

A comparative study between all-electron scalar relativistic calculation and all-electron calculation on the adsorption of hydrogen molecule onto small gold clusters

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Abstract. A comparative study between all-electron relativistic (AER) calculation and all-electron (AE) calculation on the H₂ molecule adsorption onto small gold clusters has been performed. Compared with the corresponding Au_nH₂ cluster obtained by AE method, the Au_nH₂ cluster obtained by AER method has much shorter Au–H bond-length, much longer H–H distance, larger binding energy and adsorption energy, higher vertical ionization potentials (VIP), greater charge transfer, higher vibrational frequency of Au–H mode and lower vibrational frequency of H–H mode. The delocalization of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for Au_nH₂ cluster obtained by AER method is obvious. All these characteristics suggest that the scalar relativistic effect might strengthen the Au–H bond and weaken the H–H bond. It is believed that the scalar relativistic effect is favourable to the H₂ molecule adsorption onto small gold cluster and the reactivity enhancement of H₂ molecule. It may be one of the reasons why the dissociative adsorptions take place in some Au_nH₂ clusters. With increasing size of Au_nH₂ clusters, the influence of scalar relativistic effect becomes more significant. Some further studies focused on the influence of scalar relativistic effect on the adsorption behaviour of other small molecules onto gold clusters are necessary in the future.

Keywords. Small gold cluster; hydrogen molecule; adsorption; scalar relativistic effect.

1. Introduction

Small gold clusters have attracted much attention from both industrial and scientific areas due to their unique physical and chemical properties strongly dependent on the cluster size.^{1–3} Although the bulk gold is one of the most chemically inert metals, gold clusters, the size of which is as small as 2–3 nm, are efficient catalysts for various chemical reactions.^{4–7} Previous studies have reported that small gold catalysts could be applied to many oxidation and hydrogenation reactions at low temperatures. These reactions include CO and NO oxidations,⁸ partial oxidation of propylene,⁹ partial hydrogenation of acetylene,¹⁰ hydrogenations of ethylene,¹¹ and so on. Even more interesting is the partial oxidation of propylene to propylene oxide, by a mixture of hydrogen and oxygen, which is catalysed by small gold clusters supported on TiO.^{12–16} The presence of hydrogen in the oxidation reaction is rather unusual and still not understood well.¹⁷ Consequently, some further study on

the role of hydrogen in this process may have practical applications.

Stimulating by this unusual phenomenon, the adsorption behaviour of hydrogen molecule onto small gold clusters has been studied experimentally and theoretically.^{17–24} Varganov *et al.* have studied the reaction of molecular hydrogen with the dimer and trimer gold clusters by using DFT, second order perturbation theory and coupled cluster methods.¹⁷ They report that H₂ molecules can be easily bonded with neutral Au₂ and Au₃ clusters but can not form stable complexes with Au₂[–] and Au₃[–] clusters. Okumura *et al.* have carried out a hybrid density functional calculation on Au₁₃H₂ cluster to discuss the catalytic behaviour of Au cluster.¹⁸ It is suggested that the Au nanoparticle has a stable chemisorption state of H atom and has the ability to dissociate H₂ at low temperature. Ghebriel *et al.* have presented a theoretical investigation on the adsorption of H₂ and H₂S molecules onto small neutral and cationic gold clusters by using density functional theory with the generalized gradient approximation.¹⁹ It has been shown that H₂ molecule weakly bonds to the neutral gold clusters as compared to the corresponding cationic clusters. The adsorbed molecules get attached to a

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single gold atom and there is no preference to get adsorbed at places between the gold atoms. In most cases, the geometry of the lowest energy gold cluster remains planar structure even after the adsorption. Kang *et al.* have investigated the adsorption and dissociation of H₂ on the neutral and charged gold clusters by using the density functional theory Perdew–Wang 1991 (PW91) functional.²⁰ They find that H₂ interacts very weakly with Au_{*n*}⁻¹, whereas the interaction with Au_{*n*}⁺¹ is relatively strong. The H₂ molecule dissociates facily at low temperatures on both neutral and cationic Au₄ and Au₅ clusters.

Although there are some studies on the adsorption behaviour of hydrogen molecule onto small gold clusters, some questions concerning the H₂ dissociation remain unclear.^{25–29} Corma *et al.* investigate the H₂ dissociation on gold by using three different models.²⁵ They find that on four-coordinated Au atoms, H₂ dissociation is facile while on five-coordinated Au atoms or surfaces, the dissociation is difficult. They conclude that the existence of low coordinated Au atoms would be the sufficient and necessary condition for H₂ dissociation. However, Strømsnes *et al.* report a quite high dissociation barrier of 1.95 eV on a four-coordinated Au atom.²⁶ Hence the relationship between the coordination number of the Au atom and the feasibility of H₂ dissociation is still inconclusive. Recently, Kan *et al.* indicate that the reason of H₂ dissociation is not the higher dissociation barrier and weak bond of H₂.²⁰ The coordination number of the Au atom may not play a determining role in H₂ dissociation. For the first time, they suggest that H₂ dissociation may involve the valley-ridge inflection points on some clusters. Besides the questions of dissociative adsorption toward H₂, another important research point is the influence of scalar relativistic effect on the adsorption behaviour of small gold clusters. Gold being a heavy element, the scalar relativistic effect of outer shell electrons is obvious and can not be neglected.^{30–34} Furthermore, previous studies.^{35,36} indicate that the reason for the preference of planar structures by gold clusters up to large size may be attributed to the scalar relativistic effects that cause a shrinking of the size of the *s* orbitals and thus enhance the *s*–*d* hybridization. This phenomenon also can be observed in other coinage metal clusters, such as Ag, Cu, and is most strikingly evident in gold cluster and called ‘gold maximum’.³⁷ So for coinage metal cluster in general, and gold cluster in particular, it is essential to study the scalar relativistic effect on the adsorption behaviour. In this paper, we perform a comparative study between all-electron scalar relativistic (AER) calculation and all-electron (AE) calculation on the hydrogen molecule adsorption onto small gold clusters (*n* =

1 – 13) by using density functional theory with the generalized gradient approximation at PW91 level and try to answer the question whether and how the scalar relativistic effect will affect the adsorption behaviour of small gold clusters toward hydrogen molecule. We hope that our study can help people understand the interaction between small gold clusters and hydrogen molecule better. The paper is arranged as follows: the computational method and cluster model are described in section 2, calculation results and discussions are presented in section 3 and the main conclusions are summarized in section 4.

2. Computational method and cluster model

All calculations are based on spin-polarized density functional theory (DFT) in the DMOL 3 program package.^{38,39} A high quality double-numerical with polarization (DNP) basis set is chosen to describe the electronic wave functions. Within the generalized gradient approximation (GGA), the Perdew–Wang 91 exchange–correlation (XC) functional (PW91),⁴⁰ combined with the DFT-basis all-electron treatment and all-electron relativistic four-component Dirac–Kohn–Sham procedure for clusters containing heavy elements is adopted in the calculations.^{41,42} These potentials do not replace core electrons; instead they supplement the core potentials with approximate relativistic effects. Such effects are important for heavier elements, and are certainly required starting with the second row of transition metals. Using these potentials may yield the most accurate results, though at the highest cost.^{38–42}

The self-consistent field (SCF) tolerance is set to be 1.0×10^{-6} eV. In order to accelerate the calculation, the direct inversion in iterative subspace (DIIS) approach is used and the smearing value is set to be 0.005 Ha. During the structure optimization, the spin is unrestricted and the symmetry of the structure has no constraint. The convergence tolerance of max force, max energy and max displacement is 0.002Ha/Å, 1.0×10^{-5} Ha and 0.005 Å, respectively. During the structure relaxation, the spin multiplicity will be considered at least 2, 4 and 6 for odd-electrons Au_{*n*}H₂ clusters (*n* = 1, 3, 5, 7, 9, 11 and 13) and 1, 3, 5 for even-electrons Au_{*n*}H₂ clusters (*n* = 2, 4, 6, 8, 10 and 12). If the total energy decreases with the increasing of spin multiplicity, the high spin state will be considered until the energy minimum with respect to the spin multiplicity is reached. In addition, the stability of the optimized geometry is confirmed without any imaginary frequency by computing vibrational frequencies at the same level of theory.

The choice of distinct initial geometries is important to the reliability of obtained lowest energy structures. In this work, we get the initial structures by the following way: First, considering previous studies on the configurations of pure gold clusters,^{43–45} we optimize the structures of pure Au_n clusters and free H_2 molecule by using the AER method and AE method, respectively. Based on the optimized equilibrium geometries of pure gold clusters and free H_2 molecule, we obtain the initial structures of Au_nH_2 clusters by adding H_2 molecule directly on each possible non-equivalent site of Au_n cluster including all possible bonding patterns. All these initial structures are fully optimized by relaxing the atomic positions until the force acting on each atom vanishes (typically $|F_i| \leq 0.002$ Ha/Å) and by minimizing the total energy by using the AER and AE method, respectively.

In order to check the intrinsic reliability of various functional forms, we chose Au_2 , Au_3 and AuH as examples to calculate some properties (the corresponding experimental data are available for these clusters) by using the GGA-PW91, GGA-(Becke-Perdew) BP, GGA-(Perdew, Burke and Enzerhof) PBE, GGA-(Becke-Lee-Yang-Parr) BLYP and (Local Density Approximation-Perdew-Wang 1992) LDA-PWC, LDA-(Vosko-Wilk-Nusair) VWN functional forms, respectively. From the AER calculation, the results listed in table 1, we can see that the results obtained by using the GGA-PW91 functional form are more close to the available experimental data.^{43–48} This indicates that among all these available functional forms, the GGA-PW91 functional is the most reliable and accurate one for the study of pure Au_n clusters and Au_nH_2 clusters. Although there is possibly no available experimental data for comparison between experimental and theoretical results, some previous research reports^{44,49–52} used similar techniques demonstrate that the AER and AE method adopted in this paper are recognizable.

3. Results and discussion

3.1 Geometrical structures

In order to acquire the initial structures of Au_nH_2 clusters, we optimize the pure Au_n clusters and single H_2 molecule by using AER and AE method, respectively. The optimized geometries of Au_n clusters and single H_2 molecule are shown in figure 1. For single H_2 molecule, the H–H bond-lengths of AER calculation and AE calculation, which are adopted to compare with those of H_2 after adsorption, are the same value of 0.728 Å and in good agreement with the experimental value of 0.7414 Å.⁵³ This situation indicates that the scalar relativistic effect almost has no influence on single H_2 molecule. For pure Au_n clusters, the planar structures obtained by AER method are in good agreement with previous works.^{43–45} But, the average Au–Au bond-length of planar structure obtained by AE method is much longer than that of corresponding planar structures obtained by AER method. This indicates that the scalar relativistic effect may enhance the Au–Au bond significantly. Then, based on the optimized lowest energy structures of Au_n clusters, we perform an extensive lowest energy structure search for H_2 molecule adsorption onto small gold cluster according to the way described in section 2. The lowest energy structures of Au_nH_2 ($n = 1 - 13$) clusters obtained by AER and AE method are displayed in figure 1 comparatively. For the lowest energy geometries of Au_nH_2 ($n = 1 - 13$) clusters obtained by AE method, the H–H bond-lengths are slightly longer than that of single H_2 molecule. The H_2 structures in these Au_nH_2 clusters are slightly perturbed and still keep the structure like single H_2 molecule. This picture indicates that only molecular adsorptions take place in these Au_nH_2 clusters without including scalar relativistic effect. For the lowest energy geometries of Au_nH_2 ($n = 1 - 13$) clusters obtained by AER

Table 1. AER calculation results comparison between different functional forms for some properties of Au_2 , Au_3 and AuH clusters.

Cluster Properties	Au_2				Au_3	AuH	
	R (Å)	E_b (eV/atom)	VIP (eV)	ν (cm^{-1})	VIP (eV)	R (Å)	E_b (eV/atom)
GGA-PW91	2.487	1.221	9.381	183.1	7.443	1.521	1.671
GGA-BP	2.489	1.138	9.372	181.5	7.375	1.514	1.653
GGA-PBE	2.488	1.189	9.376	181.7	7.369	1.516	1.652
GGA-BLYP	2.528	1.104	9.192	169.8	7.285	1.519	1.646
LDA-PWC	2.437	1.505	9.611	201.2	7.694	1.502	1.923
LDA-VWN	2.436	1.502	9.613	200.9	7.699	1.501	1.926
Exp	2.470	1.225	9.400	191.0	7.500	1.524	1.680

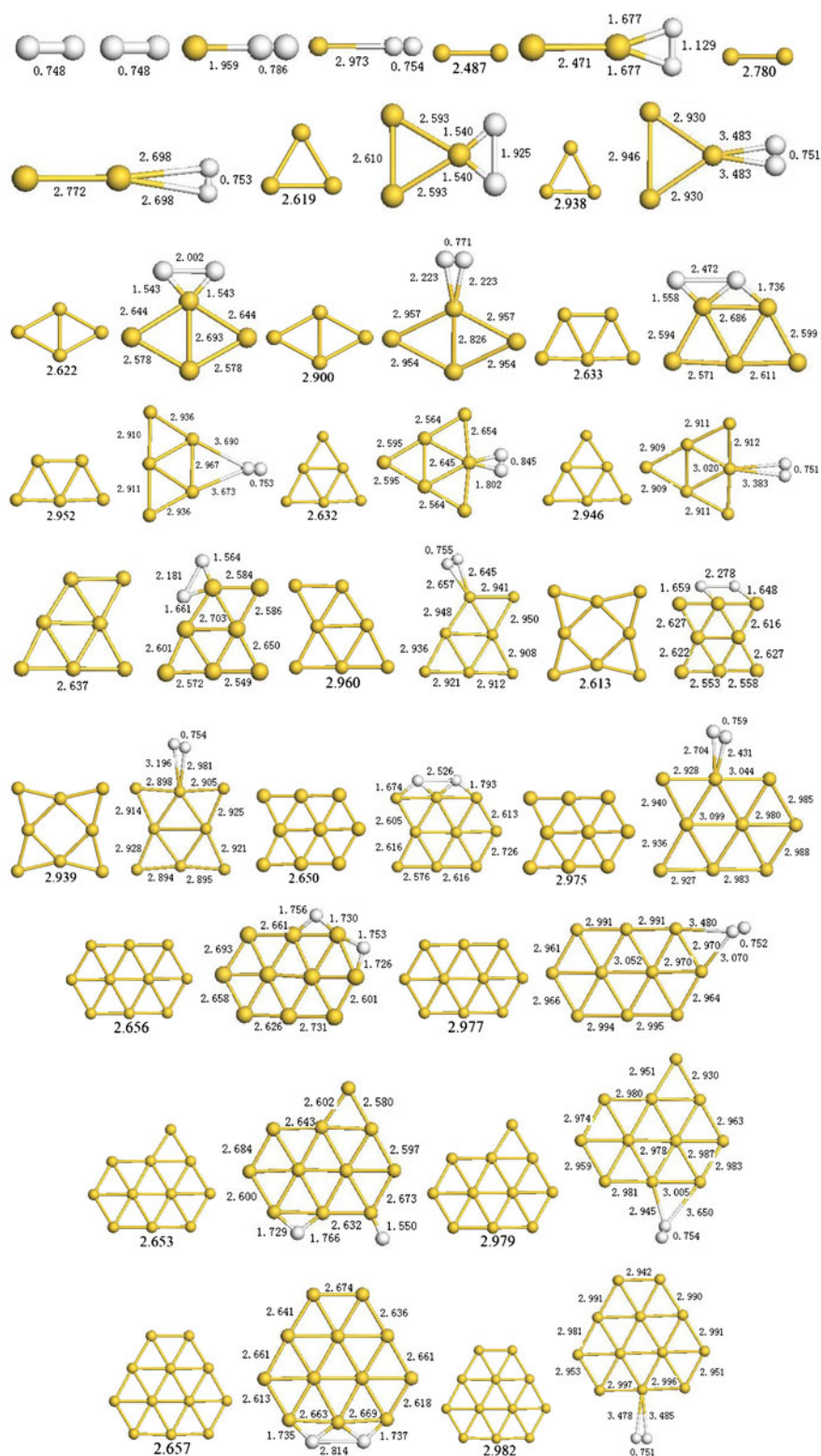


Figure 1. Lowest energy geometries for pure Au_n clusters and Au_nH_2 ($n = 1-13$) clusters. Every cluster has two figures, first one for AER calculation and second one for AE calculation.

method, the lengthening of H–H distance is very obvious and significant. The H–H distance in Au_nH_2 cluster obtained by AER is much longer than that of corresponding Au_nH_2 cluster obtained by AE. For AuH_2 ,

Au_2H_2 and Au_6H_2 clusters, the H–H distances are the values of 0.786 Å, 1.129 Å and 0.845 Å, respectively. The H_2 still can be regarded as molecule and molecular adsorptions take place in these clusters. But, in other

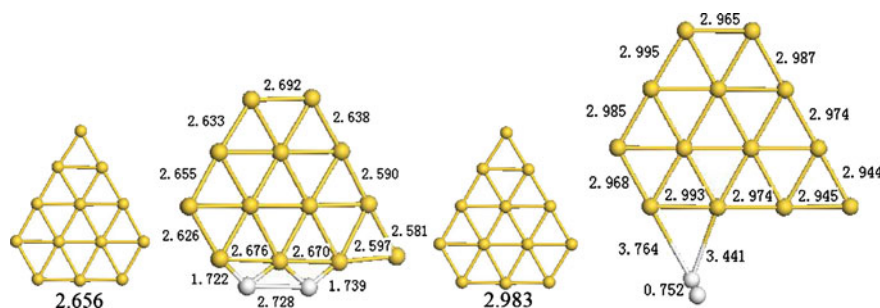


Figure 1. (contd.)

Au_nH_2 clusters, the H–H distances are elongated from 0.748 Å to the value of more than 2.000 Å. The H_2 is obviously dissociated and dissociative adsorptions take place in these Au_nH_2 clusters definitely. All these dissociative adsorptions are found to be favourable to two, three and four-coordinated Au atoms, no dissociative adsorption on five and six-coordinated Au atoms can be found. The low-coordinated Au atoms are more reactive toward H_2 molecule than the high-coordinated Au atoms. This situation is consistent well with previous work²⁵ and may be understood in terms of the lack of charge transfer channels and electron pairing chance for low-coordinated Au atoms. Meanwhile, we can also see that the Au–H bond-length in Au_nH_2 cluster obtained by AER method is significantly shorter than that of corresponding Au_nH_2 cluster obtained by AE method, indicating that the strength of Au–H bond in Au_nH_2 cluster obtained by AER method is greatly stronger than that of Au–H bond in Au_nH_2 cluster obtained by AE method. For Au_nH_2 ($n = 1 - 8$) clusters, the Au–H bond-length and H–H bond-length obtained by AER method in our work are shorter and longer than the corresponding bond-length in previous work¹⁹ (see figures 2 and 3), respectively. All these characteristics of geometrical structure demonstrate that the scalar relativistic

effect might have obvious influence on the adsorption behaviour of small gold cluster toward H_2 molecule. It may significantly strengthen the Au–H bond and weaken the H–H bond, thus, promote the adsorption strength of small gold cluster toward H_2 molecule, enhance the dissociation and reactivity of H_2 molecule.

3.2 Energy and electronic structures

The binding energy (BE), adsorption energy (E_{ads}) and vertical ionization potentials (VIP) for pure Au_n cluster and Au_nH_2 cluster are displayed in figures 4–7, where we define:

$$\begin{aligned} BE(Au_n) &= [nE(\text{Au}) - E(Au_n)] / n \\ BE(Au_nH_2) &= [nE(\text{Au}) + 2E(\text{H}) - E(Au_nH_2)] / (n+2) \\ E_{\text{ads}} &= [E(Au_n) + E(H_2) - E(Au_nH_2)] \\ VIP &= E(Au_nH_2)^+ - E(Au_nH_2). \end{aligned}$$

Generally speaking, the binding energy of a given cluster is a measurement of its thermodynamic stability. From figure 4, we can find that the binding energy of pure Au_n cluster obtained by AER method is obviously larger than that of pure Au_n cluster obtained

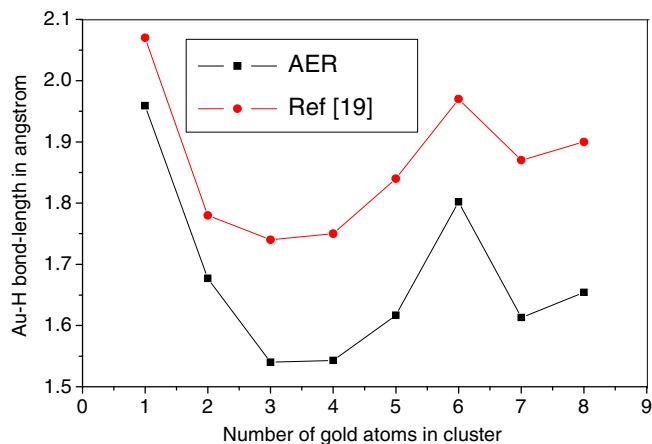


Figure 2. Au–H bond-length comparison between AER calculation and Ref. 19 for Au_nH_2 ($n = 1-8$) clusters.

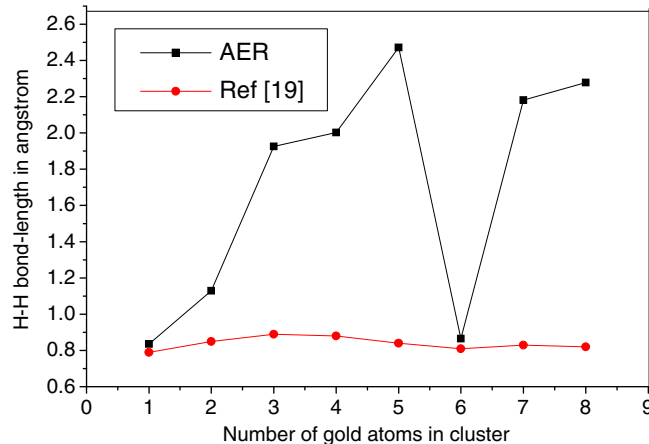


Figure 3. H–H bond-length comparison between AER calculation and Ref. 19 for Au_nH_2 ($n = 1-8$) clusters.

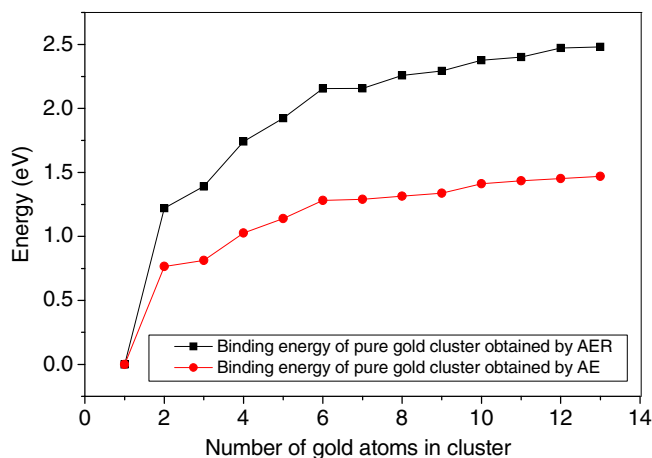


Figure 4. Size dependence of binding energy for pure Au_n cluster.

by AE method. With increasing size of pure Au_n cluster, the binding energy difference becomes large and then stable gradually, indicating that the scalar relativistic effect enhances the stability of pure Au_n cluster and furthermore this effect is strengthened gradually with increasing size of gold cluster. Similar with pure gold clusters, the binding energy of Au_nH_2 cluster obtained by AER method is also obviously larger than that of Au_nH_2 cluster obtained by AE method (see figure 5). With increasing size of Au_nH_2 cluster, the binding energies of Au_nH_2 clusters obtained by AE method fluctuate around the value of 1.500 eV and exhibit an odd-even oscillation which can be explained based on the electron pairing effect.⁵⁴ But, the binding energies of Au_nH_2 clusters obtained by AER method increase gradually and no obvious odd-even oscillation can be found. The binding energy difference between AER method and AE method becomes larger gradually (see figure 5). All these characteristics infer that the scalar relativistic effect enhances the stability of Au_nH_2

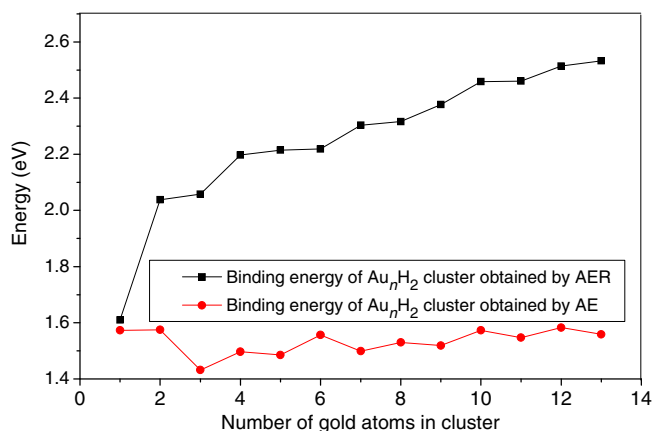


Figure 5. Size dependence of binding energy for Au_nH_2 cluster.

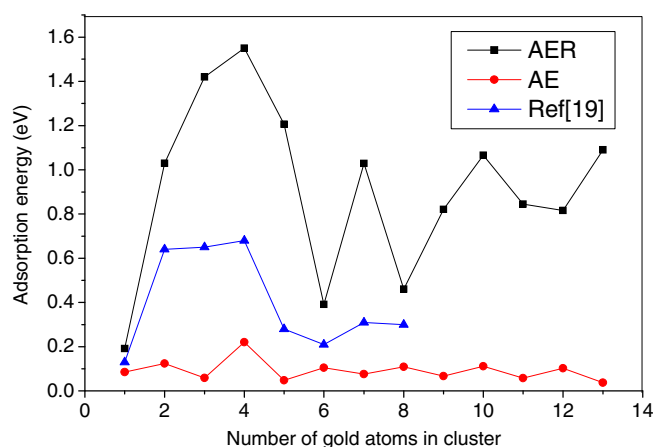


Figure 6. Size dependence of adsorption energy for Au_nH_2 cluster.

cluster and with increasing size of Au_nH_2 clusters the influence of scalar relativistic effect becomes more and more significant, and conceal the influence of the electron pairing effect gradually.

From the adsorption energies displayed in figure 6, we can see that the adsorption energies of Au_nH_2 clusters obtained by AE method are very small and the adsorption energy of Au_nH_2 cluster obtained by AER method is much larger than that of Au_nH_2 cluster obtained by AE method, but also for Au_nH_2 cluster obtained by AE method, the adsorption energy reaches the maximum value at $n = 4$. Similar with the variation of binding energies, an odd-even oscillation of adsorption energies obtained by AE method can be observed, indicating that the electron pairing effect might play an important role in variation of adsorption energies obtained by AE method. However, with increasing size of Au_nH_2 clusters, the adsorption energies obtained by AER method fluctuate acutely and no obvious odd-even oscillation can be found. In addition, the

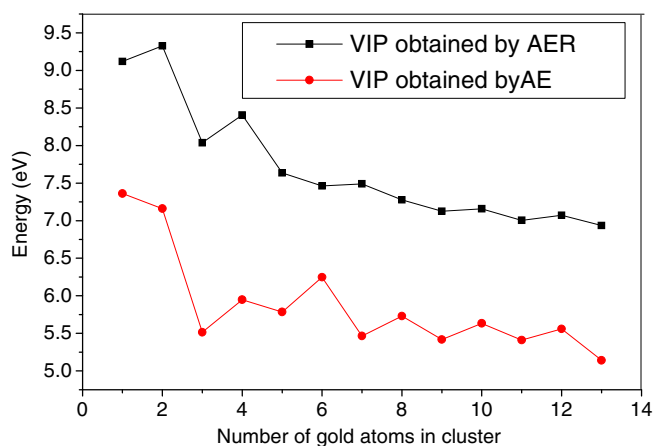


Figure 7. Size dependence of VIP for Au_nH_2 cluster.

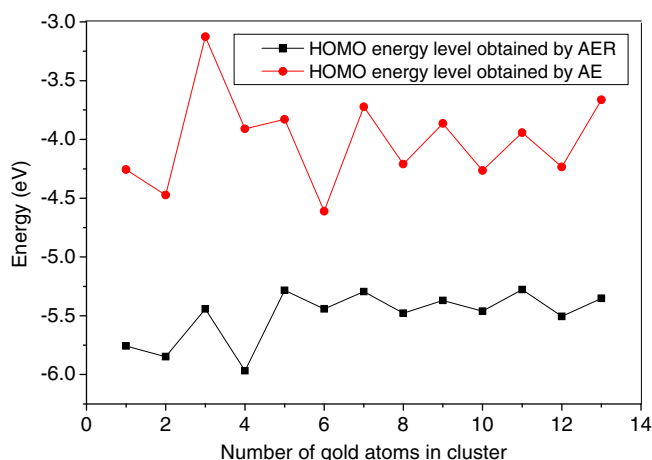


Figure 8. Size dependence of HOMO energy levels for Au_nH_2 cluster.

adsorption energy for Au_nH_2 ($n = 1 - 8$) clusters obtained by AER method in our work is larger than the corresponding adsorption energy in previous work¹⁹ (see figure 6). All these facts suggest that the scalar relativistic effect greatly enhances the adsorption strength of hydrogen molecule onto small gold clusters and plays a more important role than the electron pairing effect. The influence of scalar relativistic effect on the size dependence of adsorption energies is obvious.

The vertical ionization potential (VIP) is often used to investigate the chemical stability of small clusters, the larger of the VIP, the deeper of the HOMO and LUMO energy level, which leads to less reactivity or higher chemical stability. This can be confirmed by Au_nH_2 clusters in our work. From figures 7, 8 and 9, we can see that the VIP of Au_nH_2 cluster obtained by AER method is larger than that of Au_nH_2 cluster obtained by AE method, and the HOMO (LUMO) energy level of Au_nH_2 cluster obtained by AER method is deeper than

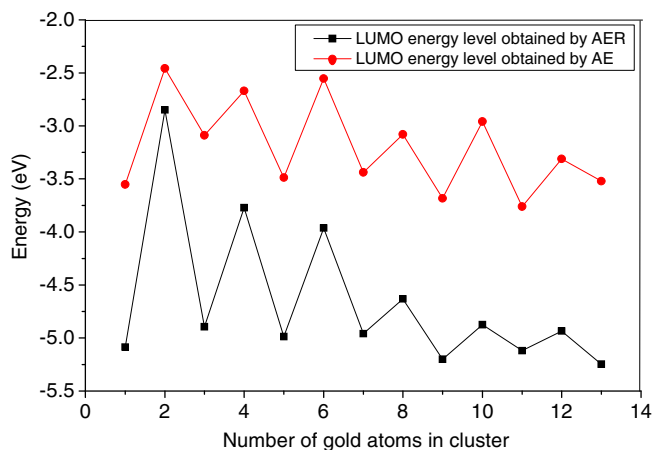


Figure 9. Size dependence of LUMO energy levels for Au_nH_2 cluster.

that of Au_nH_2 cluster obtained by AE method, indicating that the scalar relativistic effect promotes the chemical stability of Au_nH_2 cluster. For all Au_nH_2 clusters obtained by AE method, the obvious odd–even oscillations of VIPs and HOMO (LUMO) energy levels can be observed clearly. But, for all Au_nH_2 clusters obtained by AER method, only the obvious odd–even oscillation of HOMO (LUMO) energy levels can be seen. The strong scalar relativistic effect in gold lowers the energy of the 6s orbital relative to the 5d orbital⁵⁵ and then has obvious influence on the size dependence of VIPs. However, the odd–even oscillation of HOMO (LUMO) energy levels is mainly the reflection of electron pairing effect and reasonably almost has nothing to do with the scalar relativistic effect.

The interaction between small gold cluster and H_2 molecule also can be reflected through charge transfers. We perform a Mulliken charge analysis for Au_nH_2 clusters and list the effective charges on Au_n and two H atoms in table 2. For the lowest energy Au_nH_2 clusters obtained by AER, the values of charge transfers suggest a mechanism to favour electron donation, that is, charge transfer from two H atoms to gold cluster. Some previous works^{56–58} indicated that the charge transfer has the linear correlation with the adsorption energy, the larger charge transfer often leads to the larger adsorption energy, and the variation trend of adsorption energies also can be explained in the light of the charge transfer between gold cluster and H_2 molecule. From table 2, we can clearly see that the variation trend of charge transfer between gold cluster and H_2 molecule obtained by AER and AE is in general consistent with the variation trend of adsorption energy obtained by AER and AE, respectively (see figure 6). The largest charge transfer belongs to the Au_4CO cluster with the largest adsorption energy. However, we must point out that the adsorption energy is also related with the geometries of the cluster, donation and back-donation of electrons, and the overlap of orbital electron cloud.⁵⁹ All these factors might have influence on the adsorption strength. Obviously, the charge transfer from two H atoms to Au_n obtained by AER is much greater than that obtained by AE, this leads to the larger adsorption energy in Au_nH_2 clusters obtained by AER. It is suggested that the scalar relativistic effect might promote the charge transfers from H_2 to Au_n , strengthen the Au–H bond and the adsorption strength of small gold cluster toward H_2 and thus give more prominence to the 2π molecular orbitals of H_2 molecule characterized by the anti-bonding between two H atoms. In turn, the H–H bond is weakened and the reactivity of H_2 molecule is enhanced, appearing as the much longer H–H distance and dissociation of H_2 molecule.

Table 2. Calculated charge transfer for Au_nH_2 clusters.

Cluster	Charge						
	AER			AE			
	Au_n	H	H	Au_n	H	H	H
AuH_2	-0.066	0.068	-0.002	0.009	-0.013		0.004
Au_2H_2	-0.094	0.057	0.037	-0.046	0.023		0.023
Au_3H_2	-0.108	0.054	0.054	-0.004	0.002		0.002
Au_4H_2	-0.124	0.062	0.062	-0.060	0.030		0.030
Au_5H_2	-0.097	0.052	0.045	0.021	-0.019		-0.002
Au_6H_2	-0.078	0.044	0.034	0.022	-0.021		-0.001
Au_7H_2	-0.105	0.079	0.026	-0.017	0.010		0.007
Au_8H_2	-0.064	0.042	0.022	0.020	-0.022		0.002
Au_9H_2	-0.079	0.048	0.031	-0.016	0.012		0.004
Au_{10}H_2	-0.102	0.059	0.043	0.024	-0.017		0.007
Au_{11}H_2	-0.086	0.055	0.031	0.011	-0.016		0.005
Au_{12}H_2	-0.080	0.049	0.031	0.021	-0.019		0.002
Au_{13}H_2	-0.106	0.059	0.047	0.011	-0.015		0.004

From table 3, we can see that all the Au_nH_2 clusters obtained by AER and AE method prefer low spin multiplicity M ($M = 1$ for even-numbered Au_nH_2 clusters and $M = 2$ for odd-numbered Au_nH_2 clusters). The even-numbered Au_nH_2 clusters are found to exhibit zero magnetic moment and the odd-numbered Au_nH_2 clusters are found to possess magnetic moment with the value of $1 \mu_B$ (mainly contributed by Au_n). The odd-even alteration of magnetic moments for Au_nH_2 clusters is very obvious. This situation can be explained in terms of the electron pairing effect. Previous studies^{59–62} have shown that charge transfer and hybridization of valence electrons stemming from host and impurity influence the properties significantly. The stability of the scandium doped gold system is strengthened because of the strong pairing effect between the scandium $3d$ electrons and gold $6s$ electrons. It is similar with the situation of

the pairing effect between the $6s$ electrons of Au_n and the $1s$ electrons of H_2 molecule in Au_nH_2 clusters of our work. Meanwhile, we can also find that the magnetic moment of Au_n obtained by AER method is obviously larger than that obtained by AE method, this picture of magnetic moments may be understood based on the more chance to be paired of $6s$ electrons in Au_n and less chance to be paired of $1s$ electrons in H_2 caused by larger charge transfer from H_2 to Au_n .

In order to understand the nature of chemical bonding in these systems, we have plotted the spatial orientation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for Au_nH_2 clusters obtained by AER and AE method in figure 10. At first glance, the HOMOs and LUMOs of free H_2 molecule obtained by AER method and AE method which are characterized by the anti-bonding

Table 3. Calculated magnetic moments for Au_nH_2 clusters.

Cluster	M	Magnetic moment (μ_B) AER				M	Magnetic moment (μ_B) AE			
		Au_n	H	H	Total		Au_n	H	H	Total
AuH_2	2	0.918	-0.032	0.114	1	2	0.982	0.004	0.014	1
Au_2H_2	1	0	0	0	0	1	0	0	0	0
Au_3H_2	2	0.910	0.045	0.045	1	2	0.998	0.001	0.001	1
Au_4H_2	1	0	0	0	0	1	0	0	0	0
Au_5H_2	2	0.831	0.010	0.159	1	2	0.981	0.012	0.007	1
Au_6H_2	1	0	0	0	0	1	0	0	0	0
Au_7H_2	2	0.902	0.003	0.095	1	2	0.993	0.003	0.004	1
Au_8H_2	1	0	0	0	0	1	0	0	0	0
Au_9H_2	2	0.970	0.019	0.011	1	2	0.996	0.002	0.002	1
Au_{10}H_2	1	0	0	0	0	1	0	0	0	0
Au_{11}H_2	2	0.920	0.007	0.073	1	2	0.991	0.004	0.005	1
Au_{12}H_2	1	0	0	0	0	1	0	0	0	0
Au_{13}H_2	2	0.950	0.040	0.010	1	2	0.998	0.001	0.001	1

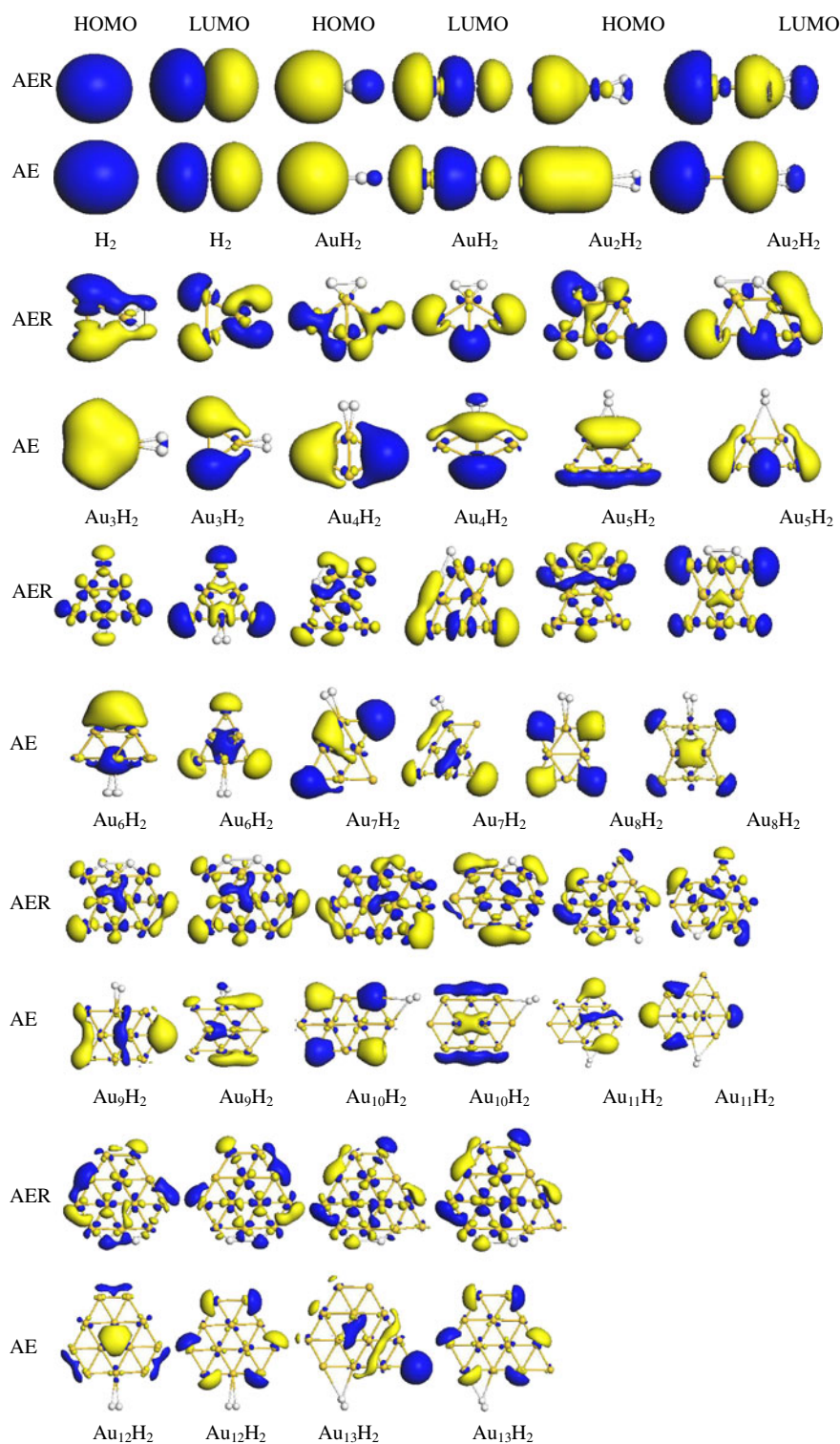


Figure 10. Spatial orientations of HOMO and LUMO for Au_nH_2 ($n = 1-13$) clusters.

orbital between two H atoms are almost same, indicating that the scalar relativistic effect has no influence on the free H_2 molecule. It is consistent with the same value of 0.728 \AA obtained by AER and AE. For the Au_nH_2 clusters obtained by AER, the HOMO and LUMO are delocalized obviously with the con-

tribution from almost all atoms in the cluster. With increasing size of Au_nH_2 clusters, the delocalization becomes stronger and the distribution of electron cloud is well-mixed and relatively uniform. Besides the strong $s-d$ hybridization in Au atom, the spd hybridization between the s, d orbital of Au atom and the s orbital

of H_2 molecule also exists and is very strong in some Au_nH_2 clusters. The electron cloud overlap between the $p\pi^*$ orbital of H_2 and the $d\sigma + sp$ hybridized orbital of Au for some Au_nH_2 clusters is also illustrated. But, the electron cloud overlap between the frontier orbital of two H atoms can not be found in most Au_nH_2 clusters. On the contrary, the obvious delocalization of HOMOs and LUMOs only can be found in some small Au_nH_2 clusters obtained by AE method. With increasing size of Au_nH_2 clusters, the HOMO and LUMO have become more and more localized with the contribution from only a few atoms in the cluster. This discrepancy may be explained in terms of the strong scalar relativistic effect in small gold cluster. The strong scalar relativistic effect caused by the high speed motion of out shell electrons and the spin-orbit coupling leads to the shrinking of the size of the s orbitals, lowers the corresponding energy level and enhances the shielding effect of inner electrons. Thus, promotes the outward expanding of the d , f orbitals and makes the s , d electrons closer. The enhancement of $s - d$ hybridization is very obvious and the frontier orbitals become dispersive. The total energy of system decreases and the stability enhancement may be expected. Meanwhile, H_2 molecule adsorption onto a gold cluster can be seen that it is only partly involving an excitation of the formerly unoccupied orbital in the cluster, since the open shell has to be ‘pushed up’ when the cluster-H bond is formed. The same argument can also be found in connection with the bond preparation method used in the cluster surface model⁶³ and is also the reason why the H orbitals can not be seen in many HOMOs and LUMOs of Au_nH_2 clusters.

3.3 Frequency analysis

Since many experiments on the adsorption behaviour of nanosized gold clusters were based on the FTIR method and focused on the vibrational frequency of different mode in the adsorption system. Higher vibrational frequency often corresponds to the stronger interaction between the specified bonded atoms. From table 4, it is easy to be found that the highest frequency of Au–H mode obtained by AER method is significantly higher than that of Au–H mode obtained by AE method and the highest frequency of H–H mode obtained by AER method is obviously lower than that of H–H mode obtained by AE method. Meanwhile, all the highest vibrational frequencies of H–H mode obtained by AER and AE methods are lower than those of single H_2 molecule. It is believed that after adsorption, the H–H interaction is weakened and reactivity of H_2 is enhanced for all Au_nH_2 clusters obtained by AER and AE method. The scalar relativistic effect might

Table 4. The calculated highest frequencies of Au–Au, Au–H and H–H mode for Au_nH_2 clusters.

Cluster	ν_{Au-H} (cm^{-1})		ν_{H-H} (cm^{-1})	
	AER	AE	AER	AE
H_2			4387.2	4392.7
AuH_2	336.8	179.1	3656.5	4274.3
Au_2H_2	304.9	180.8	2447.0	4314.3
Au_3H_2	485.7	108.4	2368.4	4360.2
Au_4H_2	443.4	119.3	2313.0	3986.1
Au_5H_2	417.5	124.5	2202.0	4317.0
Au_6H_2	272.6	128.2	3052.8	4351.3
Au_7H_2	416.0	130.8	2081.1	4281.3
Au_8H_2	401.9	137.6	1615.8	4301.7
Au_9H_2	378.2	174.4	1481.4	4187.5
$Au_{10}H_2$	315.5	144.4	1475.7	4315.3
$Au_{11}H_2$	397.6	143.6	1419.1	4281.7
$Au_{12}H_2$	391.0	127.0	1432.6	4356.7
$Au_{13}H_2$	380.8	123.8	1439.2	4329.4

strengthen the Au–H interaction and weaken the H–H interaction, appearing as the much shorter Au–H bond-length and much longer H–H distance. It also proves again that the scalar relativistic effect is favourable to the dissociative adsorption of H_2 molecule onto small gold cluster and the reactivity enhancement of H_2 molecule.

4. Conclusions

In this paper, a comparative study between all-electron relativistic (AER) calculation and all-electron (AE) calculation on the H_2 molecule adsorption onto small gold clusters has been made. Compared with the corresponding Au_nH_2 cluster obtained by AE method, the Au_nH_2 cluster obtained by AER method has much shorter Au–H bond-length, much longer H–H distance, larger binding energy and adsorption energy, higher VIP, greater charge transfer, higher vibrational frequency of Au–H mode and lower vibrational frequency of H–H mode. All these characteristics suggest that the scalar relativistic effect might strengthen the Au–H bond and weaken the H–H bond, appearing as the much shorter Au–H bond-length and much longer H–H distance. The delocalization of HOMO and LUMO for Au_nH_2 cluster obtained by AER method is obvious. It is believed that the scalar relativistic effect is favourable to the H_2 molecule adsorption onto small gold cluster and the reactivity enhancement of H_2 molecule. It is also one of the reasons why the dissociative adsorptions take place in some Au_nH_2 clusters. With increasing size of Au_nH_2 clusters, the influence of scalar relativistic effect becomes more significant. Some further studies

focused on the influence of scalar relativistic effect on the adsorption behaviour of other small molecules onto gold clusters are necessary in the future.

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