Electron Transfer from Hydrogen Molecule to Au(111) During Dissociative Adsorption: A First-Principles Study

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We investigate the electron transfer from a dissociatively adsorbed H₂ molecule to a Au(111) surface using the first-principles methods. A fractional electron transfers from a molecule to a substrate, and potential energy increases during the process. The initial energy increase coincides with that of the isolated, separated, and positively charged H₂ molecule calculated by the real-space density functional method. The barrier formation is due to the destabilization of the molecule induced by the electron transfer. The electronegativity difference between the adsorbate and the substrate determines the direction of the electron transfer.

KEYWORDS: electronegativity difference, dissociation, direction of electron transfer, adsorption, hydrogen molecule, surface, electron transfer, energy barrier

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1. Introduction

Understanding and controlling the reactivity of adsorbed molecules are one of the central issues in the field of surface science. The term "reactivity" refers to surfaces' ability to break bonds of molecule approaching surfaces and to adsorb fragments that are forming a new bond with atoms on the surfaces. Bond breaking is a rate-limiting step in catalytic reactions. If there is no barrier during the adsorption, then a molecule has high reactivity when fragments have large chemisorption energies; if there is a barrier, then a molecule has low reactivity.

Among the adsorptions of molecules on metal surfaces, the adsorption of H\textsubscript{2} molecules on metals is a typical example of catalytic reactions, since they have been used in fuel cells. The adsorption barriers have been confirmed theoretically to exist for the H\textsubscript{2} adsorption on simple metal surfaces such as Al\textsuperscript{1,2} and Mg\textsuperscript{1,3,4} and on the noble metals such as Cu,\textsuperscript{2,5–10} Ag,\textsuperscript{11} and Au\textsuperscript{7,8,12} surfaces with filled d-orbitals. No barrier has been confirmed on the Ni,\textsuperscript{4,5,7,8,10,13} Pd,\textsuperscript{4,14,15} Pt,\textsuperscript{2,7,8,16} and W\textsuperscript{17,18} surfaces that have unfilled d-bands.

The origin of the formation of these barriers has been first given by Nørskov’s group.\textsuperscript{1,3,19} They explained the barriers to be due to kinetic energy repulsion, that had proposed by Zaremba and Kohn,\textsuperscript{20} to explain the interaction between closed shell adsorbates, such as isoelectronic He atoms, and metal surfaces. Harris and Anderson,\textsuperscript{5} who have first used Pauli repulsion for the barrier formation, showed that a barrier appears in a Cu\textsubscript{2}H\textsubscript{2} cluster and no barrier appears in a Ni\textsubscript{2}H\textsubscript{2} cluster. They explained that since the atoms with d-holes such as the Ni atom accept an s-electron from the H atom, no barrier appears by canceling the Pauli repulsion. A copper atom has the filled d-orbitals, so the Pauli repulsion produces the barrier. Feibelman et al.\textsuperscript{21} and Hammer et al.\textsuperscript{2,7} have also shown the barriers of the H\textsubscript{2} molecule on the Al and Mg metal surfaces and on the Cu, Ag, and Au metal surfaces to be attributed to the Pauli repulsion and no barrier for the Ni, Pd, and Pt surfaces to the cancellation. Hammer et al. have also explained the barriers for the Al and Mg metal surfaces to be due to the "weak chemisorption" case reported by Newns and Anderson.\textsuperscript{22,23}

In 1995, Nørskov et al. have given an explanation for the barrier formation using projected density of states.\textsuperscript{2,7} On the one hand, when both the bonding and the anti-bonding states are situated below the Fermi level, then the barrier appears owing to the Pauli repulsion. This is the case for the Cu and Au metal surfaces. On the other hand, when the Fermi level is located between the anti-bonding and the bonding states, the hybridization is attractive, counteracting the Pauli repulsion and deleting the energy barrier. These are the cases for the Ni and Pt surfaces that have d-band holes.\textsuperscript{7}

Since the extensive discussion of the explanations for the barrier formation from 1981 to 1995, all first-principles studies have explained the barrier formation using both the Pauli repulsion and the d-band hole.\textsuperscript{1–3,7,19–21}

There have been only two studies on the difference electron density of the dissociated
H₂ molecules on the metal surfaces.²⁴,²⁵ Bird et al. have shown an increase of the electron density of the dissociated H₂ molecule on Mg(0001) surface through the difference electron density map.²⁴ Huda and Ray have shown electron transfer from the Pu(111) surface to the H₂ molecule.²⁵

The aim of the present study is to investigate how the electron population varies during the process and to elucidate the relation between the electron transfer and the barrier formation. There has been no earlier study, to the authors's best knowledge, that has investigated such a relation.

We evaluate electron density using the first-principles calculations for the dissociation of the H₂ molecule on a Au(111) surface. There have been earlier studies of the dissociative adsorption of the H₂ molecule on the periodic Au surfaces.⁷,²⁶ This system has been found to have a large dissociation barrier.⁷

2. Computational Details

We perform first-principles density functional calculations using the generalized gradient approximation of Perdew, Burke and Ernzerhof (GGA-PBE).²⁷ The interactions between the ion cores and electrons are described using the ultrasoft pseudopotential²⁸ for Au atoms and the norm-conserving pseudopotential²⁹ for H atoms. We use the valence 5d¹⁰6s¹6p⁶ configuration with partial core correction for Au pseudoatoms and the valence 1s¹2p³d⁰ configuration for H atoms. A partial core correction is necessary for partitioning the space with the minimum electron densities around each atom (see below). The cutoff radius of the partial core for Au atoms is 0.582 Å. Brillouin-zone integration is performed using a Monkhorst-Pack grid³⁰ of 4×3×1 k-points. We use a planewave-based pseudopotential formalism with a periodic boundary condition to calculate the electronic structures of the dissociation of the H₂ molecule.

We use a slab structure to model the surface of the Au bulk system. The surface consists of a √3 × 2 structure with four Au atoms and the slab contains four Au layers. Figure 1(a) shows the geometry of the H₂/Au(111) system that we investigated and the numbers of Au atoms on the first layer. The integrated electron charge variation, as we will show later, within the second layer has been negligible during the dissociative adsorption. Thus this number of layers is sufficient for the present purpose of calculation. The slab structure is sandwiched by two vacuum layers whose thickness is 6.59 Å, which corresponds to the vacuum region with 13.18 Å. We select the origin of the reaction path at Z=4 Å above the first layer, at which the binding energy between the H₂ molecule and the Au surface has been only 0.0247 eV which is sufficiently low compared with the maximum barrier height of 1.55 eV, as will be shown in Fig. 3; the present size of the vacuum region is sufficient for the present analyses. The slab structure has been relaxed; the distance between the first and second layers is 2.615 Å, and the distance between the second and the third layers is 2.603 Å.
We determine the cutoff energy of the planewave expansion of the wavefunction for the Fourier expansions of both the pseudowavefunctions and the pseudopotentials to converge. The cutoff energy for the electron density is chosen to be nine times the value of the wavefunction to incorporate the partial core charge. The number of basis functions decreases with increasing cell size at a fixed energy cutoff, which increases total energy with increasing cell size leading to an incorrect equation of states. Thus we calculated the equation of states for a fixed number of bases. The cutoff energy is chosen to be 27.79 Ry at 3.98 Å of cell size. The maximum barrier height has increased only by 0.039 eV at an increased cutoff energy of 40 Ry. Thus, the selected cutoff energy is sufficient for the present analyses. The H$_2$ molecule is located above the top site of the Au$_0$ atom with its molecular axis kept parallel to the surface and is oriented towards the bridge sites, as shown in Fig. 1(b). To calculate the potential energy surface of the dissociated H$_2$ molecule on the slab structure, we constrain the atom positions of the whole system.

To evaluate the electron transfer between the H atoms and the surface atoms, we use Bader analysis,$^{31}$ in which the space is partitioned along minimum-charge-density surfaces, which is called zero-flux planes around the atoms. By integrating the charges inside each region, we evaluate the electrons that belong to each atom and then evaluate the electron transfer through the difference from those of reference systems. We have confirmed the existence of the zero-flux planes in the present investigation except for the plane between the H atoms in an undissociated equilibrium H$_2$ molecule, since they form covalent bonding. Thus, we integrate the electron densities around the two H atoms to show the electron transfer from the molecule to the surface. We compare the stabilities of the dissociatively adsorbed and charged H$_2$ molecule in the whole system with those of the isolated, separated, and charged H$_2$ molecules in real-space. We calculate the energies of the molecule using a real-space density functional method with the same electron-correlation functionals as the periodic system.

We use the PHASE code$^{32}$ for the planewave calculations and the Amsterdam Density Functional (ADF) code$^{33}$ for the real-space calculations using Slater-type orbitals with triple-zeta basis sets and doubly polarized basis functions, which are the same conditions as those used in our previous investigation for the hydrated silicon cluster.$^{34}$

3. Results

Figure 2 shows the potential energy surface for the dissociatively adsorbed H$_2$ molecule. The energies are shown as a function of the bond length $d$ and the height $Z$ of the molecule above the surface. A reaction path is defined in the potential energy surface. The barrier top is located at a height of 1.5 Å above the top layer of the slab with a H-H distance of 1.5 Å. The top shown with an open triangle mark appears after the molecule has dissociated, since the equilibrium H$_2$ distance is 0.74 Å. The open square mark in the figure will be discussed in Figs. 5-7.
In order to show the potential energy variation $\Delta E$ along the path $s$, we use the equation

$$\Delta E = E[H_2, \text{Au}(111)] - E[H_2] - E[\text{Au}(111)],$$  \hspace{1cm} (1)$$

where the first term is the formation energy of the whole system and the other terms are the energies of the $H_2$ molecule and the $\text{Au}(111)$ slab structure in the supercell with the same sizes as the first term. The first term is expressed by

$$E[H_2, \text{Au}(111)] = E_T[H_2, \text{Au}(111)] - 2\mu_{H} - 16\mu_{\text{Au}},$$  \hspace{1cm} (2)$$

where the first term is the total energy of the whole system and the other ones are the chemical potentials of the H and Au atoms. Inserting the same type equations for the other terms into the eq. (1), we obtain the following equation for the potential energy variation;

$$\Delta E = E_T[H_2, \text{Au}(111)] - E_T[H_2] - E_T[\text{Au}(111)],$$  \hspace{1cm} (3)$$

This corresponds to the energy zero to be selected for the $H_2$ molecule to be located at an infinitely separated position above the surface. The energy $\Delta E$ along the path $s$ is shown in Fig. 3. The origin of the path $s$ is chosen at $Z=4.0$ Å above the surface. The barrier height is 1.55 eV per single $H_2$ molecule, which is comparable with the earlier calculated value of $\sim$1.2 eV per single $H_2$ molecule given by Hammer and Nørskov\textsuperscript{7} calculated using an earlier version\textsuperscript{35} of the GGA-PBE\textsuperscript{27} functionals that we used. Barrier heights have been recognized to be sensitive to electron-correlation functionals.\textsuperscript{6,36,37}

To investigate the origin of the barrier, we first evaluate the electron transfer from the two H atoms in the dissociated $H_2$ molecule using the Bader analysis.\textsuperscript{31} In order to show the electron population variation, we define the equation

$$\Delta x_{2H} = x_{2H}[H_2, \text{Au}(111)] - x_{2H}[H_2],$$  \hspace{1cm} (4)$$

where the first term is the electron population of the two H atoms in the whole system and the second term is that in the supercell with the same size as the first term. Figure 4 shows the electron population variation $\Delta x_{2H}$ along the reaction path $s$ together with the potential energy variation $\Delta E$ shown in Fig. 3. The electron variation of the two H atoms decreases with increasing energy barrier indicating the electron transfer to the Au substrate. The path $s$ at the minimum of the population of the dissociate $H_2$ coincides with $s$ at the maximum energy $\Delta E$. The maximum electron transfer from the $H_2$ molecule to the surface has been 0.129e per molecule. Thus the maximum barrier height of the energy corresponds to the most depleted electron state of the dissociation of the $H_2$ molecule, indicating that a correlation exists between the barrier formation and the electron transfer.

Figure 5 shows the variation in $\Delta E$ as a function of the difference electron population $\Delta x_{2H}$, in which we used the quantities shown in Fig. 4. The energy increases linearly with decreasing electron variation in the dissociated $H_2$ molecule, deviates from the increase at -0.087e shown by an open square mark, and increases to the barrier maximum shown by an
open triangle. The slope is -9.37 eV/e. The electron transfer from the molecule to the Au surface is proportional to the energy increase of the system in the region.

However, a question arises: how can this barrier $\Delta E$ be explained. We have just found that the dissociated H$_2$ molecule transfers the electron to the Au substrate. Here, we examine how the barrier is related to the energy of isolated, separated, and charged H$_2$ molecules. To estimate the energy, we evaluate the binding energy of the molecules by the real-space density functional method. By fixing both the charge states of the dissociated H$_2$ molecules given in Fig. 4 and their bond lengths $d$ given in Fig. 2, we calculate the energies of the molecules in real-space. Figure 6 shows the calculated binding energy $E_b$ of the molecules as a function of the path $s$, together with the energy $\Delta E$ of the whole H$_2$/Au(111) system. The energy $E_b$ increases with the path $s$ and coincides with the energy $\Delta E$ curve almost up to the open square mark, shown in Figs. 2 and 5. This implies that the increase in the energy $\Delta E$ of the whole system correlates to the destabilization of the dissociated molecule. The energy of the interaction between the dissociated H$_2$ molecule and the Au surface is negligible in this region.

Figure 7 shows the difference electron population $\Delta x_{\text{Aug}}$ of each Au$^\#$ atom on the first layer of the slab. Here we define the difference electron population $\Delta x_{\text{Aug}}$ using the equation

$$\Delta x_{\text{Aug}} = x_{\text{Aug}}[\text{H}_2, \text{Au}(111)] - x_{\text{Aug}}[\text{Au}(111)],$$

(5)

where $\#$ is the positions of each Au atoms in the slab. We also show in this figure the variation of the electron population $\Delta x_{2\text{H}}$ in Fig. 4 and the energy variation $\Delta E$ in Fig. 3 for comparison. On the one hand, the electron of the top Au0 atom in the slab decreases with increasing path $s$. The electron variation increases after the minimum -0.053e. On the other hand, the electron variations of the other coordinated Au1, Au2, and Au3 atoms on the first layer increase with the path $s$ and decrease after their maxima. The variations of the Au2 and Au3 atoms are the same, since they are symmetrical with respect to the two H atoms, as is shown in Fig. 1(a).

The path $s$ at the maxima of the populations for the Au1, Au2, and Au3 atoms coincides with that at the minimum population for the Au0 atom. At this turning point, the deficit population of the top Au0 atom is 0.053e. The deficit electron population of the dissociated H$_2$ molecule at the point $s$ amounts to 0.087e. The coordinate position that corresponds to the point is $(d, Z)=(1.0\,\text{Å},1.7\,\text{Å})$, which is shown in Figs. 2, 5, and 6 as the open square marks. The point is far below the energy barrier maximum. The decrease in the electron variation in the top site Au0 atom is caused by the Coulomb repulsion between the electrons around the dissociated H$_2$ molecule and those around the top Au0 atom. The coordinated Au1, Au2, and Au3 atoms accept the repelled electrons from the top Au0 atom. Thus, the electron transfers from the molecule to the top Au0 atom and from the top Au0 atom to other Au atoms in the first layer. The path $s$ at the maximum variation for Au0 coincides with the minimum variation for the 2H corresponding to the energy barrier maximum of $\Delta E$ in Fig. 4. The difference electron population of the second layer Au atoms are negligible compared
with those of the first layer.

4. Discussion

We have used both the real-space DFT method and the periodic DFT method to identify the origin of the barrier height. The real-space method uses a lower number of basis functions comparing with the number of basis functions in the periodic methods. The real-space methods have a lower accuracy in the electronic structure calculation than the periodic methods. The magnitude of the barrier, however, has been large enough and amount to 1.55 eV. So the incompleteness of the wavefunctions in the real-space method would be negligible in the present study.

We have evaluated the potential energy barrier during the dissociative adsorption of the H$_2$ molecule to the Au(111) surface. The electron in the dissociated H$_2$ molecule has transferred from the H$_2$ molecule to the surface during the energy barrier formation. The energy curve along the reaction path has coincided with that of the charged, separated, and isolated H$_2$ molecule that has been calculated by the real-space method. They have coincided up to the turning point as shown in Fig. 6. So the energy barrier is formed by the destabilization of the dissociated molecule in the region. The reaction path $s$ at the minimum of the difference electron population in the dissociated H$_2$ molecule has coincided with that $s$ at the maximum potential energy $\Delta E$. The energy increase has been proportional to the electron transfer from the dissociated H$_2$ molecule to the Au surface up to the turning point. The barrier formation is due to the destabilization of the dissociated molecule.

The present results have shown that the electron in the molecule transfers to the Au(111) surface, although the Au surface has the filled $d$-band. Even the Au surface with the filled $d$-band has received the electron from the dissociated H$_2$ molecule.

There may exist two other contribution to the potential energy variation for the dissociation of H$_2$ molecule on the Au substrate; they are the energy contribution from the interaction between the molecule and the substrate and the one from the electron increase in the substrate. At present it is unclear whether they are cancelled each other or they are negligible in the magnitudes.

Here we discuss the origin of the transfer that has caused the barrier formation. There were a few earlier studies on the electron transfer during the dissociative adsorption of the molecules on the metal surfaces, although these studies gave no relation between the transfer and the energy barrier formation. Bird et al. showed the increase in electron variation in the dissociated H$_2$ molecule on the Mg(0001) surface,$^{24}$ showing that the electron transferred from the Mg surface to the H$_2$ molecule. Huda et al. indicated that the electron transferred from the Pu(111) surface to the dissociated H$_2$ molecule.$^{25}$ In the present case, in contrast, the electron has transferred from the H$_2$ molecule to the Au surface. This is in the reverse direction of the transfers in the earlier two cases. However these directions can be explained consistently
by the electronegativity differences between the H atoms and the metal substrates. Since the electronegativity is larger for H than for Mg, the electron transferred from the Mg surface to the H atoms. The electronegativity is larger for H than for Pu, so the electron transferred from the Pu surface to the H atoms. The electronegativity is larger for the Au than for the H, so the electron transferred from the H atoms to the Au surface. Thus the electronegativity difference between the H atom and the metal substrates determines the direction of the transfer.

Figure 2 has shown the maximum barrier in the $\Delta E$ to appear at $(d,Z) = (1.5\text{Å},1.5\text{Å})$. The distance $d$ is fairly larger than the equilibrium distance 0.74 Å of the H$_2$ molecule, which we call dissociative adsorption. This indicates that when the H$_2$ molecule approaches the Au surface, the difference in electronegativity induces electron transfer. Then the H$_2$ molecule has dissociated owing to an electron deficit that raises the energy of the positively charged H$_2$ molecule. When the H$_2$ molecule conserves the equilibrium distance, the energy variation is higher than that of the reaction path $s$, as shown in Fig. 2.

For H$_2$ molecule adsorption on Pt surfaces, there has been no barrier or low barriers in the potential energy surfaces. The H atoms have been adsorbed with almost the same interhydrogen distance as that in the equilibrium H$_2$ molecule, i.e., without dissociating the molecule, which we call nondissociative adsorption. This is because these elements have the same electronegativity. This is another evidence of the origin of the barrier formation found in the present investigation.

The energy increase of the whole system has coincided with that of the separated, charged, and isolated H$_2$ molecule up to the turning point, as shown in Fig. 4. The extent of the coincidences will depend on the adsorption sites on the Au substrates, since the distance between the H$_2$ molecule and the substrate depends on adsorption sites.

We have investigated the electron transfer from the H$_2$ molecule, whose axis is kept parallel to the surface, to the Au substrate. We predict the extent of the transfer from a vertically oriented H$_2$ molecule to the substrate. Since the electron has transferred from the H$_2$ molecule to the Au substrate, we expect that the lower H atom transfers more electrons than the upper H atom to the substrate. An unsymmetrical electron transfer will cause a higher energy barrier than the symmetrical case when we have calculated.

The electron transfer found in the present investigation may be related to Pauli repulsion. The investigation of the relation is beyond the scope of the present study.

5. Conclusions

We have investigated the electron transfer from the dissociatively adsorbed H$_2$ molecule to the Au(111) surface by evaluating the electron that belongs to atoms in crystals and molecules. We have found that electrons transfer from the molecule to the surface. The difference of the electronegativities determines the direction of the electron transfer not only in the H$_2$/Mg(0001) and H$_2$/Pu(111) systems, but also in the present H$_2$/Au(111) system.
The calculated dissociation energy curve along the reaction path has coincided with that of the isolated, separated, and positively charged H$_2$ molecule that has been calculated by the real-space density functional method. The energy increase has been proportional to the charge deficit of the H$_2$ molecule up to the turning point. The barrier formation in the present system is due to the destabilization of the dissociated molecule induced by the transfer.

Acknowledgments

The authors thank Professor Masahiro Yamamoto of Kyoto University for discussions. The numerical calculations were partly carried out using SCore cluster system in Meiji University and Altix3700 BX2 at YITP in Kyoto University.
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Fig. 1. Schematic drawing of the surface structure and the adsorption sites of hydrogen molecule $H_2$ on the Au(111) surface. (a) The periodic supercell consists of four Au layers each containing four atoms with a $\sqrt{3} \times 2$ structure sandwiched by two vacuum layers. The dashed line corresponds to the unit cell. The closed small circles indicate the H atoms, and the open circles the Au atoms. The numbers 0 to 3 correspond to Au0, Au1, Au2, and Au3 atoms, respectively. (b) Side view intersected at the dotted plane in the left figure. The distance $d$ is the separation between the two H atoms and the distance $Z$ is the height of the molecule.

Fig. 2. Contour plot for the potential energy surface for the dissociation of the hydrogen molecule $H_2$ on the Au(111) surface as a function of the H-H bond length $d$ and the height $Z$ of the molecule above the surface. The contour spacing is 0.1 eV. The top of the potential energy barrier appears at $(d, Z) = (1.5\text Å, 1.5\text Å)$, shown as an open triangle mark. The open square mark shown at $(d, Z) = (1.0\text Å, 1.7\text Å)$ is referred in the text. The equilibrium adsorption site of H atoms is located at $(d, Z) = (2.8\text Å, 1.1\text Å)$.

Fig. 3. Potential energy variation $\Delta E$ along the reaction path $s$ of the hydrogen molecule $H_2$ on the Au(111). The origin of the $s$ is chosen to be $Z = 4.0\text Å$ above the center of the first layer of the Au surface. The lines are for visual guidance.

Fig. 4. Difference electron population $\Delta x_{2H}$ along the reaction path $s$ in $H_2$/Au(111) system together with the potential energy variation $\Delta E$ shown in Fig. 3. The maximum population $\Delta x_{2H}$ is $-0.129e$ and the maximum barrier is 1.55 eV. The lines are for visual guidance.

Fig. 5. Potential energy variation $\Delta E$ as a function of the difference electron population $\Delta x_{2H}$. The open square mark at the beginning of the deviation corresponds to the square mark shown in Fig. 2. The open triangle mark corresponds to the maximum barrier height of the potential energy.

Fig. 6. The variation in the binding energy $E_b$ of the isolated, separated, and charged $H_2$ molecule as a function of the reaction path $s$, together with the potential energy variation $\Delta E$ shown in Fig. 3 for comparison. The binding energies (solid line) are calculated with the same bonding distances and charged states as those of the $H_2$ molecule in the whole $H_2$/Au(111) system shown in Fig. 4. Both the energies are plotted with the same scales. The open square mark corresponds to the same mark shown in Fig. 5, and the open triangle to the barrier top. The lines are for visual guidance.

Fig. 7. Difference electron population $\Delta x_{Au}$ (solid lines) of each Au atom on the first layer of the slab structure along the reaction path $s$. The positions of the Au0 to Au3 atoms have shown in Fig. 1. The energy variation $\Delta E$ (dashed line) and difference electron population of the two H atoms are also shown for comparison. The vertical dashed line (left) corresponds to the reaction path $s$ that corresponds to the open square marks shown in Figs. 2, 5, and 6. The chained line (right) corresponds to the maximum barrier height of the potential barrier.
in the earlier figures. The lines are for visual guidance.
Fig. 1. Schematic drawing of the surface structure and the adsorption sites of hydrogen molecule H$_2$ on the Au(111) surface. (a) The periodic supercell consists of four Au layers each containing four atoms with a $\sqrt{3} \times 2$ structure sandwiched by two vacuum layers. The dashed line corresponds to the unit cell. The closed small circles indicate the H atoms, and the open circles the Au atoms. The numbers 0 to 3 correspond to Au0, Au1, Au2, and Au3 atoms, respectively. (b) Side view intersected at the dotted plane in the left figure. The distance $d$ is the separation between the two H atoms and the distance $Z$ is the height of the molecule.
Fig. 2. Contour plot for the potential energy surface for the dissociation of the hydrogen molecule H$_2$ on the Au(111) surface as a function of the H-H bond length $d$ and the height $Z$ of the molecule above the surface. The contour spacing is 0.1 eV. The top of the potential energy barrier appears at $(d,Z)=$ (1.5Å, 1.5Å), shown as an open triangle mark. The open square mark shown at $(d,Z)=$ (1.0Å, 1.7Å) is referred in the text. The equilibrium adsorption site of H atoms is located at $(d,Z)=$ (2.8Å, 1.1Å).
Fig. 3. Potential energy variation $\Delta E$ along the reaction path $s$ of the hydrogen molecule $H_2$ on the Au(111). The origin of the $s$ is chosen to be $Z=4.0$ Å above the center of the first layer of the Au surface. The lines are for visual guidance.
Fig. 4. Difference electron population $\Delta x_{2H}$ along the reaction path $s$ in $\text{H}_2/\text{Au}(111)$ system together with the potential energy variation $\Delta E$ shown in Fig. 3. The maximum population $\Delta x_{2H}$ is $-0.129e$ and the maximum barrier is 1.55 eV. The lines are for visual guidance.
Fig. 5. Potential energy variation $\Delta E$ as a function of the difference electron population $\Delta x_{2H}$. The open square mark at the beginning of the deviation corresponds to the square mark shown in Fig. 2. The open triangle mark corresponds to the maximum barrier height of the potential energy.
Fig. 6. The variation in the binding energy $E_b$ of the isolated, separated, and charged H$_2$ molecule as a function of the reaction path $s$, together with the potential energy variation $\Delta E$ shown in Fig. 3 for comparison. The binding energies (solid line) are calculated with the same bonding distances and charged states as those of the H$_2$ molecule in the whole H$_2$/Au(111) system shown in Fig. 4. Both the energies are plotted with the same scales. The open square mark corresponds to the same mark shown in Fig. 5, and the open triangle to the barrier top. The lines are for visual guidance.
Fig. 7. Difference electron population $\Delta x_{\text{Au}}$ (solid lines) of each Au atom on the first layer of the slab structure along the reaction path $s$. The positions of the Au0 to Au3 atoms have shown in Fig. 1. The energy variation $\Delta E$ (dashed line) and differential electron population of the two H atoms are also shown for comparison. The vertical dashed line (left) corresponds to the reaction path $s$ that corresponds to the open square marks shown in Figs. 2, 5, and 6. The chained line (right) corresponds to the maximum barrier height of the potential barrier in the earlier figures. The lines are for visual guidance.