Molecular Modeling of Ammonia Gas Adsorption onto the Kaolinite Surface with DFT Study

Cheng, Qi; Li, Yongbing; Qiao, Xiaojuan; Guo, Yang; Zhao, Yang; Zhang, Qiuyuan; Ju, Yiwen; Shi, Yaolin

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Abstract: With high porosity and being one of the most abundant clay minerals, dried kaolinite may be an excellent adsorbent to remove ammonia gas (NH₃). Here, the plane wave pseudopotential method based on density functional theory (DFT) was used to explore the mechanism of ammonia gas adsorption on the dried kaolinite, the Mulliken electric charge, and the partial density of states of atoms of the NH₃/kaolinite (001) system. NH₃ adsorption on kaolinite can happen in three different types of adsorption positions: “top”, “bridge” and “hollow”. The “hollow” position is enclosed by two “upright” hydroxyl groups perpendicular to the (001) surface of kaolinite and a “lying” hydroxyl group parallel to the surface. At this position, the adsorption is the most stable and has the highest adsorption energy. The nitrogen atom of the NH₃ molecule bonds with the hydrogen atom in the “upright” hydroxyl group on the (001) surface and its hydrogen atom forms H-N...O hydrogen bond with oxygen atom in the “lying” hydroxyl group, which leads to the NH₃ stably adsorbed on kaolinite (001) surface. A small part of electrons transfer between NH₃ molecules and kaolinite creates weakly electrostatic adsorption between them.

Keywords: kaolinite; NH₃; adsorption; density functional theory (DFT)

1. Introduction

Sulfate, nitrate, and ammonium are the main chemical components of the increasing smog weather. Increasing atmospheric pollution caused by gases such as ammonia gas has been proven to be a global problem, and received widespread attention [1,2]. Due to the large amount of industrial exhaust emissions, domestic pollutants, and livestock farming, ammonia gas produced by these pollutants has increased dramatically, and the volatilization from decomposing livestock waste are the main sources of NH₃ in the atmosphere [3,4]. As a colorless and irritating alkaline gas with low volatility, NH₃ is the most abundant alkaline trace gas in the atmosphere and also the third most nitrogen-containing gas after N₂ and NO₂ [5]. The phenomena involved in the atmospheric circulation of NH₃ are complex in nature. At normal temperatures, pressures, and alkaline conditions, the equilibrium gas phase concentration of ammonia in dilute solution of ammonia + ammonium obeys Henry’s law and agrees well with the NBS thermodynamic data, its concentration is about 0.002–0.10 M [6,7]. Ammonia gas can cause serious pollution to the environment and seriously damages human skin tissue and respiratory system. When ammonia gas concentration reaches 0.5–1.0 mg/m³, it can be felt by the human body and
adheres to human skin tissue to absorb water from skin tissue and destroy the structure of proteins, thereby destroy cells [8], which make ammonia gas to be one of the common problems faced by all countries in the world.

As a means of treating gas emissions, adsorption is effective even at low contaminant levels and can recover contaminants by desorption [9]. For ammonia gas, even if the equipment is simple, it can be effectively removed by the adsorption method and the useful components can be recovered [10,11]. Previous studies have included clay minerals, activated carbon, zeolites, alumina and so on [12–18]. For kaolinite, one of the most abundant components in clay minerals [19,20], many previous researches have been conducted about its surface absorption of the CO$_2$, methane, ammonia ions and heavy metals [21–28], but few studies have dealt with the adsorption mechanism of ammonia gas on kaolinite.

In this paper, the first-principles density functional theory (DFT) [29,30] was used to study the adsorption mechanism of ammonia gas on the surface of kaolinite. The electronic distribution difference of the mineral surface before and after adsorption, the adsorption amount of adsorbed ammonia on the surface of kaolinite and the interaction between atoms in the adsorption process were obtained in order to explore the microscopic mechanism during adsorption. This study may help to reveal the microscopic coupling mechanism between gas and solid.

2. Calculational Methods and Models

2.1. Computational Methods

The calculation is based on the density functional theory (DFT) [31,32], local density approximation (LDA) [33] and general gradient approximation (GGA) [34] are used to approximate the exchange-associated energy. The Perdew-Burke-Ernzerhof (PBE) functional has high accuracy in the hydrogen bond description [35] and is used to model the electron exchange and correlation interaction within the GGA.

The Cambridge Sequential Total Energy Package (CASTEP) module was used to optimize the initial unit cell of kaolinite [36,37], and different exchange correlation functions and plane wave cut off energy was selected to determine its simulation optimization data. Density Function Theory-Dispersion force correction (DFT-D) [38] is performed on the basis of exchanging associated functionals to balance the strong van der Waals forces in the system. The interaction between electrons and ions is described by UltraSoft Pseudo Potential (USPP) [39,40]. The valence electrons in the calculation of the pseudo-potentials involved in the calculation are H-1s; O-2s$^2$2p$^4$; Al-3s$^2$3p$^1$; Si-3s$^2$3p$^2$. The atomic position optimization algorithm uses Broyden-Fletcher-Goldfarb-Shanno (BFGS) [41]. The Brillouin zone integral uses the Monkhorst-Pack [42] method. The positions of all the atoms in the calculation are relaxed according to Hartee-Fork [43] in the reciprocal space, and the k-point grid is set to (4 × 2 × 3). The whole process uses a cut off energy of 400 eV. The self-consistent field (SCF) [44] convergence accuracy is 2.0 × 10$^{-6}$ eV/atom, and the optimal convergence criterion of the total energy change of the system is set to 1.0 × 10$^{-5}$ eV/ Atom. The maximum force between atoms is 0.05 eV/Å, the maximum internal stress between atoms is 0.1 GPa, and the maximum displacement between atoms is 0.002 Å. The calculated lattice parameters and cell angles and Bish’s experimental results [45] are shown in Table 1, and the calculated data are consistent with the experimental data.
Table 1. Optimized results of the bulk of kaolinite.

| Exchange-Correlation Functions/eV | Lattice Parameter (Å) | Cell Angles (°) | Total Energy/eV |
|----------------------------------|-----------------------|-----------------|-----------------|
|                                  | a         | b         | c         | α         | β         | γ         |                |
| LDA + CA-PZ/400                 | 5.082     | 8.820     | 7.155     | 91.734    | 105.078   | 89.839    | -8689.188     |
| LDA + CA-PZ (DFT-D)/400         | 5.045     | 8.752     | 7.099     | 91.966    | 105.389   | 89.885    | -8689.142     |
| GGA + PBE/400                   | 5.209     | 9.068     | 7.485     | 91.675    | 104.836   | 89.726    | -8682.448     |
| GGA + PBE (DFT-D)/400           | 5.176     | 8.977     | 7.339     | 91.724    | 105.037   | 89.962    | -8682.408     |
| GGA + PW91                      | 5.176     | 8.984     | 7.371     | 91.757    | 105.445   | 89.813    | -8693.178     |
| GGA + WC                        | 5.183     | 9.024     | 7.347     | 91.652    | 105.077   | 89.740    | -8667.929     |
| GGA-PBESOL                      | 5.182     | 9.030     | 7.335     | 91.634    | 104.928   | 89.743    | -8656.095     |
| Experimental results [45]       | 5.154     | 8.942     | 7.391     | 91.926    | 105.046   | 89.797    |                |

2.2. Computational Models

Kaolinite is a layered aqueous aluminosilicate mineral with a triclinic system and belongs to the 1:1 type dioctahedral clay mineral. Its crystal structure is \( \text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8 \). The basic unit of kaolinite consists of a \( \text{Si}_4\text{O}_{10} \) tetrahedral layer and an \( \text{AlO}_2(\text{OH})_4 \) octahedral layer with its tetrahedron and octahedron interconnected by common oxygen ions, and its unit layers are connected to each other by a hydrogen bond with a van der Waals force between the molecules. A \( 2 \times 1 \times 1 \) kaolinite supercell model is established by expanding the well-optimized kaolinite bulk twice in the \( a \)-axis direction, which contains 68 atoms: 8Al, 8Si, 36O, 16H. The large monolayer of the kaolinite model consists of six atomic “sublayers”, which are \( \text{H}–\text{O}–\text{Al}–\text{O}–\text{Si}–\text{O} \) from top to bottom. The upper three layers constitute the “Alumina layer”, and the lower three layers constitute the “Silica layer” (Figure 1a). From the kaolinite (001) surface, the hydroxyl group on its inner surface could be two types: one third “lying” hydroxyl (\( \text{O}_l\text{H} \)) oriented parallel to the kaolinite (001) surface and two thirds “upright” hydroxyls (\( \text{O}_u\text{H} \)) oriented perpendicularly to the surface (Figure 1b).

![Figure 1](image_url) (a) the main view of kaolinite single layer model. Each kaolinite single layer contains six atomic “sublayers” which are \( \text{H}–\text{O}–\text{Al}–\text{O}–\text{Si}–\text{O} \) from top to bottom, the upper three layers constitute the “Alumina layer” and the lower three layers constitute the “Silica layer”; (b) the hydroxyl which parallel to the surface of kaolinite—“lying” hydroxyl (\( \text{O}_l\text{H} \)), the hydroxyl which perpendicular to the surface of kaolinite—“upright” hydroxyl (\( \text{O}_u\text{H} \)).

The kaolinite crystal can be cleaved in three directions of (001), (010) and (110) planes [46,47], among which the layer (001) is the most cleavable and the surface of layer (001) should be the largest proportion of the total surface area of the kaolinite particles for adsorption [48], so the subsequent studies were focused on this surface. For calculating the \( \text{NH}_3 \) adsorption on kaolinite surface, the lower part of the \( \text{O}–\text{Si}–\text{O} \) three sub-layers (silicon oxide layer) of this monolayer surface model is fixed, the upper part of the \( \text{H}–\text{O}–\text{Al} \) three sub-layers (aluminum oxide layer) is relaxed, and a 20 Å vacuum layer on the surface model (Figure 2) was built.
Figure 2. A vacuum layer of 20 Å was created on the surface of kaolinite (001). The left part is an enlarged kaolinite, in which red is a fixed three sub-layers and gray is a relaxed three sub-layers.

Similar to Hu [49] and Zhao [26], three categories of NH₃ adsorption position of were established on the kaolinite surface (Figure 3) based on the configuration and symmetry of the relaxed (001) surface of kaolinite. They are “top” positions (the adsorbed atom N directly above the active atom O), “bridge” positions (the adsorbed atom N between the two active atoms O) and “hollow” positions (the adsorbed atom N is bounded by three or more active atoms O). Considering the adsorption properties of NH₃, the “top”, “bridge” and “hollow” positons have three, three and four different adsorption positions respectively. Since NH₃ has no periodicity, build a 15 × 15 × 15 Å³ periodic cell to optimize NH₃ molecular which is placed in the center of the cell. The model parameters used in the optimization of the kaolinite surface model are from the optimized kaolinite unit cell of this study.

Figure 3. Top view of the kaolinite (001) surface. (A) three “Top” adsorption positions (T1-T3); (B) three “Bridge” adsorption positions (B1-B3); (C) four “Hollow” adsorption positions (H1-H4) (the white ball: H; the red ball: O; the purple ball: Al).
3. Results and Discussion

3.1. Adsorption Energy and Stable Adsorption Configuration

The adsorption energy can reveal the adsorption stability of NH$_3$ on the surface of kaolinite quantitatively, and the adsorption energy can be calculated as Equation (1):

$$E_{\text{ads}} = E_{\text{adsorbate/slab}} - E_{\text{adsorbate}} - E_{\text{slab}}$$  \hspace{1cm} (1)

Among them, $E_{\text{ads}}$ is the adsorption energy of NH$_3$ on the surface of kaolinite; $E_{\text{adsorbate/slab}}$ is the total energy of NH$_3$ on the surface of kaolinite; $E_{\text{adsorbate}}$ is the total energy of NH$_3$ before adsorption and $E_{\text{slab}}$ is the total energy of the kaolinite surface. If the adsorption energy is negative, it means that adsorption can occur, and the larger the absolute value of negative value, the more stable the adsorption. Thus, the adsorption configuration optimization is to find the adsorption configuration where the adsorption energy is the lowest. In this process, unfixed atoms change their positions, which makes the distance between the atoms change, until the convergence criterion of the calculation setting is satisfied. The adsorption energies corresponding to different adsorption positions were listed in Table 2.

Table 2. Summary of NH$_3$ adsorption energy corresponding to different adsorption positions on kaolinite surface.

| Surface | Adsorption Position | NH$_3$ on Kaolinite Final Enthalpy (eV) | Adsorption Energy (eV) |
|---------|---------------------|----------------------------------------|-----------------------|
| (001)   | Top1                | −17,689.03                            | −0.19                 |
|         | Top2                | −17,689.29                            | −0.45                 |
|         | Top3                | −17,689.12                            | −0.27                 |
|         | Bridge1             | −17,689.27                            | −0.43                 |
|         | Bridge2             | −17,689.33                            | −0.48                 |
|         | Bridge3             | −17,689.36                            | −0.52                 |
|         | Hollow1             | −17,689.38                            | −0.54                 |
|         | Hollow2             | −17,689.37                            | −0.53                 |
|         | Hollow3             | −17,689.35                            | −0.51                 |
|         | Hollow4             | −17,689.11                            | −0.27                 |

The calculated adsorption energies of three different adsorption positions show that the adsorption capacity of the “hollow” (the site of the adsorbed atom N among three active atoms O) is the largest, which indicates that the “hollow” positions of the three positions are the most stable adsorption positions for NH$_3$ on the kaolinite surface. The adsorption of “top” position is relatively weak. For “hollow” positions, the best adsorption position in is “hollow1”, and its adsorption energy is 0.54 eV, which means that NH$_3$ adsorption is the most stable here. The “Hollow1” is the middle position of a triangle, which surrounded by two “upright” hydroxyl groups perpendicular to the surface of kaolinite and a “lying” hydroxyl group parallel to the surface of kaolinite, and the “lying” direction of the H atom in the “lying” hydroxyl group is closest to the N atom in NH$_3$. The lowest adsorption energy in the “hollow” position is “hollow4” where H atom in the “lying” hydroxyl group is the farthest from the N atom in NH$_3$, and its adsorption energy is 0.27 eV. It seems that the distance between the H atom in the “lying” hydroxyl group and the N atom in NH$_3$ has a decisive influence on the adsorption energy. The closer distance between the H atom in the “lying” hydroxyl group and the N atom in NH$_3$, the greater adsorption energy of NH$_3$ adsorbed on the surface. For “top” and “bridge” adsorption, the most stable adsorption positions are “Top2” and “Bridge3” respectively, and their corresponding adsorption energies are 0.45 eV and 0.52 eV.

Figure 4 is the atom positional changes of kaolinite and NH$_3$ before and after their adsorption of the “hollow1” with the largest adsorption energy and the “top1” with the lowest adsorption energy. NH$_3$, which originally located in “hollow1”, shifted to “bridge2” after adsorption, and the N atom of NH$_3$ is closer to the kaolinite surface “vertically”. H$_{N1}$, H$_{N2}$ and H$_{N3}$ are the H atoms of NH$_3$ molecule,
they are far from the surface. All the H atoms of the hydroxyl group on the surface of kaolinite are gathered in the direction of the middle N atom (Figure 4A,a). The position of NH$_3$ adsorbed on “Top1” was nearly unchanged before and after adsorption, and the surface of kaolinite did not change greatly (Figure 4B,b). So, the larger the adsorption energy, the greater the NH$_3$ positional shift, and the stronger the reaction with the adsorbent.

![Figure 4](image-url)  
**Figure 4.** Top view of the positional change of NH$_3$ molecules before and after adsorption. (A,a) the positional change of NH$_3$ before and after adsorption at the “Hollow1” of the kaolinite (001) surface; (B,b) the positional change before and after adsorption at the “Top1” (the white ball: H; the red ball: O; the purple ball: Al).

### 3.2. Bond and Mulliken Electric Charge

Kaolinite crystals are electrically neutral, but the surface electrical properties of the kaolinite crystal faces are not, thus the surface of the kaolinite crystal may be the ability to catch the NH$_3$ molecules to balance their own electrical properties. Similarly, the atomic charge distribution inside the mineral crystal before and after adsorption may different and can be used to reveal the adsorption mechanism. Here, the most stable adsorption points of these three adsorption positions “top”, “bridge”, and “hollow” were selected to understand the change of atomic charge distribution and bond change after NH$_3$ adsorption on kaolinite (001) surface. Table 3 lists the longest and shortest N–H bond lengths, the largest and smallest H–N–H angles of NH$_3$ molecular adsorbed on “top2”, “bridge3”, and “hollow1” of the kaolinite surface. All the N–H bond lengths after adsorption are shorter than before (1.110 Å), and the longest N–H bond length is always the N–H$_{N1}$ bond. The longest bond N–H lengths corresponding to the “top2”, “bridge3” and “hollow1” are 1.030 Å, 1.033 Å and 1.036 Å, respectively. With the increase of adsorption energy, lengths of the longest and the shortest N–H bond are all increases. It demonstrates that the strongest repelling by H atoms on the kaolinite (001) surface results in the largest change of N–H$_{N1}$ bond. All H–N–H bond angles after adsorption are smaller than before (109.471°), and under the action of H atom of the kaolinite surface, H–N–H structure shift to the vacuum zone. The maximum H–N–H bond angles are all H$_{N1}$–N–H$_{N2}$, which are 107.885°, 108.112°.
and 108.550° respectively. The smallest bond angles were affected less by H atoms of the kaolinite surface, and decrease 2.203°, 3.249° and 2.965° after adsorption.

The Mulliken population can show the charge distribution of the overlapping regions between the bonding atoms (the relevant atomic orbitals), and the charge distribution of each atomic orbital, so the relative value of the atomic charge generated by the Mulliken population may provide useful information for the charge transfer and bond strength between different atoms [37]. The larger population between bonds is, the stronger bonding is. The N–H bonds became shorter and the population value between the N–H bonds became about 0.65 larger after adsorption, showing a significant covalent effect. Table 4 and Figure 5 show the change of Mulliken population between the atomic bonds of NH₃ after adsorption on the kaolinite (001) surface of “Top2”, “Bridge3” and “Hollow1”. The population between the N–H atoms shows positive, negative and zero values. Usually, the bond between atoms contains a bond or an anti-bond orbit and the contribution of the bond orbit is positive, while the contribution of the anti-bond orbit is negative. If the bond orbit is mainly filled, the Mulliken population between the N–H bonds was positive and contributes to bonding between atoms, or else it is a negative value, and no bonding between atoms. The combination of the N atom of NH₃ with the H atom of the surface of kaolinite has a big impact on the electron arrangement of orbits. For the “Top2” adsorption position, the Mulliken population between the N atom of NH₃ and the H₁ atom of the kaolinite just is 0.09, and they can form an N–H₁ bond. For the “Bridge3” position, the N atom of NH₃ interacted with two different H atoms of the kaolinite surface, H₂ and H₃, their population values are 0.06 and −0.01 respectively. It’s worth noting that only the N atom and the H₂ atom can form an N–H₂ bond. For the “hollow1” position, the N atom of NH₃ interacted with three different H atoms of the kaolinite surface—H₁, H₂ and H₃, their population values are 0.06, 0.02, and −0.02 respectively, so they can only form N–H₁ and N–H₂ bonds. In addition, the Mulliken population between Hₙ₁ and O₃ is 0.03, and can then form hydrogen bond.

Table 3. The structural parameters for NH₃ adsorbed on “Top2”, “Bridge3”, and “Hollow1” of the kaolinite (001) surface.

| Bond Length and Band Angle | Adsorption Before | Top2 | Bridge3 | Hollow1 |
|----------------------------|-------------------|------|---------|---------|
| Longest N–H bond length (Å) | 1.110             | 1.030| 1.033   | 1.036   |
| Shortest N–H bond length (Å) | 1.028             | 1.029| 1.030   |         |
| Largest H–N–H angle (°)     | 109.471           | 107.885| 108.112| 108.550 |
| Smallest H–N–H angle (°)    |                   | 107.268| 106.522|         |
| Adsorption energy (eV)       |                   | 0.45 | 0.52    | 0.54    |

Table 4. Mulliken bond population of atoms before and after NH₃ adsorption on kaolinite (001) surface (Top2, Bridge3 and Hollow1).

| Adsorption Site | Bond | Population (bulk/after) | Bond Length (bulk/after)/Å |
|-----------------|------|-------------------------|---------------------------|
| adsorption before |      |                         |                           |
| N–H₁            | 0.64/0.65 |                         | 1.039/1.036               |
| N–H₂            | 0.64/0.65 |                         | 1.035/1.030               |
| N–H₃            | 0.64/0.66 |                         | 1.039/1.030               |

| Top2 | N–H₁ | 0.09 | 1.887 |
|      | N–O₁ | −0.10| 2.869 |

| Bridge3 | N–H₁ | 0.00 | 2.960 |
|         | N–H₂ | 0.06 | 2.037 |
|         | N–H₃ | −0.01| 2.599 |
|         | N–O₂ | −0.06| 2.979 |

| Hollow1 | N–H₁ | 0.06 | 2.016 |
|         | N–H₂ | 0.02 | 2.326 |
|         | N–H₃ | −0.02| 2.552 |
|         | Hₙ₁–O₃ | 0.03 | 2.094 |
After adsorbing NH$_3$ on the kaolinite (001) surface, the Mulliken populations between N atoms of NH$_3$ and H atoms in the “upright” hydroxyl (O$_3$H) perpendicular to the kaolinite surface are positive, but the population between N atoms and H atoms in the “lying” hydroxyl (O$_1$H) parallel to the kaolinite surface is negative. This indicated that there is a tendency for the N atom to form an N–H bond with the H atom in the “upright” hydroxyl group (O$_3$H). For the “lying” hydroxyl (O$_1$H), the O atom exposed to the surface due to the “recumbent” of the H atom has a tendency to form hydrogen bonds with the H atoms closest to NH$_3$. The N–H bond length after adsorption is significantly shorter.

The electron density difference between adjacent atoms can describes the electron rearrangement and the electron transfer before and after surface adsorption. The “Hollow1” site has the largest adsorption energy in NH$_3$/kaolinite system and Figure 6 plots the electron density difference of “Hollow1” site before and after surface adsorption. In Figure 6, the yellow region between atoms represents the accumulation of electrons, and the blue region represents the depletion of electrons, and the color distribution showed a significant electron density depletion around the N atom and accumulates around H$_1$ and H$_2$, while the electron density around the H$_{N1}$ atom accumulates and the electron density around the O$_3$ atom is consumed.

Table 5 lists the charge of atoms’ Mulliken populations before and after NH$_3$ adsorption on “Hollow1” of (001) surface of kaolinite, including the N and H atoms of NH$_3$ and the H and O atoms of the kaolinite surface. H$_1$ and H$_2$ are the hydrogen atoms in “upright” hydroxyl group that bonded with...
N atom of NH₃, and the exposed oxygen atom (O₃) in the “lying” hydroxyl group forms a hydrogen bond with H₁₁ of NH₃ (Figure 5). Before adsorption, the charges of N and H atoms in the initial adsorbent NH₃ were respectively −1.23e and 0.41e, and the charges of H₁, H₂ and O₃ on the surface of the initial adsorbent kaolinite were respectively 0.45e, 0.46e and −1.05e. After the adsorption reaction, the charge of each atom changes.

In Table 5, a positive value means that electrons are lost, while a negative value means that electrons are gain. In NH₃, the N atom loses 0.05 electrons, in which the N 2s orbitals provide 0.02 electrons and the N 2p orbitals provide 0.03 electrons. The lost electrons of NH₃ are transferred to H₁ and H₂ on the kaolinite surface, resulting in H₁ charge changes from 0.45 to 0.43 and H₂ from 0.46 to 0.45. The H₁₁ atom of NH₃ obtains 0.02e form the 2p orbitals of O₃ atom on the surface of kaolinite, which results in the charge change of O₃ from −1.05e to −1.02e. A small part of the electron transference between ammonia molecules and kaolinite results in weakly electrostatic adsorption between them.

### Table 5. Mulliken charge populations of atoms before and after NH₃ adsorption on “Hollow1” of kaolinite (001) surface.

| Adsorption Site | Atom | Adsorption State | s  | p  | Total | Charge (e) |
|-----------------|------|------------------|----|----|-------|------------|
| Hollow1 H₁₁     | Before | 0.59             | 0  | 0.59 | 0.59  | 0.41       |
|                 | After  | 0.61             | 0  | 0.61 | 0.61  | 0.39       |
|                 | Δ(After-Before) | 0.02             | 0  | 0.02 | −0.02 |
| Hollow1 H₁₂     | Before | 0.59             | 0  | 0.59 | 0.59  | 0.41       |
|                 | After  | 0.58             | 0  | 0.58 | 0.58  | 0.42       |
|                 | Δ(After-Before) | 0.01             | 0  | −0.01| 0.01  |
| Hollow1 H₁₃     | Before | 0.59             | 0  | 0.59 | 0.59  | 0.41       |
|                 | After  | 0.59             | 0  | 0.59 | 0.59  | 0.41       |
|                 | Δ(After-Before) | 0.00             | 0  | 0.00 | 0.00  |
| Hollow1 N       | Before | 1.74             | 4.49| 6.23| 6.23  | −1.23      |
|                 | After  | 1.72             | 4.46| 6.18| 6.18  | −1.18      |
|                 | Δ(After-Before) | −0.02            | −0.03| −0.05| −0.05 |
| Hollow1 H₁      | Before | 0.55             | 0  | 0.55 | 0.55  | 0.45       |
|                 | After  | 0.57             | 0  | 0.57 | 0.57  | 0.43       |
|                 | Δ(After-Before) | 0.02             | 0  | 0.02 | −0.02 |
| Hollow1 H₂      | Before | 0.54             | 0  | 0.54 | 0.54  | 0.46       |
|                 | After  | 0.55             | 0  | 0.55 | 0.55  | 0.45       |
|                 | Δ(After-Before) | 0.01             | 0  | 0.01 | −0.01 |
| Hollow1 O₃      | Before | 1.85             | 5.20| 7.05| 7.05  | −1.05      |
|                 | After  | 1.86             | 5.16| 7.02| 7.02  | −1.02      |
|                 | Δ(After-Before) | 0.01             | −0.04| −0.03| −0.03 |

Δ is the difference of Mulliken charge populations of atoms before and after NH₃ adsorption on “Hollow1” of kaolinite (001) surface.

### 3.3. Density of State and Electron Transfer

Density of state (DOS) is one of the most important parameters for describing the state of motion of electrons in solid physics [50,51]. Figure 7 is a partial density of state (PDOS) image of NH₃ before and after adsorption at different adsorption sites on the kaolinite (001) surface. Figure 7A–D represent the PDOS diagram of the s, p orbital energy levels and the sum of two orbital energy levels of the free NH₃ molecules before adsorption and those of “top”, “bridge” and “hollow” (“Top2”, “bridge3” and “hollow1”) positions on the kaolinite surface after adsorption. For comparison, we also calculated the PDOS diagram of the H and O two-layer atoms involved in the adsorption of kaolinite (001) surface. Figure 7a is the image before adsorption and Figure 7b–d is the image after adsorption, including the s, p orbital energy levels and the sum of the two orbital energy levels.
The sum of PDOS (blue dotted line in the Figure 7) shows there are three peaks before NH$_3$ adsorption on the kaolinite surface, which are $-14.97$ eV, $-5.12$ eV and $-0.0055$ eV, but $-0.0055$ eV is very close to the Fermi level (0 eV) and is not considered in this study. The left peak mainly represents the 2s-orbital level, while the right peak mainly represents the 2p-orbital level. When the NH$_3$ molecule adsorbed to kaolinite surface on the “Top” position, the energy of the two orbitals of NH$_3$ reduced by 2.11 eV and 2.10 eV, and the wave crest reduced by 0.61 eV and 1.27 eV respectively. For the “bridge” position, the center of the peaks moved to the right by 1.26 eV and 1.21 eV, with wave crest decreasing by 0.54 eV and 2.21 eV. For the “hollow” position, the center of the peaks moved 1.65 eV and 1.58 eV to the right, and the wave crest reduced by 0.56 eV and 3.95 eV. The peaks of the three positions were all moved toward the low energy direction, and the distances which the center positions of the two peaks moved similar, that means the electron orbital energy decreases after adsorption and the adsorption system tends to be more stable. The wave crest change of 2s-orbital is small, but the wave crest of the 2p-orbital changes greatly, and as the adsorption energy increases, the wave crest of the 2p-orbital gradually decreases, which implies that during the adsorption process of NH$_3$, the influence of the p-orbital level is greater than the s-orbital energy level. The corresponding orbital energy level change of the kaolinite surface is small, the s-orbital in kaolinite surface has a little change, and there is nearly little change in the p orbital.

Figure 7. The PDOS plots for the NH$_3$ molecule and the Kaolinite surface atoms at the “Top”, “Bridge” and “Hollow” adsorption sites: (A) for NH$_3$ before adsorption; (a) for Kaolinite before adsorption; (B–D) for NH$_3$ adsorption on “Top”, “Bridge” and “Hollow” sites; (b–d) for kaolinite (001) surface after NH$_3$ adsorbed on “Top”, “Bridge” and “Hollow” positions.

Figure 8 illustrates the individual atom orbital energy level change of the most stable adsorption site (“Hollow1”) during the process of the adsorption. The zero point of energy is set at the Fermi level ($E_F$), the H$_1$ atoms is on the kaolinite surface (Figure 8a), and the H$_{N1}$ atoms is in NH$_3$ and the O$_3$ atoms is on the kaolinite surface (Figure 8b).

The partial density of states plots in Figure 8a, shows that the nonlocality of 2p-orbitals of N atoms in NH$_3$ increase after adsorption. The electron density of states disappears at Fermi level, and the whole density of states moves towards the direction of energy reduction after the interaction between N atom and H$_1$ atom of kaolinite surface, indicating that the NH$_3$/kaolinite (001) system is stable after adsorption. With Fermi level as the boundary, the bonding between 2p-orbital of N atom of NH$_3$ and 1s-orbital of H atom of kaolinite surface on the left side of Fermi level is from $-10$–$0$ eV, and the anti-bonding between them on the right side of Fermi level is 2.5–7.5 eV. According to the wave crest height of density of states, bonding is much stronger than anti-bonding, so N–H$_1$ bond. The density of states in Figure 8b shows that the anti-bonding between the 1s-orbital of H$_{N1}$ atom of NH$_3$ and the 2p-orbital of O$_3$ atom on surface is very weak, and the bonding effect is relatively strong, so H$_{N1}$–O$_3$ can bond. As a result, NH$_3$ can strongly adsorb on the (001) surface of kaolinite.
As a result, NH$_3$ can stably be adsorbed on the kaolinite surface and kaolinite is a suitable adsorbent choice. The interaction of ammonia gas with water is more complicated, and the interaction of ammonia gas with kaolinite demands further study.

For the “lying” hydroxyl group (O$_1$H), the H atom is “lying”, the O atom is exposed to the outermost surface and can forms a hydrogen bond with the H$_N$ atom of the NH$_3$ which closest to it. Moreover, a small part of electron transfer between NH$_3$ and kaolinite surface causes electrostatic adsorption between them. As a result, NH$_3$ can stably be adsorbed on the kaolinite surface and kaolinite is a suitable adsorbent choice. The interaction of ammonia gas with water is more complicated, and the interaction of water, ammonia gas and kaolinite demands further study.

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