Theoretical Study of Hydrogen Adsorption on Ruthenium Clusters

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Abstract The geometries, stabilities, electronic, and magnetic properties of hydrogen adsorption on Ruₙ clusters have been systematically investigated by using density functional theory with generalized gradient approximation. The result indicates the absorbed species does not lead to a rearrangement of the basic cluster. For n > 2, three different adsorption patterns are found for the RuₙH₂ complexes: One H atom binds to the Ru top site, and another H binds to the bridge site for n = 3, 5, 6, 8; bridge site adsorption for n = 4; hollow site and top site adsorption for n = 7. The adsorption energies display oscillation and reach the peak at n = 2, 4, 7, implying their high chemical reactivity. The small electron transferred number between H atoms and Ruₙ clusters indicates that the interaction between H atoms and Ruₙ clusters is small. When H₂ is absorbed on the Ruₙ clusters, the chemical activity of corresponding clusters is dramatically increased. The absorbed H₂ can lead to an oscillatory behavior of the magnetic moments, and this behavior is rooted in the electronic structure of the preceding cluster and the changes in the magnetic moment are indicative of the relative ordering of the majority and minority LUMO’s. The second order difference indicates 5 is magic number in RuₙH₂ and Ruₙ clusters.

Keywords RuₙH₂ cluster · Electronic properties · Equilibrium geometries
Introduction

In the past 20 years, small metal clusters have been used to model the adsorption of different molecules with the purpose to obtain a good description of the activity of many metal catalysts. Due to the small particles size of a well dispersed catalysts, most or almost all of its atom are surface atoms, so they exhibit structural and reaction properties different from those of the bulk, they are appropriate to surface reactions as the most process in catalysis are. Many previous researches showed that the catalytic properties of clusters are structure dependent, leading to different adsorption energies and sites for different structures of clusters [1–6]. Hydrogen is employed in many modern technologies [7–21], so surface reactions of hydrogen molecules in transition metals have been carried out over the adsorption and desorption of hydrogen and deuterium molecules on well-defined single crystal metals. Axel Pramann et al. [22] studied hydrogen chemisorption rates and electronic structures of small NbₙAl⁻ clusters by photoelectron spectroscopic method. Poulain et al. [23] studied the C₂v and C₃v reaction of H₂ with a Pt₄ cluster. Hege Strømsnæs et al. [24] studied the chemisorption of molecular hydrogen on a seven atom gold cluster using explicitly correlated wave functions. On the other hand, an area that has attracted recent attention is the effect of chemisorption on the magnetic properties of clusters. For example, Whetten et al. [25] studied the reactivity of Feₙ clusters toward H₂ and D₂, and found the Fermi energy and the band filling could be modulated by adding hydrogen suggests that one could expect interesting effects on magnetic properties. Indeed, Knickelbein et al. [26] recently investigated the effect of hydrogen on the magnetic moment of Feₙ clusters in molecular beam experiments and found intriguing results. Knickelbein et al. generated Feₙ clusters containing 10–25 atoms in molecular beams and the clusters were saturated with hydrogen. The hydrogenated clusters were subsequently passed through the Stern Gerlach gradient fields. They found that unlike the case of larger nanoparticles and thin films where the hydrogen adsorption quenches the magnetic moment [27], the magnetic moments of the saturated hydrogenated clusters containing 12–25 atoms were higher than those of the free clusters.

Ruthenium is the main element used for hydrogenation and dehydrogenation catalytic reactions. Liu et al. [28] studied adsorption characteristics of atomic nitrogen on ruthenium surfaces, they found that atomic nitrogen always preferably occupies the high coordination sites on Ru surfaces. Carmelo Crisafulli et al. [29] have studied Ni-Ru bimetallic catalysts for the CO₂ reforming of methane. Romain Berthoud et al. [30] have studied hydrogen and oxygen adsorption stoichiometries on silica supported ruthenium nanoparticles. Zheng et al. [31] have investigated NH₃ decomposition kinetics on supported Ru clusters. Tu et al. [32] have studied the interaction of oxygen with ruthenium clusters by density functional study. Suss-Fink et al. [33] investigated the cluster dication [H₆Ru₄(C₆H₆)₄]²⁺ using the a low-temperature ¹H-NMR and density functional theory (DFT) calculations, and found the cluster dication [H₆Ru₄(C₆H₆)₄]²⁺(1) tends to lose molecular hydrogen to form the cluster dication [H₄Ru₄(C₆H₆)₄]²⁺(2). The equilibrium between 1 and 2 can be used for catalytic hydrogenation reactions. Adams et al. investigated the Activation of hydrogen by mixed transitional metal cluster complex [34–37]. Poteau et al. [38]
studied spectroscopic and thermodynamic properties of surfacic hydrides on Ru (0001) model surface: the influence of the coordination modes and the coverage by density functional theory and this study partially opens the route to DFT studies of multistep hydrogenation reactions at the surface of ruthenium nanoparticles monitored by spectroscopic techniques. Torsten Gutmann et al. [39] studied hydrido-ruthenium cluster complexes as models for reactive surface hydrogen species of ruthenium nanoparticles by solid-state $^2$H NMR and quantum chemical calculations and found that the $^2$H nuclear quadrupolar interaction is a sensitive tool for distinguishing the binding state of the deuterons to the transition metal.

To our knowledge, the study on the adsorption properties of small molecule on ruthenium clusters is still lacking either experimentally or theoretically so far. It would be interesting to know the adsorption ability of ruthenium clusters to small molecules such as the H$_2$ molecule. More precisely, where are the optimal adsorption sites of ruthenium clusters to H$_2$ molecule? Moreover, how does the adsorption of H$_2$ molecule affect the magnetism of the clusters? To answer these questions, we have performed density functional theory (DFT) computations to explore the adsorption behavior of H$_2$ molecule on Ru$_n$ clusters. The purposes of this paper include the following: (a) Locate the optimal adsorption sites and (b) analyze the size-dependent structural, electronic, and magnetic properties of the Ru$_n$H$_2$ complexes, and compare with the bare ruthenium clusters.

### Computational Methods

Full geometry optimizations were performed using the spin-polarized density functional theory (DFT) implemented in a DMOL package [40]. In the electronic structure calculations, all electron treatment and double numerical basis including d-polarization function (DNP) [40] were chosen. The exchange–correlation interaction was treated within the generalized gradient approximation (GGA) using PBE functional. Self-consistent field calculations were done with a convergence criterion of $10^{-5}$ Hartree on the total energy. The density mixing criterion for charge and spin were 0.2 and 0.5, respectively. The Direct Inversion in an Iterative Subspace (DIIS) approach was used to speed up SCF convergence. A 0.001 Hartree of smearing was applied to the orbital occupation. In the geometry optimization, the converged thresholds were set to 0.004 Hartree/A˚ for the forces, 0.005Å for the displacement and $10^{-5}$ Hartree for the energy change. Harmonic vibrational frequencies were calculated for the promising stationary points from a direct structural optimization; if an imaginary vibrational mode was found, a relaxation along coordinates of imaginary vibrational mode was carried out until the true local minimum was actually obtained. Therefore, all isomers for each cluster are guaranteed as the local minima. The on-site charges and magnetic moment were evaluated via Mulliken population analysis [41].

To test the accuracy of the theoretical method, we have calculated the dimers for Ru$_2$ and H$_2$ by using different functionals. For Ru$_2$, the bond length $r = 2.26$ Å, $\omega = 364.46$ cm$^{-1}$; the calculated results using PBE functional are in agreement with the previous theory values obtained by all-electron calculation ($r = 2.41$Å,
\[
\omega = 380 \text{ cm}^{-1}) \quad [42] \text{ and experimental value by Resonance Raman matrix isolation } \\
\text{studies of mass-selected (347.1(9) cm}^{-1}) \quad [43]. \text{ For H}_2, \text{ the bond length } r = 0.748 \text{Å,} \\
\text{binding energy } E_b = 4.665 \text{ eV, } \omega = 4410.896 \text{ cm}^{-1}. \text{ The calculated results using } \\
PBE \text{ functional are in good agreement with experiment values } (r = 0.741\text{Å,} \\
E_b = 4.519 \text{ eV } \omega = 4401.21 \text{ cm}^{-1}) \quad [44]. \text{ It indicates that the employed PBE } \\
scheme is reliable for the dimer Ru}_2 \text{ and H}_2. \text{ Consequently, the PBE functional are } \\
\text{reliable and accurate enough to be applied to describe the properties of the Ru}_n\text{H}_2 \text{ in } \\
\text{this paper.}
\]

**Results and Discussions**

**Equilibrium Structures**

The low-lying isomers of Ru\(_n\)H\(_2\) complexes and their naked counterparts Ru\(_n\) are 

displayed in Figs. 1 and 2. The structure and the bond length of the lowest energy 

structures for Ru\(_n\) and Ru\(_n\)H\(_2\) are given in Table 1. Here we only present the longest 

and the shortest interatomic distances between two Ru atoms, two H atoms and 

Ru–H in Ru\(_n\)H\(_2\) and in the corresponding bare Ru\(_n\). The geometries of Ru\(_n\)H\(_2\) and 

Ru\(_n\) clusters with considered spin configuration are performed by DFT. The lowest 

energy geometry of Ru\(_2\) is a linear structure. For Ru\(_3\), the result is different from 

those of empirical methods by Tu et al. [45] who have all concluded that the 

structure of Ru\(_3\) is an equilateral triangle. The lowest energy structure we obtained 

is a triangle (C\(_s\)) whose binding energy is 0.819 eV lower than that of equilateral 

structure. The lowest energy geometry of Ru\(_4\) is a quadrangle structure with D\(_{4h}\) 

symmetry. The distorted tetrahedron is 0.348 eV higher than that of the lowest 

energy geometry. For Ru\(_5\), the lowest energy structure is a square pyramid. The 

trigonal bi-pyramid is an isomer with 0.853 eV higher than the square pyramid. A 

trigonal prism is the lowest energy structure of Ru\(_6\) cluster. The square bipyramid is 

0.358 eV higher than that of trigonal prism. The lowest energy structure of Ru\(_7\) is a 

twin square pyramid. The trigonal prism structure face capped a Ru atom is a 

matastable isomer, it’s energy is 0.0269 eV higher than that of the twin square 

pyramid. A square prism is the lowest energy structure of Ru\(_8\) cluster. Most of 

lowest energy structures we obtained are similar to the result obtained by Tu et al. 

[45].

For RuH\(_2\), the ground state corresponds to a H–H distance of 2.428 Å. The H 

molecular is therefore activated. For Ru\(_2\), the additional hydrogen molecular 

occupies the on-top site. The Ru–Ru bond length (R\(_{\text{Ru–Ru}}\)) is 2.322 Å, 4.31% greater 

than that in the bare Ru\(_2\) dimer. The two Ru–H bond lengths are 1.573 and 1.574 Å, 

respectively. Two Ru–Ru–H angles are both around 90 degree. The H–H bond 

length (R\(_{\text{H–H}}\)) is 2.173 Å, again indicates that the H\(_2\) is activated compared with free 

H\(_2\) molecular.

For \(n > 2\), three different adsorption patterns are found for the Ru\(_n\)H\(_3\) complexes: 

one H is absorbed on the Ru top site, and another H is absorbed on the bridge site 

which H atom sits over the Ru–Ru bond for \(n = 3, 5, 6, 8\); bridge site adsorption for 

\(n = 4\); hollow site and top site adsorption for \(n = 7\). The longest R\(_{\text{Ru–Ru}}\) bond
Fig. 1 Ground state and some metastable geometries of Ru$_n$ clusters. $\Delta E$(eV) is the excess energy of an isomer as compared to the energy of the most stable one. The multiplicity is given in parentheses.
Fig. 2 Ground state and some metastable geometries of RuₙH₂ clusters. The dark circles are the Ru atoms while the white circles are the H atoms. ΔE(eV) is the excess energy of an isomer as compared to the energy of the most stable one. The multiplicity is given in parentheses. The symmetry groups of RuₙH₂ clusters are C₁ except that of the most stable RuₙH₂ (n = 1, 4) (C₃v, Cᵥ).
lengths range from 2.493 to 2.598 Å and the shortest from 2.326 to 2.399 Å, the longest RRu–H bond lengths vary from 1.743 to 1.849 Å and the shortest from 1.154 to 1.722 Å, and the bond lengths of H–H are in the range of 2.320 to 3.419 Å, which indicates the H₂ is activated.

For Ru₂H₂, the ground state is quintet state with H–H bond length of 2.173 Å. When one H atom is drawn to one Ru atom and the other H atom to the other Ru atom, the optimized structure (Fig. 2b) is 0.18 eV higher than the ground state. In this structure, both of Ru–Ru–H angles are about 90°.
The most stable structure of Ru$_3$H$_2$ is a triplet state with C$_1$ symmetry. The structure with a H is absorbed on the different top site is metastable isomer, its energy is 0.0861 eV higher than that of the lowest energy structure. In case of Ru$_4$H$_2$, the first and the second H are both absorbed on the adjacent bridge sites. In the lowest energy structure with a triplet state, the H–H distance is 2.530 Å, and the H$_2$ is also activated. The structure with two H atoms absorbed on the top site on the lowest energy structure of Ru$_4$ is metastable isomer, its energy is 0.126 eV higher than that of the lowest energy structure. For Ru$_5$H$_2$, a square pyramid-based structure in a singlet state is most stable, followed by a singlet, triplet and triplet state with 0.293, 0.416 and 0.457 eV higher in energy, respectively.

For Ru$_6$H$_2$, the most stable structure is a trigonal prism-based structure in a triplet state, followed by a singlet with 0.0218 eV higher in energy than the most stable structure. The structure with two H atoms absorbed on the bridge site on the trigonal prism is metastable isomer, its energy is 0.0368 eV higher than that of the lowest energy structure. For Ru$_7$H$_2$, a square pyramid-based structure in a singlet state is most stable, followed by a singlet, triplet and triplet state with 0.293, 0.416 and 0.457 eV higher in energy, respectively.

In the case of Ru$_8$H$_2$, the most stable structure is a trigonal prism-based structure in a triplet state, followed by a singlet with 0.0218 eV higher in energy than the most stable structure. The structure with two H atoms absorbed on the bridge site on the trigonal prism is metastable isomer, the energy is 0.0368 eV higher than that of the lowest energy structure. For Ru$_7$H$_2$, the most stable structure is a singly capped trigonal prism-based structure in a quintuple state, formed by a hollow site adsorption in which one H atom sits above the plane of three Ru atoms and another H atom locates on the Ru atom top. The secondary low-lying isomer of Ru$_7$H$_2$ is a singly capped square bi-pyramid-based structure, which actually corresponds to the third low-lying isomer of pure Ru$_7$ isomer. Other isomers are also presented in Fig. 2. The lowest energy structure of Ru$_8$H$_2$ is square prism-based structure in a quintet state, the single state is 0.0772 eV higher in energy.

According to above analysis, it is shown that the lowest energy structure of Ru$_n$H$_2$ can be obtained by adsorbing H$_2$ in the lowest energy and some meta-table isomers of Ru$_n$ clusters. It is interesting to notice that in all cases, the absorbed species does not lead to a rearrangement of the basic cluster, but the hydrogen atom adsorbs to the edge of a Ru–Ru bond with the bond lengthening. The longest and the shortest R$_{Ru-Ru}$ (increase with the cluster size overall) as well as R$_{Ru-H}$ vary in small ranges overall. In the Ru$_n$H$_2$, H–H bond length is about 2.173–3.419 Å. The values

Table 1. The longest (Max$_{R_{Ru-Ru}}$, Max$_{R_{Ru-H}}$) and the shortest (Min$_{R_{Ru-Ru}}$, Min$_{R_{Ru-H}}$) bond lengths(Å) and H–H bond length(Å)(R$_{H-H}$) of the lowest energy structures of Ru$_n$ clusters and Ru$_n$H$_2$ complexes.

| n  | Symmetry | Max$_{R_{Ru-Ru}}$ | Min$_{R_{Ru-Ru}}$ | Max$_{R_{Ru-H}}$ | Min$_{R_{Ru-H}}$ | R$_{H-H}$ |
|----|----------|-------------------|-------------------|-------------------|-------------------|----------|
| 2  | C$_1$    | D$_{x,y}$         | 2.322             | 1.574             | 1.573             | 2.173    |
| 3  | C$_1$    | C$_s$             | 2.598             | 1.748             | 1.581             | 2.443    |
| 4  | C$_s$    | D$_{4h}$          | 2.587             | 1.780             | 1.722             | 2.530    |
| 5  | C$_1$    | C$_{2v}$          | 2.584             | 1.787             | 1.154             | 2.407    |
| 6  | C$_1$    | C$_1$             | 2.542             | 1.795             | 1.661             | 2.571    |
| 7a | C$_1$    | C$_s$             | 2.898             | 1.849             | 1.632             | 3.419    |
| 7b | C$_1$    | C$_1$             | 2.610             | 1.810             | 1.750             | 2.988    |
| 8  | C$_1$    | D$_{3d}$          | 2.493             | 1.743             | 1.633             | 2.320    |
are larger than the bond length of optimized H₂ (0.748 Å), which indicates the hydrogen molecular is activated.

Relatives Stability and Electronic Properties

It is known that the relative stability of the different sized cluster can be predicted by calculating the averaged binding energy. The averaged binding energy can be defined as the following formula:

\[
E_b[\text{Ru}_n\text{H}_2] = (-E[\text{Ru}_n\text{H}_2] + nE[\text{Ru}] + 2E[\text{H}])/(n + 2)
\]

\[
E_b[\text{Ru}_n] = (-E[\text{Ru}_n] + nE[\text{Ru}])/n
\]

where \( E_T(\text{Ru}_n\text{H}_2), E_T(\text{Ru}), E_T(\text{H}) \) and \( E_T(\text{Ru}_n) \) represent the total energies of the \( \text{Ru}_n\text{H}_2, \text{Ru}, \text{H}, \text{Ru}_n \) clusters, respectively. The calculated results on the averaged energies for \( \text{Ru}_n\text{H}_2 \) and \( \text{Ru}_n \) clusters are plotted in Fig. 3. When H₂ is adsorbed on the \( \text{Ru}_n \) clusters, the average binding energy is larger than that of \( \text{Ru}_n \) clusters for \( n = 2–3 \), the average binding energy is smaller than that of \( \text{Ru}_n \) clusters with cluster size increasing. For \( n = 2–3 \), the H atom mainly act with Ru atom. The calculated binding energy (3.577 eV) of Ru–H are larger than that of Ru–Ru (3.19 eV), which indicates the interaction between Ru and H is larger than that of Ru–Ru. So the averaged energy for \( \text{Ru}_n\text{H}_2 \) clusters is larger than that of \( \text{Ru}_n \). When \( n > 3 \), the H atoms are mainly bond \( \text{Ru}_n \) by the weak interaction, which causes the averaged binding energies of \( \text{Ru}_n\text{H}_2 \) are smaller than that of \( \text{Ru}_n \) clusters.

The relative stabilities of these clusters can be better understood by calculating the incremental formation energies, i.e., the second order difference of cluster energies, we defined the \( \Delta_2E(n) \) as the following formula:

\[
\Delta_2E = E(n-1) + E(n+1) - 2E(n)
\]
where $E_T(n)$ is the total energy of clusters. The second order difference of cluster energies for Ru$_n$H$_2$ and Ru$_n$ clusters are all presented in Fig. 4. According to Fig. 4, for Ru$_n$ clusters, the peak values appear at $n = 3, 5$, it shows apparently that the maximum magic number of the relative stability is $n = 3, 5$ among investigated Ru$_n$ clusters. For Ru$_n$H$_2$, particularly high peaks for are found at $n = 5$, reflecting that the Ru$_5$H$_2$ cluster is more stable than its neighboring clusters. The same magic number 5 indicates the effect of H molecular to the bonding natures of Ru$_n$ clusters is small for $n \geq 3$, which is consistent with the result of the averaged energy.

To measure the strength of the interaction of H with each of the clusters, we calculated the binding energy of H to each cluster according to:

$$E(H) = E(\text{Ru}_n\text{H}_2) - \frac{E(\text{Ru}_n)}{2} - 2E(\text{H})$$

(4)

The calculated binding energies of H to cluster corresponding to the most energetically favorable chemisorption site are show in Fig. 5, which has a strong dependence on the clusters and increase until $n = 2$, and then decrease to the lowest value of 5.847 eV at $n = 3$. The bind energies of H to Ru$_n$ cluster then increase in general as the size of the clusters increase, attaining the local maxima for $n = 2, 4$ and 7. The larger binding energies of H to Ru$_n$ cluster ($n = 2, 3$) indicate the stronger inaction of Ru–H, which is consistent with the result of the averaged energy. The values for bind energies of H to Ru$_n$ cluster are 5.847–7.024 eV, and these is larger than that of Ru$_n$ cluster(1.597–4.295 eV), which also shows the interaction of Ru–H is larger than that of Ru–Ru.

The electronic properties of clusters are discussed by examining the energy gap between the HOMO and LUMO. The HOMO-LUMO gaps for Ru$_n$H$_2$ and Ru$_n$ clusters of the most stable structure are shown in Fig. 6. As can be seen from Fig. 6, when H$_2$ is absorbed on the Ru$_n$ clusters, the gaps are usually smaller than those of

![Fig. 4 Second finite difference of the total energies for Ru$_n$H$_2$ and Ru$_n$ clusters](image-url)
Ru\textsubscript{n} cluster, which indicates that the adsorption of the H atoms improves the chemical activity of the host clusters in most cases. However, the exceptional case is \( n = 2 \) in which the values of the gap for Ru\textsubscript{2} are much larger than those of the Ru\textsubscript{2}H\textsubscript{2} cluster. Interestingly, the energy gap of Ru\textsubscript{8}H\textsubscript{2} is close to that of Ru\textsubscript{8}, which shows that the adsorption has little effect on the chemical activity with \( n = 8 \). Consequently, the Ru\textsubscript{n}H\textsubscript{2} clusters exhibit remarkable difference in terms of the variation of the energy gap as the H atoms are adsorbed onto the Ru\textsubscript{n} clusters.
In light of the particular phenomenon mentioned above, it is necessary to further study the reason about the changing trend of the gap. Meanwhile, the energy level of the molecular orbital for Ru$_2$ (Ru$_2$H$_2$), Ru$_5$(Ru$_5$H$_2$), which is displayed in Fig. 7, were investigated to further illustrate the electronic property. The obvious characteristic of the molecular orbital for Ru$_2$ is the appearance of the degeneracy of the energy level in the vicinity of the HOMO–LUMO. With the H atoms being adsorbed onto the Ru$_2$ cluster, the degenerate energy level is completely disappeared. Moreover, compared with Ru$_2$, the energy level of the LUMO for Ru$_2$H$_2$ is elevated strongly (about 0.938 eV). In case of Ru$_5$, there is also degenerate orbital in the vicinity of HOMO–LUMO. However, the HOMO and LUMO for Ru$_5$H$_2$ both consist of two degenerate orbitals, respectively. When H atoms are adsorbed onto the Ru$_5$ cluster, the LUMO of Ru$_5$H$_2$ is also reduced (about 0.669 eV) in comparison to Ru$_5$. Apparently, the similar behavior of the reduction of the LUMO for $n = 3, 4, 6, 7$, results in the decrease of their energy gap.

In Fig. 8, we give the adsorption energy for Ru$_n$H$_2$ complex. The absorbed energy can be defined as the following formula:

$$E_{\text{adv}} = E_{\text{H}_2} + E_{\text{cluster}} - E_{\text{cluster}+\text{H}_2}$$  \hspace{1cm} (5)

It is well-known that the chemisorption energies can be used to quantitatively describe the reactivity of H$_2$ on the Ru$_n$ clusters. The calculated chemisorption energies corresponding to the most energetically favorable chemisorption site are show in Fig. 8, which has a strong dependence on the clusters and increase until $n = 2$, and then decrease to the lowest value of 1.182 eV at $n = 3$. The chemisorption energy then increase in general as the size of the clusters increase, attaining the local maxima for $n = 2, 4$ and 7. The present results show the Ru$_3$ cluster is of high inertness with respect to the H$_2$ chemisorption, while Ru$_2$, Ru$_4$, and Ru$_7$ clusters are of high activity with respect to the H$_2$ chemisorption. Note that

![Fig. 7 One electron energy levels in the vicinity of the HOMO and LUMO of the Ru$_2$H$_2$, Ru$_5$ (The dotted lines represent the LUMO levels, and the solid lines represent HOMO levels)
Dhilip Kumar et al. [46] also calculated that the H\textsubscript{2} chemisorption energy was found to be the lowest for the stable Ti\textsubscript{7} cluster but highest for the most stable cluster Ti\textsubscript{13}. Experimental measurements indicate that when Ti\textsubscript{13} cluster is added as a catalyst to increase the reaction rate of hydrogenation and dehydrogenation processes in alanates [47]. Whether the Ru\textsubscript{2} is added as a catalyst to increase the reaction rate of hydrogenation and dehydrogenation processes is to be studied further theoretically and experimentally.

The charge transfer from the Ru\textsubscript{n} cluster to H\textsubscript{2} molecule is an essential factor to determine the H\textsubscript{2} adsorption behavior on Ru\textsubscript{n} clusters. Here we give the charge populations from natural population analysis on H atoms (Fig. 9). According to the NPA charge population, electron transfer will occur from H atoms to Ru\textsubscript{n} clusters. The electron transferred number between H atoms and Ru\textsubscript{n} clusters is about 0.0475–0.158e, this means the interaction between H atoms and Ru\textsubscript{n} clusters is small. When \( n = 2, 7 \), the charges from H atoms to Ru\textsubscript{n} clusters are more, which is consist with the large absorbed energy in these clusters. For Ru\textsubscript{6}H\textsubscript{2}, the charges from H atoms to Ru\textsubscript{n} clusters are smallest among Ru\textsubscript{n}H\textsubscript{2} complex, this indicates the adsorption has little effect on Ru\textsubscript{6}, which is the reason that the energy gap of Ru\textsubscript{6}H\textsubscript{2} is close to that of Ru\textsubscript{6}.

**Magnetic Properties**

Figure 10 gives the spin magnetic moment of pure and hydrogenated clusters. For Ru\textsubscript{3}, the H atoms decrease the spin magnetic moment. For Ru\textsubscript{2}, Ru\textsubscript{4} and Ru\textsubscript{7}, the H atoms increase the spin magnetic moment. In case of Ru\textsubscript{n} (\( n = 5, 6, 8 \)), the H atoms have little impact on the spin magnetic moment. In a previous paper, Fournier et al. have proposed H\textsubscript{2} affect on spin magnetic moment of transitional metal clusters can be understood within a simple model [48, 49]. The change in moment is related to
the location of the lowest unoccupied orbital of the preceding cluster. The H atom can be considered as a proton and an electron. The additional electron goes to the spin state with lowest LUMO while the proton is screened by the $d$-states of the neighboring Ru sites. This however, is not the only consideration. If the LUMO of the preceding cluster belongs to the minority manifold (spin down) and the LUMO of majority (spin up) is only slightly higher, the additional electron may still go to majority manifold since the exchange coupling could lead to a rearrangement of the manifolds. To put it simply, it is the difference, $\delta E$, between the LUMO of the
majority and the minority spin manifolds that controls the change in moment. When this quantity is positive, one expects the moment to increase. On the other hand, when this quantity is highly negative, an addition of H would lead to a decrease in the magnetic moment. To show this correlation, we list in Table 2, the HOMO and LUMO of all the clusters. Note that when $dE$ is less than 0 eV, the spin magnetic moment does decrease upon addition of H$_2$. When $dE$ is close to or more than 0 eV, the spin magnetic moment increases or varies little upon addition of H$_2$.

According to above analysis, it again identify the difference between the LUMO of the majority and the minority spin manifolds that controls the change in magnetic moment, the change rule in magnetic moment is different when H$_2$ is adsorbed on different transitional metal clusters. The model may be predict the change in magnetic moment when small molecular is adsorbed on the transitional metal clusters.

### Conclusions

We have presented a systematic study on the interaction of the hydrogen atoms with the small Ru$_n$ clusters in the size range of two to eight Ru atoms. The lowest energy structures of Ru$_n$H$_2$ clusters can be obtained by substituting H$_2$ in the lowest energy and some meta-stable isomers of Ru$_n$ clusters. For $n > 2$, three different adsorption
patterns are found for the Ru$_n$H$_2$ complexes: One H atom binds to the Ru top site, and another H binds to the bridge site for $n = 3, 5, 6, 8$; bridge site adsorption for $n = 4$; hollow site and top site adsorption for $n = 7$. The adsorption energies display oscillation and reach the peak at $n = 2, 4, 7$, implying their high chemical reactivity. The small electron transferred number between H atoms and Ru$_n$ clusters indicates the interaction between H atoms and Ru$_n$ clusters is small. It is interesting to note that in all cases, the absorbed species does not lead to a rearrangement of the basic cluster. When H$_2$ is absorbed on the Ru$_n$ clusters, the chemical activity of corresponding clusters is dramatically increased. The present studies show that the H absorption can lead to an oscillatory behavior of the magnetic moments. This behavior is rooted in the electronic structure of the preceding cluster and the changes in the magnetic moment are indicative of the relative ordering of the majority and minority LUMO’s. The second order difference indicates 5 is magic number in Ru$_n$H$_2$ and Ru$_n$ clusters.

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