) surfaces strongly depends on the choice of GGA XC functional: Results for the dissociation probability when using the PW91 or RPBE functionals are significantly different. The comparison of the latter results with experimental data does not lead to a firm conclusion as to which functional provides the best PES.

We have performed a more detailed analysis of the dynamics by following the time evolution of the impinging molecules. This analysis led us to conclude that the RPBE functional produces a too repulsive PES far from the surface. The latter observation does not conflict with the conclusion of earlier works as to the increased accuracy of RPBE with respect to PW91 close to the surface. Indeed, we found indications that the RPBE functional better describes the PES in the vicinity of the molecular chemisorption well. The use of the RPBE functional decreases significantly the role of dynamic trapping in dissociation as a consequence of two effects: (i) A hindered access to the top vertical well due to the increased repulsion far from the surface and (ii) a lower probability to escape this well toward dissociation.

In summary even though there is evidence that the RPBE provides a better description when the molecule is

close to the surface (as observed for adsorption energies), it seems to fail badly in the low density region far from the surface, of key importance for the dynamics of molecule/surface interactions. We hope that our findings will stimulate further studies of the RPBE functional to check whether these assumptions can be theoretically supported.

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