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# First principles study of adsorption of O<sub>2</sub> on Al surface with hybrid functionals

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Adsorption of O<sub>2</sub> molecule on Al surface has been a long standing puzzle for the first principles calculation. We have studied the adsorption of O<sub>2</sub> molecule on the Al(111) surface using hybrid functionals. In contrast to the previous local-density approximation/gradient-corrected approximation, the present calculations with hybrid functionals successfully predict that O<sub>2</sub> molecule can be absorbed on the Al(111) surface with a barrier around 0.2–0.4 eV, which is in good agreement with experiments. Our calculations predict that the lowest unoccupied molecular orbital of O<sub>2</sub> molecule is higher than the Fermi level of the Al(111) surface, which is responsible for the barrier of the O<sub>2</sub> adsorption. © 2011 American Institute of Physics. [doi:10.1063/1.3665032]

## I. INTRODUCTION

The adsorption and dissociation of oxygen molecule on metal surfaces is a phenomenon of large relevance to materials processing such as catalysis and corrosion.<sup>1</sup> Because of the absence of d-electrons and simple geometric structure, the O<sub>2</sub>/Al(111) system is considerably simpler than transition metals and thus generally proposed as a prototype system for oxidation. In order to gain some insights into the microscopic mechanism of the oxidation of Al(111) surface, extensive experimental<sup>2–6</sup> and theoretical<sup>7–10,12–16</sup> studies had been done during the past several decades.

However, even for such a simple O<sub>2</sub>/Al(111) system, dramatic disagreement lies between experiments and up-to-date theoretical results based on the density functional theory (DFT) calculations. Experimentally, independent molecule beam scattering experiments had consistently shown<sup>2,3</sup> that the initial sticking probability of oxygen molecule on Al(111) surface, defined as the ratio of sticking events to the total number of molecule-surface collisions, is small ( $\approx 10^{-2}$ ) at low incident translation energy, which indicates a barrier around 0.3 eV along the adsorption trajectory. On the other hand, according to the adiabatic potential energy surface (PES) obtained from the DFT calculations,<sup>7–10</sup> the adsorption of oxygen molecule on the Al(111) surface is exothermic and no sizable barriers was found.

It seems to be widely established that the failure of DFT to reproduce the experimental results is due to the adiabatic approximation, which plays a fundamental role in the frame of DFT. From this point of view, during the initial adsorption the charge transfer from the Al(111) surface to O<sub>2</sub> molecule would be forbidden by Wigner's spin-selection rules,<sup>11</sup> and as a result the O<sub>2</sub>/Al(111) system is confined to some kind of excited states, the description of which is beyond the scope of the DFT. Many models designed to account for the non-adiabatic effects had been proposed and barriers can indeed

be produced along the initial adsorption trajectories.<sup>12–16</sup> To invoke all these methods, one has to abandon the single PES picture and to at least partially abandon the DFT, the cost of which is thus not very satisfactory and has been under debate.<sup>17,18</sup>

The other possible reason for the lack of barriers in the previous DFT calculations, which appears to be overlooked, is that the accuracy of the exchange-correlation (XC) functionals used before are not good enough to correctly describe the O<sub>2</sub>/Al(111) system. Although DFT methods have impressively proven their computational relevance during the last decades and won great success in the description of various systems, the frequently used local-density approximation (LDA) and gradient-corrected approximation (GGA) functionals have several severe shortcomings.<sup>19–21</sup> For example, the calculated formation energy and reaction energy between small molecules exhibit significant deviations from experimental results. Considering the structures, the LDA tends to underestimate the bond length while the GGA often yields a too large value. Moreover, LDA and GGA always severely underestimate the band gap for insulators and semiconductors. The highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO) gap for small molecules may also be underestimated in these functionals. For the reaction between oxygen molecule and aluminum clusters, it has been shown<sup>22,23</sup> recently that the presently widely used GGA functionals are not adequacy enough. It has also been shown that for the O<sub>2</sub>/Al<sub>13</sub><sup>+</sup> case, the situation can be improved by using hybrid density functionals.<sup>22</sup>

In hybrid functionals the local- or semi-local (gradient-corrected) functional is modified by adding a fraction of the exact exchange energy. This represents a sensible compromise between the two simple mean-field methods [DFT and Hartree-Fock (HF)] and often, probably due to its partial correction of the self-interaction error in local and semi-local DFT functionals, yields fairly good agreements with state of the art many-body methods such as configuration interaction and perturbation theory as well as with experimental results.

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The formation energy and geometries of small molecules, for instance, are in better agreement with experiments compared to LDA and GGA, and even the prediction of the band gap and band structure can also be improved.<sup>24–26</sup>

In this paper, the initial adsorption of oxygen molecule on Al(111) surface is studied by three different functionals, one is the semi-local Perdew-Burke-Ernzerhof (PBE) functional and the other two are hybrid functionals (HSE06 and PBE0). The PBE calculation shows a barrier-less reaction path while both of the two hybrid functionals produce barriers along the adsorption trajectories, with the barrier height in good agreement with experimental results. The relative position of the Fermi surface of the Al(111) surface and the LUMO level of oxygen molecule is shown to play an essential role in the existence of such barriers.

## II. THE CALCULATION METHOD

The calculations presented in this paper are based on the DFT and performed by means of the plane-wave-pseudopotential code Vienna *ab initio* simulation package (VASP).<sup>27–29</sup> The wave functions are expanded in a plane-wave basis set and pseudopotentials are used to describe the electron-ion interactions. The cutoff kinetic energy for the plane-wave basis is chosen to be 400 eV for all the calculations. The geometric structures of the ions are optimized by the conjugate gradient method. To obtain the electronic minimization, all band simultaneous update of wave functions is selected as the algorithm for the oxygen molecule, and a damped velocity friction algorithm is used for the calculations on the Al(111) surface and the O<sub>2</sub>/Al(111) system. The occupation numbers are updated by the Methfessel-Paxton scheme and a finite electronic temperature of 0.1 eV is used. All total energies are then extrapolated to zero electronic temperature. The semi-local Perdew-Burke-Ernzerhof (PBE) functional is used as the basic XC functional in all the calculations. The hybrid calculations are done with PBE0 and HSE06 functionals.<sup>30–32</sup>

The calculations on the O<sub>2</sub>/Al(111) system are restricted to triplet state in order to account for the open shell nature of the O<sub>2</sub> molecule.<sup>33</sup> The Al(111) surface is modeled by a seven layer thick slab with a 2×2 surface cell. The vacuum between slabs is 23 Å, which is large enough to make the interaction between different slabs negligible. The calculations for Al(111) surface and O<sub>2</sub>/Al(111) systems are carried out using a 4×4×1 Monkhorst-Pack (MP) grid of special k-points. To check the convergence with respect to the number of k-points, the calculations for some special points along the reaction paths such as the positions of the barriers are redone using a 10×10×1 MP grid of k-points. The differences between the adsorption energies obtained by the two grids are within just a few meV and thus negligible compared to the adsorption energies, which are typically greater than 100 meV. To map out a reaction path, we have optimized the structures for O<sub>2</sub> molecule with fixed distance to the surface between 1.8 and 3.0 Å, while at each step the two oxygen atoms and top three layers of Al atoms are relaxed by the PBE functional. For hybrid calculations the total energies are obtained

TABLE I. The equilibrium spin, bond length, and binding energy for free O<sub>2</sub> molecule by different functionals along with experimental results. The calculation results by two hybrid functionals are in good agreement with experiment.<sup>34</sup>

	Spin	Bond length (Å)	Binding energy (eV)
PBE	1	1.23	6.67
HSE06	1	1.21	5.18
PBE0	1	1.21	5.17
Experiment	1	1.21	5.20

from static calculations on the structures obtained by the PBE functional.

## III. RESULTS AND CONCLUSIONS

### A. Free O<sub>2</sub> molecule

The ground state of free O<sub>2</sub> molecule is experimentally found to be a spin triplet state, and the equilibrium bond length and the binding energy are 1.21 Å and 5.2 eV,<sup>34</sup> respectively. The theoretical findings by different functionals along with the experimental results are summarized in Table I. The results are obtained by spin-unrestricted calculations and all of three functionals can correctly predict the spin triplet state. The results by both of two hybrid functionals show significant improvement over the PBE functional especially for the prediction of binding energies and even the bond length. Our findings are consistent with previous works.<sup>24</sup>

To get more information about the electronic structure of the oxygen molecule, the density of states (DOS) of free O<sub>2</sub> molecule are calculated by the three different functionals and the results are plotted in Figure 1. The energy level of the occupied orbitals of free oxygen molecule produced by these three functionals are similar. The most significant difference between the PBE and the hybrid functionals, which can be obviously seen from Figure 1, is the gap between the highest occupied molecular orbitals and the lowest unoccupied molecular orbitals. The precise values of the HOMO-LUMO gap are 2.27, 5.28, and 6.06 eV for PBE, HSE06, and PBE0, respectively. As we will see below, the energy levels of the molecular orbitals in oxygen molecule, especially that of the LUMO, play an important role in the initial adsorption for O<sub>2</sub> on the Al(111) surface.

### B. Adsorption of oxygen molecule on Al(111) surface

With the PBE functional we have explored four starting geometries, and two distinct type of trajectories are found, the final configurations of which are given in Figure 2. Our results are consistent with previous studies.<sup>7,8</sup>

Two distinct adsorption trajectories by three different functionals are plotted in Figure 3. Two paths labeled by top and bridge correspond to those in Figure 2, respectively. The reaction coordinate is the height from Al(111) surface to oxygen molecule, oxygen molecule is parallel to the surface and the O-O bond length is optimized at each height by the PBE functional. As has been mentioned before, in all these

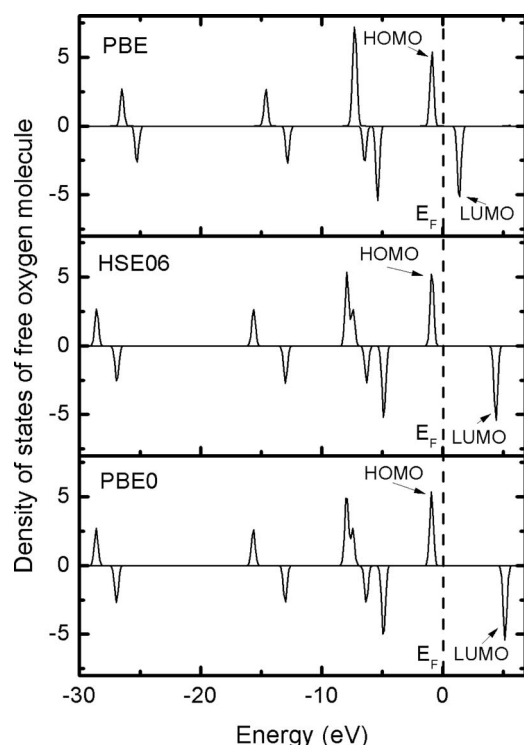


FIG. 1. Energy levels of the valence orbitals of free O<sub>2</sub> molecule calculated by three different functionals. The Fermi energy  $E_F$  is set to zero. The most obvious difference between the PBE and hybrid functionals is the HOMO-LUMO gap. Both of two hybrid functionals show a significant larger gap than the PBE functional.

calculations the O<sub>2</sub>/Al(111) system is constrained to triplet state to account for the open shell nature of the oxygen molecule. The adsorption energy is defined as

$$E_{\text{ad}} = E_{\text{O}_2/\text{Al}(111)} - E_{\text{O}_2} - E_{\text{Al}(111)},$$

where  $E$  denotes the total energy obtained by the DFT.

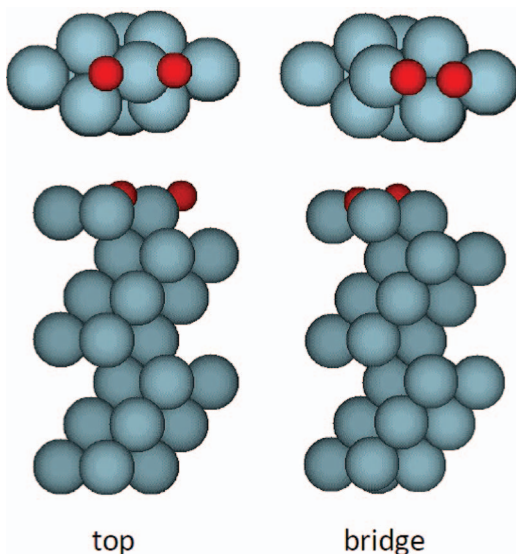


FIG. 2. Two different adsorption geometries obtained by the PBE calculation. Oxygen molecule is parallel to the surface and dissociates in both trajectories and the O-O distance is 3.3 Å in the top adsorption and 2.2 Å in the bridge adsorption. The top adsorption is energetically more favorable and the equilibrium height is around 0.9 Å, which is in consistent with previous studies and slightly higher than experimental value (0.6–0.8 Å).<sup>7,8</sup>

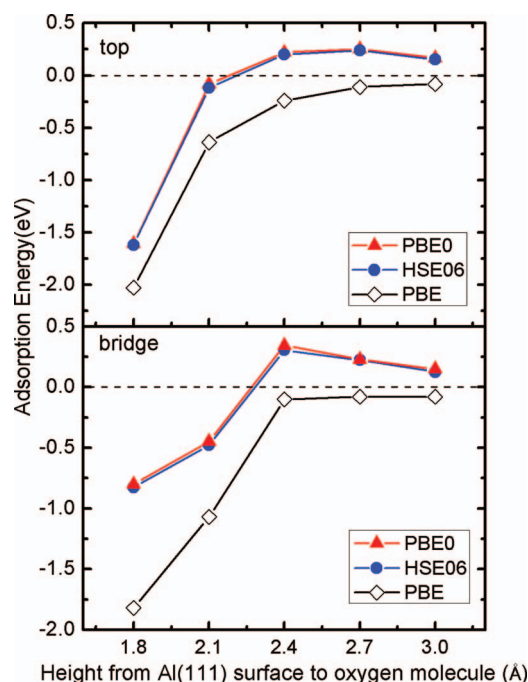


FIG. 3. Adsorption energy along two trajectories calculated by different exchange-correlation functionals. The two paths labeled by top and bridge correspond to those in Figure 2, respectively. In the PBE calculation the adsorption energy decreases monotonically for both trajectories and no barrier is found. On the other hand, both hybrid calculations produce barriers around 0.2–0.4 eV along two trajectories, which are consistent with experimental results.

It turns out that in the PBE calculation the adsorption energy decreases monotonically along the reaction coordinate for both trajectories, which indicates a non-activated reaction process. On the other hand, both hybrid calculations produce barriers around 0.2–0.4 eV along two trajectories, which are consistent with experimental results.<sup>2,3</sup>

We do the Bader charge population analysis<sup>36–38</sup> along the two trajectories by the three functionals and the results along the bridge adsorption path is plotted in Figure 4, the charge along the top adsorption path is qualitatively the same. It can be clearly seen from this figure that the charge is transferred from the Al(111) surface to the molecule, which is qualitatively consistent with previous findings.<sup>8</sup> Moreover, at large distance (the height >2.4 Å) PBE predicts more charge transfer than that of the hybrid functionals. This difference of charge transfer between the PBE and hybrid functionals could account for the different predictions of the adsorption energies and thus the existence of barriers, similar to the O<sub>2</sub>/Al<sub>13</sub> case.<sup>22</sup>

In order to understand why the hybrid functional can predict a adsorption barrier, We calculate the LUMO of free oxygen molecule and the Fermi level  $E_F$  of the clean Al(111) surface by different functionals and the results are illustrated in Figure 5. In order to compare the energy levels from different systems, the presented values of the energy levels are relative to the energy levels of vacuum. It can be seen from Figure 5 that the Fermi level of the clean Al(111) surface is nearly the same by the three different functionals. The LUMO of oxygen molecule lies below the  $E_F$  of the Al(111) surface by the PBE functional, allowing a spontaneous charge transfer



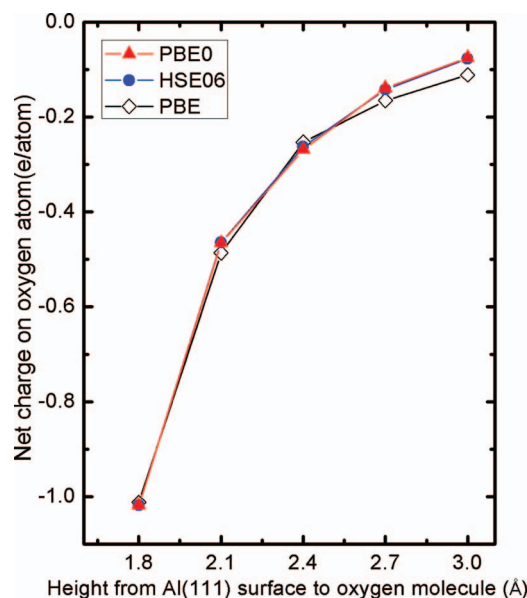


FIG. 4. Net charge on oxygen atom along the bridge adsorption path for three different functionals. It can be clearly seen that the charge is transferred from the Al(111) surface to the molecule. Moreover, at large distance ( $>2.4$ ) Å, PBE predicts more charge transfer than that of hybrid functionals.

to the LUMO of the molecule when it approaches the surface. Since the LUMO is an anti-bonding orbital, the filling of such orbital drives the dissociation of  $O_2$ . In contrast with the result of the PBE, the LUMO of oxygen molecule is above the  $E_F$  of Al(111) surface when using hybrid functionals, which gives rise to a barrier in charge transfer to the LUMO of  $O_2$  molecule and leads to the activated adsorption process. Thus the results in Figure 5 are consistent with that in Figure 4 and finally lead to the different predictions of the adsorption paths in Figure 3 by the three functionals. It would be interesting to note that for the CO/Pt(111) system, the position of the energy level of the LUMO of the CO molecule was reported to play an key role in the prediction of the preference adsorption site.<sup>35</sup>

In conclusion, we have presented DFT total-energy calculations for the adsorption of the oxygen molecule on the Al(111) surface using different exchange-correlation functionals. In contrast to semi-local functional, hybrid functionals predict a barrier for the adsorption of  $O_2$  on Al(111) surface, in agreement with experiments. Our results suggest that the LUMO of  $O_2$  molecule is higher than the Fermi level of the Al(111) surface, which is responsible for the barrier of the  $O_2$  adsorption. To the best of our knowledge, it is the first time that the barriers have been successfully produced for this reaction within the scope of the DFT. We hope that our findings can offer a new perspective for the understanding of the microscopic mechanism of the oxidation of the Al(111) surface.

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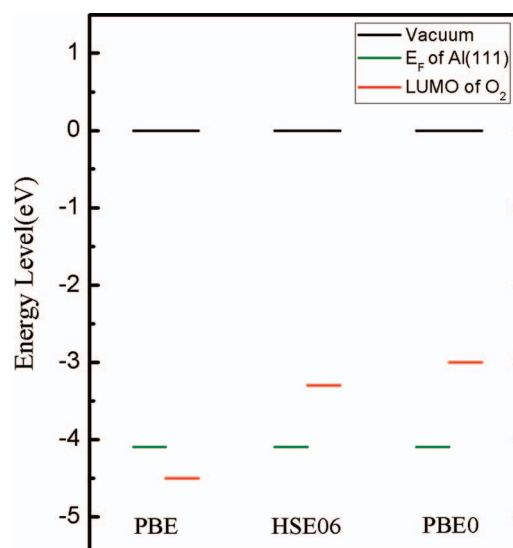


FIG. 5. The LUMO of free oxygen molecule and the Fermi level  $E_F$  of the Al(111) surface calculated by different exchange-correlation functionals. The energy level of vacuum is set to zero. The  $E_F$  of the clean Al(111) surface is nearly the same by three different functionals. The LUMO of oxygen molecule lies below the  $E_F$  of the Al(111) surface by the PBE functional. In contrast with the result of the PBE, the LUMO of the oxygen molecule is above the  $E_F$  of the Al(111) surface when using the HSE06 and the PBE0 functional.

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