Cluster and Periodic DFT Calculations: The Adsorption of Atomic Nitrogen on M(111) (M = Cu, Ag, Au) Surfaces

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First-principle density functional calculations with cluster and slab models have been performed to investigate adsorption and thermally activated atomic nitrogen on M(111) (M = Cu, Ag, Au) surfaces. Optimized results indicate that the basis set of the N atom has a distinct effect on the adsorption energy but an indistinct one on the equilibrium distance. For the N/M(111) adsorption systems studied here, the threefold face centered cubic (fcc) hollow site is found to be the most stable adsorption site. The reason for the fcc site is that the perfected adsorption site has been explained by the density of states (DOS) analysis, that is, that N(2p) has the smallest DOS population near the Fermi level on the fcc site as compared with other adsorption sites. The variations of the adsorption energy as a function of adsorption site are similar and in the following order of N−M(111) binding strengths on a given site: Cu(111) > Ag(111) > Au(111). It is found that the N atom forms essentially an ionic bond for the most stable site. Large contributions between the M(ns) and N(2p) orbitals (n = 4, 5, and 6 for Cu, Ag, and Au, respectively) are found for the cluster model at the B3LYP/LANL2DZ-6-31G(d,p) level and also found in the slab DFT-GGA calculation results, which are the main characteristics of M−N bonds. At last, the dissociation of N_2 on Cu(111) and Au(111) has also been obtained in this work, and the results showed that the dissociation of N_2 on Cu(111) is more active than that on the Au(111) surface.

1. Introduction

The adsorption of C, H, O, and N atoms on transition and noble metal surfaces are of considerable interest in connection with the nature of surface reactions involving molecular species containing these atoms, which include bulk oxidation, corrosion, ammonia synthesis, and a variety of hydrocarbon production and reforming reactions. The location of these atoms at a crystal surface is a fundamental quantity in the description of surface processes. Furthermore, the adsorption and diffusion of adatoms on metal surfaces can also be very useful knowledge in understanding many electrochemically and heterogeneously catalyzed reactions.[1] Atomic adsorption on the low index faces of metal surfaces raises superficially the simplest type of surface structural problem. At low coverage, the adatoms typically occupy the highest coordination sites on the surface with very little modification of the positions of the atoms on the surface relative to their positions on the clean surface.[2] In our previous report,[3] the interaction of C, H, O, and S atoms with the Cu(111) surface has been systematically studied from first-principle density functional calculations and the results agree well with the experiments.

The intrinsic fundamental interest of the interaction of atomic nitrogen with metal surfaces is also relevant to the catalytic chemistry of nitric oxide, whether in the context of automotive exhaust problems or the ammoxidation of olefins to nitrides.

So far, the adsorption and recombinative desorption of atomic nitrogen on Cu(100),[4−11] Cu(111),[12−16] Ag(111),[17] and Fe(*hkl*)[18] have been investigated with a variety of experimental techniques and theoretical methods, including LEED, STM, PhD, FP-LMTO, DFT, etc. Although gold has been used little as a heterogeneous catalyst, it actually plays an important role in catalysis.[19] The surface reactivity of gold changes markedly with the structure and the chemistry, which are strongly affected by the supports, although pure gold surfaces are rather inactive.[19] In contrast to experimental investigations, little is known about the binding characteristics of N/M(111) (M = Cu, Ag, Au) systems. A number of interesting issues requires more detailed studies involving well-defined single-crystal surfaces. As far as we know, only one observation of adsorption for atomic nitrogen on the Cu(100) surface was reported, and large covalent contributions between the N(2p) and Cu(3d) orbitals were found at the DFT level.[6]

A property with general interest is the difference in adsorption energy for an adsorbate on different metals. In addition, diffusion barriers for motion of adatoms on metal surfaces are important to understand the dynamics of many catalytic reactions. Density functional theory has been recently used to study the interaction of hydrogen on the M(111) (M = Ni, Pd, Pt) surfaces,[20] and the calculated results were consistent with experimental observations of the structure, energetics, and diffusion properties. We feel that model calculations of atom−surface interactions can sometimes be as accurate as experiment or at least complement each other.[21] In this paper, the adsorption of the N atom on the M(111) (M = Cu, Ag, Au) surfaces has been investigated by means of quantum chemical calculations using both cluster and slab models. We also try to probe into the correlation between

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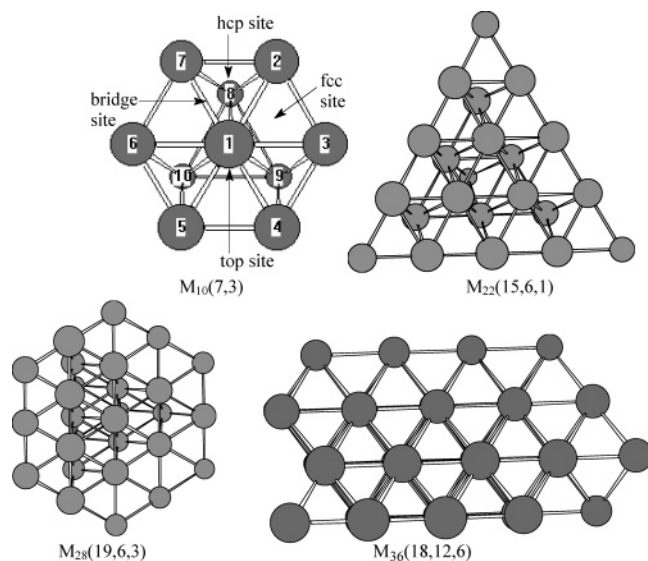§ University of Tsukuba.

Figure 1. $M_{10}(7,3)$, $M_{22}(15,6,1)$, $M_{28}(19,6,3)$, and $M_{36}(18,12,6)$ cluster models represent the M(111) surfaces with different adsorption sites (i.e., the top, bridge, hcp, and fcc sites) considered for atomic nitrogen adsorption.

some properties of these metals and the adsorption characteristics of atomic nitrogen. To the best of our knowledge, this is the first systematically electronic structure calculation dealing with the N/M(111) (M = Cu, Ag, Au) adsorption systems.

2. Method of Calculation

The development of modern surface science provided the opportunity to investigate the interaction between catalysts and molecules or atoms at the atomic scale. However, computations of molecules containing transition metal atoms have proven to be more difficult than those for first- and second-row atoms.[21] Recent advances in methodology based on the technologies of pseudopotential and plane-wave basis sets and high-speed computers have now made it possible to obtain quantitative information on the surface phenomena. In this work, cluster models of the surface have been employed to simulate the N atom adsorbed on the M(111) (M = Cu, Ag, Au) surfaces.

The cluster models of $M_{10}(7,3)$ (M = Cu, Ag, Au) (i.e., seven atoms in the first and three atoms in the second layer), M_{22}-(15,6,1), $M_{28}(19,6,3)$, and $Cu_{36}(18,12,6)$ are shown in Figure 1 and have been chosen to represent the M(111) surfaces. The M(111) surfaces are constructed using the bulk lattice constants[23] of 3.615 Å (Cu), 4.086 Å (Ag), and 4.078 Å (Au). Generally, there are four different adsorption sites on the M(111) crystal surface: the top site which resides above a surface atom, two threefold hollow sites which correspond to the "fcc site" (face centered cubic) and the "hcp site" (hexagonal close packed) (the hcp site resides above a subsurface atom in the second substrate layer, the fcc site does not), and the "bridge" site which lies halfway between the fcc and hcp sites. These sites are schematically illustrated in Figure 1. In the present calculations, a single nitrogen atom is placed on each of the different sites, namely, the top (1), bridge (1−2), hcp (1−2−7−8), and fcc (1−2−3) hollow sites (the number in parentheses is the same as the label for the metal atom in the $M_{10}(7.3)$ model of Figure 1). Geometry optimizations for the perpendicular distance of the N atom to the first metal layer are carried out while the cluster geometries are fixed at the bulk lattice parameters due to the fact that there is very little modification of the metal surface by the adatom at low coverage.[2]

The interaction of the N atom with different adsorption sites of the M(111) (M = Cu, Ag, Au) surfaces has been studied by first-principle density functional calculations that use the hybrid B3LYP exchange-correction functional[24,25] as implemented in the Gaussian94 program package.[26] For Cu atoms, the relativistic effective core potentials (ECPs) reported by Hay 3p, 3d, 4s, and 4p shells are treated explicitly. Similarly, these ECPs treat explicitly the 4s, 4p, 4d, 5s, and 5p electrons of Ag and the 5s, 5p, 5d, 6s, and 6p electrons of Au. It is customary to refer to these ECPs as LANL2. The standard double-ζ basis set, also reported by Hay and Wadt[27] and denoted as usual as LANL2DZ, is used to describe the electron density of the valence electrons of Cu, Ag, and Au, whereas the electron density of the N atom is, respectively, described with the standard 6-31G and 6-31G-(d,p) basis sets for comparison.

The natural bond orbital (NBO) procedure[28,29] provides an efficient method for obtaining bonds and lone pair electrons which compose an optimized Lewis structure of a molecule from modern ab initio wave functions. The set of orthonormal NBOs forms a compact and stable representation of the electron density in a molecule[30] and provides a convenient basis for investigating charge-transfer or hyperconjugative interactions in molecular systems.[29] Reed et al.[30] report that the natural population analysis is an alternative to conventional Mulliken population analysis and seems better to describe the charge distributions in compounds of high ionic character (i.e., those containing metal atoms), where Mulliken populations often contradict seriously the density integration and empirical measures of ionicity. In view of these cases, the NBO method[31] is employed in the analysis of electron configuration and the binding characteristics of the N/M(111) (M = Cu, Ag, Au) adsorption systems.

For the slab model calculation, it was based on a generalized gradient approximation in the density functional theory carried out using a package "STATE" (simulation tool for atom technology) which has been successfully applied to adsorption problems in the case of semiconductor and metal surfaces.[32,33] We used the Perdew, Burke, and Ernz-erhof exchange and correlation functional[34] as well as Vanderbilt's ultrasoft pseudo-potentials.[35] The energy cutoffs of the plane-wave basis sets are 25 and 400 Ry for wave functions and charge density, respectively. The unit cell of p(3 × 2) with three and six layers was used as a model of the N atom $^1/_6$ ML, and a vacuum region was defined at 10 Å thickness between two neighboring slabs. The surface Brillouin zone was sampled using a 4 × 6 special k-point for M(111). The adsorbed N atom and above three layers (for the six layers model) of substrate atoms are allowed to relax for structure optimization.

3. Adsorption on the M(111) (M = Cu, Ag, Au) Surfaces

Table 1 lists the adsorption energies, natural charges, and structural parameters of atomic nitrogen adsorbed onto each of the sites on the M(111) surfaces of Cu, Ag, and Au. The adsorption energy (E_{ads}) is calculated according to the formula

$$E_{ads} = E(M) + E(N) - E(M + N) \qquad (1)$$

where $E(M)$, $E(N)$, and $E(M + N)$ denote the calculated energy of a cluster without the N atom, the free N atom, and a cluster with the N atom, respectively. A positive value of E_{ads} implies that the adsorption of the N atom from the gas phase is thermodynamically favorable.

3.1. Preferred Site and Adsorption Energy. To find the preferred site for the N atom, we first examined its adsorption behavior on the Cu(111) surface. The optimized results show

Adsorption of Atomic Nitrogen on M(111) Surfaces

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TABLE 1: Adsorption Energies and Structural Parameters for the Adsorption of Atomic Nitrogen onto the M(111) (M = Cu, Ag, Au) Surfaces at the B3LYP/LANL2DZ Level for the M$_{10}$ Cluster[a]

	6-31G basis set		6-31G(d,p) basis set		
	Z_{eq} (Å)	E_{ads} (DFT) (eV)	Z_{eq} (Å)	E_{ads} (DFT) (eV)	Q(N)
		Cu(111) surface			
top	2.05	3.63	1.94	3.61	−0.67
bridge	1.41	4.77	1.36	4.87	−1.14
hcp hollow	1.24	5.27	1.18	5.37	−1.28
fcc hollow	1.25	5.28	1.12	5.40	−1.24
		Ag(111) surface			
top	2.47	3.38	2.17	3.31	−0.49
bridge	1.71	3.80	1.67	3.80	−0.77
hcp hollow	1.47	3.99	1.40	3.98	−1.08
fcc hollow	1.50	4.08	1.43	4.10	−0.98
		Au(111) surface			
top	2.10	2.88	2.31	2.90	−0.17
bridge	1.66	3.36	1.57	3.47	−0.63
hcp hollow	1.32	3.58	1.24	3.78	−0.91
fcc hollow	1.39	3.68	1.29	3.83	−0.87

[a] Z_{eq} is the perpendicular distance of the N atom to the first metal plane, E_{ads}, the adsorption energy of atomic nitrogen on the different site of M(111) (M = Cu, Ag, Au) surfaces, and Q(N), the natural charge on atomic nitrogen.

that the nitrogen atom prefers to stay outside the surface. The perpendicular distances between the nitrogen atom and the first metal layer are similar, all ranging from 1.24 to 1.94 Å. Early low-energy electron diffraction (LEED) studies[36−38] suggested that the nitrogen atoms are absorbed 1.45 Å above the first layer of copper atoms. And the experimental investigations[8] obtained by LEED and STM also demonstrate that nitrogen remains mostly on the sample surface and that the N concentration in bulk Cu could not exceed 1%. In fact, on the fcc(111) surface, the threefold hollow sites are so tightly packed and the metal interlayer spacing is so small that the adatoms usually do not penetrate deeply enough to form a direct bond with a metal atom in the second metal layer.[22]

It can be easily seen from Table 1 that the adsorption energies of the N atom are in the order of fcc ≈ hcp > bridge > top site, either at the B3LYP/LANL2DZ-6-31G or at the B3LYP/LANL2DZ-6-31G(d,p) level. The preferred site is the threefold fcc hollow site with an adsorption energy of 5.40 eV (5.28 eV for 6-31G) closely followed by the threefold hcp hollow site with an adsorption energy of 5.37 eV (5.27 eV for 6-31G). The adsorption energy of atomic nitrogen clearly decreases at the bridge site relative to the threefold hollow site. The least stable site is the top site with an adsorption energy of 3.61 eV (3.63 eV for the 6-31G level). In a word, the fcc and hcp hollow sites are remarkably preferential to both the bridge site and the top site for the adsorption of the N atom on the Cu(111) surface. It agrees well with the general features of atomic adsorption on the metal surfaces.[1]

In the case of the Ag(111) and Au(111) surfaces, the results are similar to those observed from the Cu(111) surface but with visibly lower adsorption energies. Thus, we will only discuss the behavior of adsorption for the N atom on the Ag(111) surface at the B3LYP/LANL2DZ-6-31G(d,p) level. The top site is the most unstable site with an adsorption energy of 3.31 eV. The fcc hollow site with an adsorption energy of 4.10 eV is slightly more stable than the hcp hollow site (3.98 eV). However, the bridge site has an intermediate value of 3.80 eV. Consequently, it can be concluded that the fcc hollow site is the preferred site for the adsorption of atomic nitrogen on the M(111) (M = Cu, Ag, Au) surfaces.
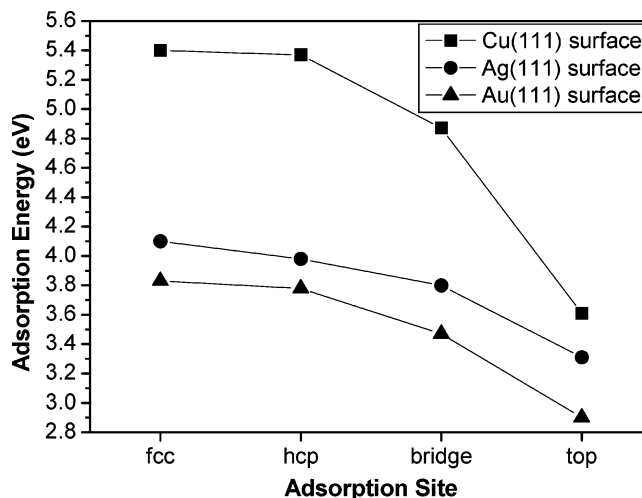
Figure 2. Adsorption energies of atomic nitrogen on the M(111) (M = Cu, Ag, Au) surfaces based on the cluster model calculation.

TABLE 2: Some Parameters in Correlation with the Adsorption Energy of Atomic Nitrogen[a]

	cluster		atomic parameters				E_{ads}
metal	HOMO	LUMO	IP (I)	EA	electronegativity	work function	(fcc site)
Cu	−3.897	−3.329	7.726	1.235	1.90	4.94	5.40
Ag	−3.903	−3.442	7.576	1.302	1.93	4.74	4.10
Au	−5.129	−4.610	9.225	2.309	2.40	5.31	3.83

[a] The HOMO and LUMO of the M(111) (M = Cu, Ag, Au) cluster models are calculated at the B3LYP/LANL2DZ level; IP (I) (the first ionization potential), EA (electron affinity), the electronegativity (on the Pauling scale), and work function are extracted from ref 23, and the electronegativity of N atom is 3.04; E_{ads} is the adsorption energy of atomic nitrogen at the most stable site; all units are in eV with the exception of the electronegativity.

3.2. Relative Strength of Adsorption. Figure 2 shows the adsorption energies of atomic nitrogen on the M(111) (M = Cu, Ag, Au) surfaces at the B3LYP/LANL2DZ-6-31G(d,p) level. Some parameters relevant to the difference in adsorption energy for the N atom adsorbed on those metal surfaces are tabulated in Table 2. It can be observed from Figure 2 that the adsorption energy of the N atom is larger on the Cu(111) surface than on Ag(111) and Au(111) for a given site, giving the following order for the N−M(111) binding strength, Cu(111) > Ag(111) > Au(111). It agrees well with the experimental investigations[17] that the adsorption of the N atom on the Ag(111) surface proceeds in a similar manner as on Cu(111) but with a weaker N−Ag bond. Similarly, the NO$_2$−M (M = Cu, Ag, Au) bond strength order, Cu−NO$_2$ > Ag−NO$_2$ > Au−NO$_2$, can also be found in Lu et al.[39] studies. It is interesting to correlate the HOMOs and LUMOs of the M$_{10}$(7,3) (M = Cu, Ag, Au) cluster models, the first ionization potential (IP (I)), the electron affinity (EA), and the electronegativity of M atoms with the N−M(111) binding strengths.

Commonly, there is a large electron transfer from the metal to the high electronegative atom in the case of atomic adsorption, as could be demonstrated by our previous studies[3,40] and by the natural charges on the N atom summarized in Table 1. On the basis of the HOMO data listed in Table 2, one may reach a conclusion that the probability of losing an electron from the M$_{10}$(7,3) cluster is Cu(111) > Ag(111) > Au(111), suggesting that the N atom will gain more electrons from Cu(111) than from Ag(111) and Au(111). The LUMO data of the M$_{10}$(7,3) cluster models also support this conclusion. This fact would account for the strongest binding of the N atom with the Cu(111)

TABLE 3: Calculated Adsorption Energies of N on Cu, Ag, and Au for the Larger Cluster Size

	6-31G		6-31G(d,p)	
	Z_{eq} (Å)	E_{ads}(DFT) (eV)	Z_{eq} (Å)	E_{ads}(DFT) (eV)
Cu22-fcc	1.26	6.36	1.22	6.30
Cu28-fcc	1.40	4.37	1.32	4.47
Cu36-fcc	1.31	4.60		
Ag22-fcc	1.39	4.57	1.39	4.64
Ag28-fcc	1.73	3.60	1.66	3.60
Ag36-fcc	1.50	3.60		
Au22-fcc	1.29	4.68	1.29	4.86
Au28-fcc	1.45	3.01	1.23	3.24
Au36-fcc	1.52	3.14		

surface, followed by the binding strength of N−Ag(111) and N−Au(111). The binding in N−Au(111) is the weakest for its highest IP (*I*), EA, and electronegativity, while the N−Cu(111) binding is found to be stronger than the N−Ag(111) binding even if the first IP of Cu is somewhat higher than that of Ag. Considering the difference between the isolated atom with bulk metal, it should be a little difficult to find a quantitative correlation between solely the first IPs of M (M = Cu, Ag, Au) atoms and the N−M(111) binding strengths but it still be correlated by EA and electronegativity of M and/or the E_{HOMO} of cluster M_{10}. Additionally, we also note that there is no quantitative correlation between the work function of the M(111) surface and the adsorption energy. We plan to make an attempt to probe the efficient parameter for correlation with the adsorption energy. No matter how, the relative strengths of adsorption for atomic nitrogen on the M(111) surfaces are in the order of Cu(111) > Ag(111) > Au(111).

3.3. Cluster Size Effect. To test the size effect of the cluster model, we also make some additional calculations using relatively large models (M_{22}, M_{28}, and M_{36}), and the results are listed in Table 3. It can be seen that the adsorption energy decreases with increasing cluster size, suggesting that the interaction between the N atom and the substrate is not a local interaction, and thus it is very sensitive to the boundary condition. In addition, we noticed that the N adsorption energy on Cu(111) based on the M_{28} model (4.47 eV) or M_{36} model (4.60 eV) is close to the previous cluster model calculation result (4.12−4.25 eV).[11] It was also found that the adsorption energy seems converged when the cluster size is larger than 36 atoms.

Considering the cluster size effect, the previous calculations reported that the M_{18} model can give a good result for the CO_2 adsorption on copper metal,[41] and the M_{18} model can also be used to simulate the HCOO/Cu(111) system very well,[42] which is different from the case of N atom adsorption on metals that it is very sensitive to cluster size. The reason might be due to the fact that the interaction of CO_2 or HCOO with metal is not as strong as the N atom (i.e., may be more local interaction), and thus it is not too dependent on cluster size.

To further consider the cluster size effect on the adsorption energy calculations, the DFT-GGA cluster model calculations based on the plane-wave basis sets were also performed in the present work. It is usually accepted that the plane-wave basis sets allow one to overcome the basis dependence as compared with the Gaussian basis sets used in the Gaussian program.[43] The cluster used to model the adsorbed system was put in a box with the size of 20 Å × 15 Å × 15 Å during the cluster model calculation, and the interaction between clusters seems neglected in such a case. Figure 3 shows the DFT-GGA results for the different cluster size, and it can be observed that calculated adsorption energy almost converged for the cluster size as large as 43 atoms, but the reason the M_{22} has so large an adsorption energy is not clear.
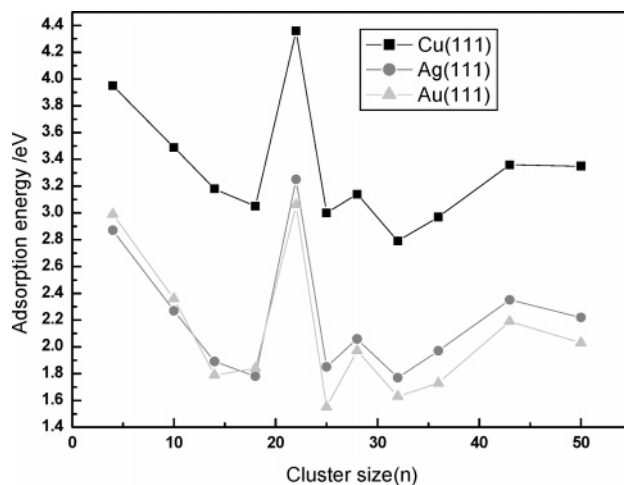
Figure 3. Size dependence of N atom adsorption energy based on the plane-wave basis sets results.

TABLE 4: DFT-GGA Results of Adsorption Energies and Structures of N on Cu, Ag, and Au Surfaces Based on the Slab Model

	three layers model		six layers model	
	Z_{eq} (Å)	E_{ads} (DFT) (eV)	Z_{eq} (Å)	E_{ads} (DFT) (eV)
Cu(111)-fcc	1.11	3.49	1.10	3.61
Ag(111)-fcc	1.17	2.41	1.11	2.56
Au(111)-fcc	1.20	2.05	1.18	2.34

In the following study, we will use the slab model to calculate the N adsorption on M(111) surfaces compared with the above cluster model results.

3.4. Slab Model Calculation Results. For the adsorption of N atom on Cu(111), a series of adsorption sites including top site, bridge site, hcp site, and fcc site were tested based on the three layers model in which the N atom and the first top layer are allowed to be relaxed. The calculated adsorption energies ware found to be 1.36, 2.91, 3.31, and 3.39 eV, respectively, suggesting that the fcc site is the most stable one. Since the fcc adsorption site is the most stable adsorption form, a larger slab model with six layers was used, and the calculated adsorption structure and adsorption energies are listed in Table 4. In here, two slab models have been used: one is the three layers model where the first layer is allowed to be relaxed and another is a six layers model where the above three layers are allowed to be relaxed. In Table 4, one can notice that the adsorption energies calculated using three layers are slightly lower than those of the corresponding data obtained using the six layers model, suggesting that the adsorption energies based on the slab model are not so dependent on the size of the slab model in the present study. Furthermore, we noticed that the adsorption energies have the order of Cu(111) > Ag(111) > Au(111), which is consistent with the trend of the cluster model. In addition, we notice that the present result of N adsorption energy on Cu(111) (3.61 eV) is quite close to the result of Biemolt et al.[16] by means of nonrelativistic local spin density approximation method (3.52 eV). Unfortunately, we cannot compare directly our calculated adsorption energies with the experimental results due to a lack of the latter.

It has long been found that the adsorbed N atom induces the metal fcc(111) or fcc(110) to a pseudo-fcc(100) structure.[2] In an effort to explore the effect of reconstruction on the adsorption energy of N on the Cu(111) surface, we also calculated the adsorption of the N atom on the reconstructed Cu(111) surface, that is, the two outermost layers adopt a geometry similar to

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TABLE 5: Natural Electron Configuration of the N/Cu(111) System at the B3LYP/LANL2DZ-6-31G(d,p) Level[a]

adsorption site	atom	no.	natural electron configuration[b]			
top site	Cu	1	[core] 4s(0.90)	3d(9.80)	4p(0.26)	5p(0.05)
	Cu	6	[core] 4s(0.98)	3d(9.94)	4p(0.04)	5s(0.01)
	Cu	8	[core] 4s(0.92)	3d(9.92)	4p(0.07)	5p(0.01)
	N	11	[core] 2s(1.96)	2p(3.70)		
bridge site	Cu	2	[core] 4s(0.70)	3d(9.80)	4p(0.07)	
	Cu	6	[core] 4s(0.96)	3d(9.94)	4p(0.04)	5s(0.01)
	Cu	8	[core] 4s(0.93)	3d(9.93)	4p(0.08)	5p(0.01)
	N	11	[core] 2s(1.93)	2p(4.20)	3p(0.01)	
hcp hollow site	Cu	2	[core] 4s(0.72)	3d(9.81)	4p(0.06)	
	Cu	6	[core] 4s(0.94)	3d(9.94)	4p(0.05)	5s(0.01)
	Cu	8	[core] 4s(0.91)	3d(9.94)	4p(0.08)	5p(0.01)
	N	11	[core] 2s(1.91)	2p(4.35)	3p(0.01)	
fcc hollow site	Cu	2	[core] 4s(0.73)	3d(9.82)	4p(0.06)	
	Cu	6	[core] 4s(0.98)	3d(9.94)	4p(0.04)	5s(0.01)
	Cu	8	[core] 4s(0.93)	3d(9.93)	4p(0.08)	5p(0.01)
	N	11	[core] 2s(1.92)	2p(4.31)	3p(0.01)	

[a] The no. of atom is the same as the label shown in Figure 1, and the tabulated number for N is 11 (not shown in Figure 1). [b] The values given are for the optimized geometries of the Cu(111)−N complex.

that of the Cu(100) structure and compared to that of the Cu(111) and Cu(100) results. A five layers model in which the first two layers have reconstructed geometry was used in the present calculation, and the calculated adsorption energy at the four-hollow site was found to be 4.20 eV, which is larger than that of Cu(111) (3.61 eV) and close to that of Cu(100) (4.65 eV) (the adsorption energies of atomic N on Cu(100) and reconstructed Cu(111) are not shown in this work).

4. Electron Configuration and Binding Characteristics

4.1. Cluster Model. In this section, we will take a closer look at the electron configuration and the binding characteristics of atomic nitrogen on the M(111) (M = Cu, Ag, Au) surfaces. At the B3LYP/LANL2DZ-6-31G(d,p) level, the NBO analysis has been performed under the optimized geometries of the M(111)−N complexes. Representative results of the natural electron configuration are only given for the N/Cu(111) system in Table 5, due to the similarity between the Cu(111), Ag(111), and Au(111) surfaces. To address the binding characteristics, we report the results from NBO analysis for the M−N bond (M = Cu, Ag, Au) with the largest occupancy in Table 6.

First, we want to establish the dominant bonding mode (i.e., covalent or ionic bond) for the N atom at its most stable adsorption site, the fcc hollow site, on the M(111) (M = Cu, Ag, Au) surfaces. The natural charges listed in Table 1 suggest that the N atom forms essentially an ionic bond according to the fcc hollow site. Likewise, it can be found in our previous studies[3,40] that atomic H forms essentially a covalent bond with the Cu(111) surface, while the S, O, and C atoms carry a relatively high negative charge and hence form an ionic bond. Also, Bagus et al.[44] reported that the Ag−halogen (F, Cl, Br) bond is essentially ionic. The binding of chlorine to a copper surface is completely ionic with hardly any trace of covalency as demonstrated by Pettersson and Bagus.[45] Considering the relationship between the amount of negative charge and the strength of ionic bond, it may be rational to conclude that the strengths of the ionic bond for the N atom on the M(111) surface are in the order of Cu(111) > Ag(111) > Au(111).

It is well-known that the electron configuration for the neutral nitrogen and copper atom in the ground state is [core]2s(2.00)-2p(3.00) and [core]4s(1.00)3d(10.00), respectively. From Table 5, one may observe that the natural electron configurations of N and Cu (directly binding with N) atoms in the top site are different from the other three sites. For the bridge, hcp, and fcc

hollow sites, the 3p orbital of the N atom gains the same amount of electron (0.01 e). However, there is 0.05 e in the 5p orbital of the Cu (directly binding with N) atom found in the top site and not in other sites. The extended orbitals of Cu(6) and Cu-(8) which indirectly bind with N are the same among the four kinds of adsorption sites but with a somewhat of a difference in the amount of electron distributions. Namely, the electrons in the 4s orbital of Cu(6) are all larger than those of the Cu(8) atoms corresponding to all the sites, while for the 4p orbital the relationship is reversed. In addition, the sequence of Cu−N binding strengths, namely, fcc ≈ hcp > bridge > top site, can also be found from the natural electron configuration of the N atom, not from Cu atoms because of the different coordination number of the N atom among the different sites. For instance, the electron number of the N atom in the fcc hollow site is more than that in the top site by 0.57 e (see Table 5). A close scrutiny of the data given in Table 5 permits us to draw a conclusion that the amount of electron in N(2p) sharply changes after the N atom is adsorbed onto the Cu(111) surface, which is closely followed by the Cu(4s) which directly binds with the N atom (i.e., Cu(1) or Cu(2) shown in Table 5).

The NBO analysis results of the N/M(111) (M = Cu, Ag, Au) systems show that both spin Lewis structures are different from each other in the exact details of M−N binding behavior. The information in Table 6 indicates that the formation of the M−N bond is only from donation of one spin system (i.e., α or β spin system). Correspondingly, the occupancies of antibonding are sharply smaller than those of the bonding of M−N (those occupancies are not shown in Table 6). For example, the contributions to the Cu−N bond are mainly from the Cu(2)−N(11) bond with an occupancy of 0.82294, rarely from the Cu-(2)−N(11) antibond with an occupancy of 0.06884 according to the fcc hollow site. For this purpose, we focus on the M−N bond analyzed by NBO method.

According to the N atom on the fcc hollow site of the Cu-(111) surface, the $100|C_A|^2$ (C_A is the polarization coefficient) of the Cu atom in the Cu−N bond is 41.19% with the contributions of Cu(4s) (91.20%), Cu(4p) (1.00%), and Cu(3d) (7.80%) and contribution of the Cu−N bond from N(2s), N(2p), and N(3d) at 1.09%, 98.84%, and 0.07%, respectively, suggesting that the formation of the Cu−N bond is primary from the contributions between the Cu(4s) and N(2p) orbitals. Similar findings hold true for other sites of the Cu(111) surface. In the case of the N atom on Cu(100), Triguero and Pettersson[6] reported that the formation of bonding and antibonding states involved a direct Cu(3d) and N(2p) interaction. The discrepancy between their results and present DFT calculations might attribute to the difference in the type of single-crystal surface involved.

It is easy to find from Table 6 that the binding characteristics of the N/Ag(111) adsorption system are very similar to that of N/Cu(111). Compared with the N/Cu(111) and N/Ag(111) systems, slight differences occur for the adsorption of the N atom on the Au(111) surface. Namely, there is no obvious bond formation between Au and N atoms for the top site, indicating that the adsorptive strength of N on the top site of the Au(111) surface is too weak to form a bond between them. On the other sites, we also note that the contributions to the Au−N bond are dominant from Au(6s) and N(2p) orbitals. For the N/M(111) systems, large contributions between the M(ns) and N(2p) orbitals (n = 4, 5, and 6 for Cu, Ag, and Au, respectively) are found at the B3LYP/LANL2DZ-6-31G(d,p) level, which are the main characteristics of the M−N bond and consistent with

TABLE 6: NBO Analysis Results for the M−N Bond (M = Cu, Ag, Au) with the Largest Occupancy Calculated at the B3LYP/LANL2DZ-6-31G(d,p) Level[a]

Cu(111) surface	spin	Cu (%)				N (%)			
		$100|C_A|^2$	4s	4p	3d	$100|C_A|^{2\ b}$	2s	2p	3d
top	β	40.75	86.81	6.76	6.43	59.25	3.27	96.73	
bridge	β	41.29	96.07	2.46	1.47	58.71	0.07	99.87	0.06
hcp hollow	β	15.50	91.33	4.05	4.62	84.50	11.47	88.46	0.07
fcc hollow	β	41.19	91.20	1.00	7.80	58.81	1.09	98.84	0.07

Ag(111) surface	spin	Ag (%)				N (%)			
		$100|C_A|^2$	5s	5p	4d	$100|C_A|^2$	2s	2p	3d
top	α	19.93	92.51	5.07	2.42	80.07	9.77	90.18	0.05
bridge	β	63.71	95.40	0.84	3.76	36.29	7.37	91.86	0.77
hcp hollow	β	51.67	94.08	0.95	4.97	48.33	0.76	99.21	0.04
fcc hollow	β	44.82	94.46	0.77	4.77	55.18	0.48	99.47	0.04

Au(111) surface	spin	Au (%)				N (%)			
		$100|C_A|^2$	6s	6p	5d	$100|C_A|^2$	2s	2p	3d
top									
bridge	β	58.10	87.14	0.53	12.34	41.90	1.32	98.58	0.09
hcp hollow	α	37.22	84.48	0.75	14.77	62.78	3.71	96.18	0.10
fcc hollow	α	19.68	91.05	1.00	7.95	80.32	14.04	85.89	0.07

[a] The values given are for the optimized geometries of the M(111)−N complexes. [b] C_A is the polarization coefficient.

the natural electron configuration of the representative N/Cu-(111) system.

4.2. Slab Model. It is well-known that the density of states (DOS) is a very useful tool for the electronic structure analysis in the slab model calculations. In here, we first use a DOS plot to analyze the perfected adsorption site of the N atom on the Cu(111) surface and then to analyze the order of adsorption energies of atomic N on Cu, Ag, and Au.

4.2.1. Perfected Adsorption Site. The DOS projected on to the N(2p) orbital for the four adsorption sites top, bridge, hcp, and fcc are given in Figure 4. It can be seen that the top site has the highest PDOS peak at the Fermi energy or near the Fermi energy level, which means that the N atom is the most unstable one among theses four sites. So, we expect that the top site has the smallest adsorption energy. In contrast, the lowest N(2p) DOS population near the Fermi level was found for the fcc site, which results in the largest adsorption energy.

4.2.2. Order of Adsorption Energy of N on Cu, Ag, and Au. In this part, we would to answer the following two questions: First is why the N atom has the largest adsorption energy at the Cu(111) surface and the second is what is the main contribution to the N adsorption energy, either the metal s-band or the metal d-band. For the first question, it may be explained as follows: Since the Cu, Ag, and Au metals are the d-filed metals, the overlap integral (or the coupling matrix element, V_{ad}^2) with the N atom orbital is important in determining the binding energy. In general, the larger the overlap, the stronger the repulsion, resulting in lower adsorption energy. Since the size of the coupling matrix element always increases down through the groups of the periodic table, making the 5d metals the most noble, the bond with adsorbates becomes weaker and weaker from copper to gold. In fact, the overlap integral (or the coupling matrix element) has the order of Cu(1.0) < Ag(2.26) < Au(3.35),[46] which agrees well with the N adsorption energy trend (see Figure 5).

For the second question, from Figure 5, we get the following fitted equation

$$E_{ads} = 4.01 - 0.62V_{ad}^2$$

where E_{ads} stands for adsorption energy. Since the definition of

V_{ad}^2 reflects the properties of the d-band, we expect that the intercept in the above equation is mainly coming from the contribution from the coupling of the N atom with the metal s-band. Because the intercepts are so large (4.01 eV or so), we may predicate that the coupling with the metal s-band is the dominant contribution to the N atom adsorption energy, which is inconsistent with our above NBO analysis and our previous conclusion based on the slab model,[47] and in agreement with other previous results based on the cluster model calculations[48] and the slab model[49] that the metal s electron is the dominant factor to the binding energy, while the d electron is the change trend for the different metals.

At last, the activation energy for the dissociation of N_2, N_2-(g) = 2N(s), was also obtained in this work, and Figure 6 shows the results based on the NEB as well as the ANEBA method.[50,51] (The model used for the reaction path calculation is p(3 × 2) with the three layers model.) It is easily found from Figure 5 that the dissociation of N_2 on Cu(111) is more active than that on the Au(111) surface, and also that the T.S structure is more like a product than the reactant, that is, it may be a *late barrier* on both Cu(111) and Au(111). This result is agreement with the general rules of linear free energy theory that it is more exothermic and more active for reactions with a similar reaction mechanism. It is also consistent with the trend of N atom adsorption energy, that is, the larger of adsorption energy of atomic nitrogen and easier for the broken N−N bond in N_2.

5. Conclusions

In the present work, the interaction of atomic nitrogen with the M(111) (M = Cu, Ag, Au) surfaces at various sites has been studied by quantum chemical DFT calculations. Optimized results show that the N atom prefers the high symmetry hollow site, the fcc site, on the M(111) surfaces. Despite their similar structure and proximity in the periodic table, the adsorption energies of the N atom are found to be considerably different for Cu compared to Ag and Au. It can be observed that the adsorption energies of the N atom on the M(111) surfaces are in the order of Cu(111) > Ag(111) > Au(111) for a given site.

The results from NBO analysis show that the N atom forms essentially an ionic bond at the most stable site, the fcc site.
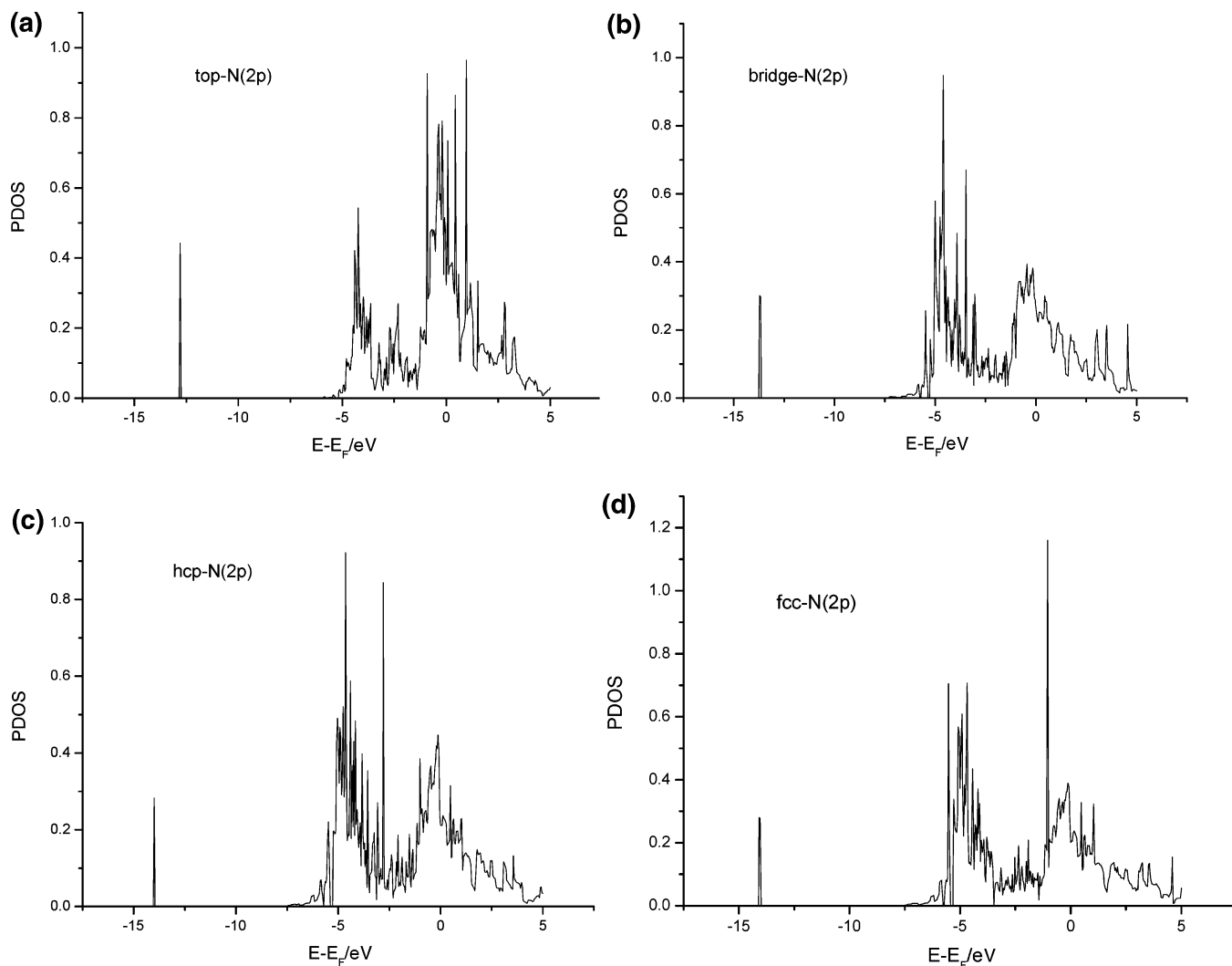
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Figure 4. Projected DOS onto N (2p) at different adsorption sites.
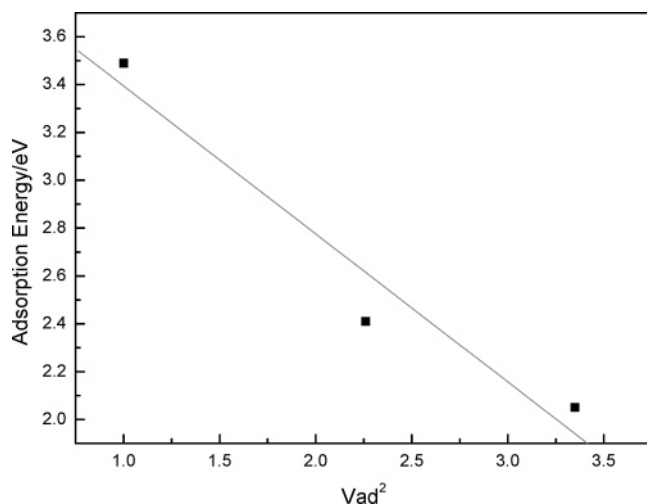
Figure 5. Correlation between adsorption energy and coupling matrix element.

Figure 6. DFT-GGA results of N_2 decomposition on Cu(111) and Au(111).

Large contributions between the M(ns) and N(2p) orbitals (n = 4, 5, and 6 for Cu, Ag, and Au, respectively) are found at the B3LYP/LANL2DZ-6-31G(d,p) level and the slab model DOS analysis, which are the main characteristics of the M−N bond. For the slab calculation results, the N adsorption energy is smaller than the cluster model, which is due to the size effect.
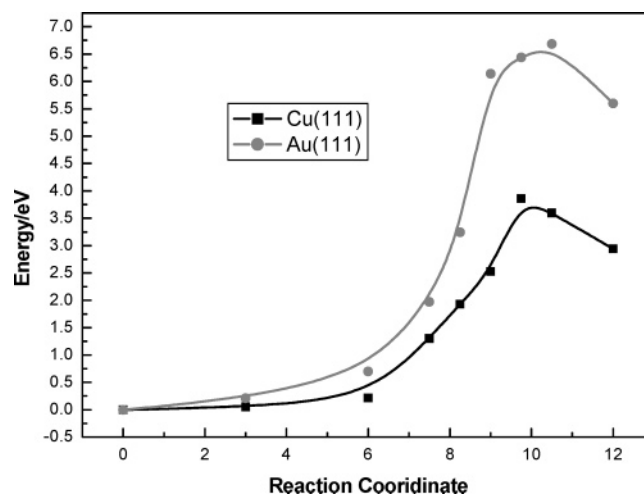
The perfected adsorption site has been analyzed by the N(2p) DOS plot, and the result suggested that the fcc site has the lowest population near the Fermi level, which means it is more stable than other adsorption sites. Furthermore, we find that the more electrons transfer to the N atom from the metal, the higher adsorption energy. At last, the dissociation of N_2 on Cu(111) and Au(111) has also been obtained in this work, and the results

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showed that the dissociation of N_2 on Cu(111) is more active than that on the Au(111) surface.

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