

# Hydrogen adsorption and magnetic behavior of $\text{Fe}_n$ and $\text{Co}_n$ clusters: Controlling the magnetic moment and anisotropy one atom at a time

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Theoretical studies to investigate the effect of H absorption on the magnetic moment of small  $\text{Fe}_n$  and  $\text{Co}_n$  clusters have been carried out using gradient corrected density-functional approach. Our studies on clusters containing up to four transition metal and 2 H atoms show that the successive addition of H atoms can lead to monotonic or oscillatory change from the free cluster magnetic moment. A detailed analysis of the density of electronic states shows that the variations in the magnetic moment can be related to the location of the lowest unoccupied molecular orbital in the parent cluster. It is shown that the addition of hydrogen can substantially change the magnetic anisotropy. In particular  $\text{Co}_3\text{H}_2$  is shown to exhibit magnetic anisotropy that is higher than any of the known anisotropies in the molecular nanomagnets.

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## I. INTRODUCTION

It is now well known that small clusters of itinerant transition metal elements  $\text{Fe}_n$ ,  $\text{Co}_n$ , and  $\text{Ni}_n$ , have higher magnetic moments than the corresponding bulk solids.<sup>1</sup> The increase in moment is largely due to surface sites that have lower coordination than the interior atoms or bulk. The reduced size also leads to new dynamical behaviors. For example, the reduction in size reduces the magnetic anisotropy energy. In clusters containing up to a few hundred atoms, the anisotropy energy is less than the ordinary thermal energies. Consequently, the magnetic moment of the cluster can undergo directional fluctuations under ordinary thermal conditions. Indeed, transition metal clusters have been found to exhibit superparamagnetic relaxations in Stern Gerlach beam experiments.<sup>2</sup>

An area that has attracted recent attention is the effect of chemisorption on the magnetic properties of clusters. It is well known that the catalytic properties of clusters can change dramatically with size. For example, Whetten *et al.*<sup>3</sup> showed that the reactivity of  $\text{Fe}_n$  clusters toward  $\text{H}_2$  and  $\text{D}_2$  was related to the ionization potentials of the free clusters. In their experiments, the clusters with the lowest ionization potential were found to be the most reactive toward chemisorption of molecular hydrogen. They argued that hydrogen chemisorption requires charge transfer from the metal cluster and therefore the reactivity is higher for clusters with lower ionization potentials. The observation that 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.*<sup>4</sup> recently investigated the effect of hydrogen on the magnetic moment of  $\text{Fe}_n$  clusters in molecular beam experiments and found intriguing results. Knickelbein *et al.* generated  $\text{Fe}_n$  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,<sup>5</sup> the magnetic moments of the saturated hydrogenated clusters containing 12–25 atoms were higher than those of the free clusters. These studies, however, are unable to address the progression of the magnetic properties as H atoms are successively added.

The purpose of the present paper is to examine the effect of hydrogenation on the magnetic properties of  $\text{Fe}_n$  and  $\text{Co}_n$  clusters containing one to four atoms, one hydrogen atom at a time. The key issue on which we want to focus is how the successive H atoms affect the magnetic moment and the magnetic anisotropy in clusters. Our first-principles studies based on the gradient corrected density-functional theory also bring out an interesting quantum effect. Depending on the cluster, the magnetic moment changes monotonically or exhibits oscillation upon successive addition of H atoms. What is exciting is that the progression of the magnetic moments can be rationalized as an addition of an electron to the electronic spectrum of the parent cluster. The variation in the magnetic moment are then related to the relative position of the unoccupied spin up or down orbital and thus a signature of the nature of the lowest unoccupied molecular orbital (LUMO's) in the parent. The presence of hydrogen also affects the magnetic anisotropy. Indeed, we identify clusters where the magnetic anisotropy energy per atom is several times larger than what is known for nanomagnets. These results suggest that the addition of hydrogen may provide unprecedented ways of controlling the magnetic moments, magnetic anisotropy, and the filling of electronic shells.

In Sec. II we describe the details of our method while Sec. III is devoted to a discussion of results. Finally, Sec. IV contains the conclusions of this work.

## II. DETAILS OF CALCULATIONS

The theoretical studies were carried out using a linear combination of atomic-orbital–molecular-orbital approach

within a gradient corrected density-functional approach.<sup>6</sup> In particular, we use the NRLMOL (Naval Research Laboratory Molecular Orbital Library) set of codes developed by Peder-son and co-workers.<sup>7</sup> As the computational procedure is well documented in previous works, here we only give relevant details. The molecular orbitals are formed from a linear combination of Gaussian functions centered at the atomic sites. The integrals required in the solution of the density-functional equation are calculated via numerical integration over a mesh of points. The exchange correlation contributions are included using a gradient corrected functional proposed by Perdew *et al.*<sup>8</sup> and all the calculations were carried out at the all electron level.

The present studies include  $\text{Fe}_n\text{H}_m$  and  $\text{Co}_n\text{H}_m$  clusters containing up to four transition metal and two H atoms. The basis set for Fe and Co had 20 primitive Gaussians contracted into  $7s$ ,  $5p$ , and  $4d$  Gaussians, and for H there were six primitive Gaussians contracted into  $4s$ ,  $3p$ , and  $1d$  Gaussians. In each case, the basis sets were supplemented by a diffuse Gaussian. We first calculated the ground state of the pure clusters. A single hydrogen was then added in the possible on-top, bridge, or hollow sites and the geometry optimized by moving atoms in the direction of forces till the Hellmann-Feynman forces were smaller than 0.001 hartree/bohr. Finally, various spin multiplicities were tried to find the spin multiplicity.

In addition to the magnetic moment we investigated the magnetic anisotropy energy in selected bare and hydrogenated clusters. As pointed out in our previous paper,<sup>9</sup> the main contribution to this quantity comes from the spin orbit coupling. An  $\mathbf{L}\cdot\mathbf{S}$  representation for the spin orbit term,  $U(\mathbf{r},\mathbf{p},\mathbf{s})$ , omits nonspherical corrections. However, the exact representation

$$U(\mathbf{r},\mathbf{p},\mathbf{S}) = -\frac{1}{2c}\mathbf{S}\cdot\mathbf{p}\times\nabla\Phi(\mathbf{r}), \quad (1)$$

where  $\mathbf{S}$  is the spin vector,  $\mathbf{p}$  is the momentum, and  $\Phi(\mathbf{r})$  is the Coulomb potential which is actually much easier to implement numerically. As we showed previously,<sup>9</sup> the calculation of the matrix elements using this expression only requires knowledge of the coulomb potential and the gradient of the basis functions. The anisotropy barrier is related to the shift of the total energy as a function of the quantization axis. For details the reader is referred to earlier papers.<sup>10-13</sup>

### III. RESULTS AND DISCUSSION

Figure 1 shows the ground-state geometry of  $\text{Fe}_n$  and  $\text{Fe}_m\text{H}_m$  clusters. We first start by comparing our results on pure  $\text{Fe}_n$  clusters with the previous density-functional studies. For  $\text{Fe}_3$  the ground state is an isosceles triangle while the ground state of  $\text{Fe}_4$  is a distorted tetrahedral structure. The Fe-Fe bond lengths in  $\text{Fe}_3$  and  $\text{Fe}_4$  vary from 2.2–2.4 Å and are higher than 2.02 Å in  $\text{Fe}_2$ . We find spin multiplicities of 5, 7, 11, and 15 for Fe,  $\text{Fe}_2$ ,  $\text{Fe}_3$ , and  $\text{Fe}_4$ . All these results are in good agreement with previous density-functional studies<sup>14</sup> on  $\text{Co}_n$  clusters by Castro *et al.* and Gutsev *et al.* on  $\text{Fe}_3$ . As pointed out before by Gutsev *et al.*, the spin multiplicity of

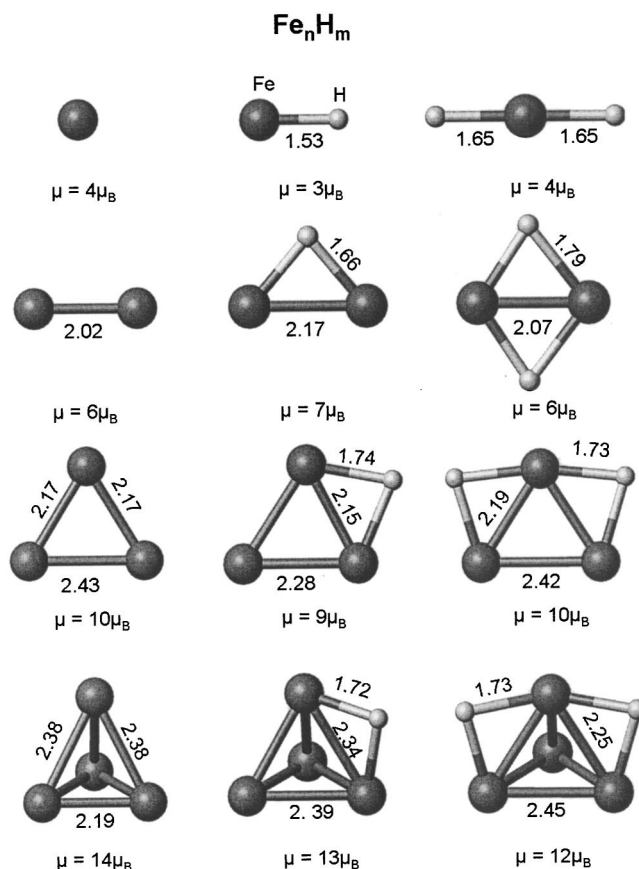


FIG. 1. Ground-state geometries of  $\text{Fe}_n\text{H}_m$  clusters. The large circles are the Fe atoms while the small circles are the H atoms. All distances are in Å.

$\text{Fe}_3$  calculated by Castro *et al.* does not account for the experimental photodetachment spectra.

The main motive of the current work is to investigate the adsorption of H. For  $\text{Fe}_2$ , the additional hydrogen could occupy the on-top or the bridge site. In case of  $\text{Fe}_3$ , one has the possibility of hollow site, in addition to the on-top and bridge. For the multiple hydrogens, the H could be adsorbed dissociatively or in the molecular form. For each cluster, we examined all the possibilities and Fig. 1 shows the ground-state geometries of all the clusters. FeH molecule has been observed in several astrophysical sources<sup>15</sup> and extensively studied both theoretically<sup>16</sup> and experimentally.<sup>17</sup> Experiments indicate that it has a spin multiplicity of 4 as obtained by us. Our calculated bond length of 1.53 Å is also in agreement with Langhoff and Bauschlicher,<sup>16</sup> who have studied the ground-state properties of FeH using CASSCF/MRCI (Complete-Active-Space Self-Consistent-Field Multi-reference Configuration-Interaction) method and find a bond length of 1.59 Å for the  $X^4\Delta$  state. For  $\text{FeH}_2$ , our calculated linear structure with a spin multiplicity of 5 is also consistent with experiments and previous calculations.<sup>18,19</sup> Note that the hydrogen occupies bridge sites in  $\text{Fe}_2\text{-Fe}_4$  and the FeH distance increases from 1.52 Å in FeH to 1.72 Å in  $\text{Fe}_4\text{H}$ . In Table I we present the binding energy of the various pure clusters and the gain in energy  $\Delta E_H$  in adding the H atom defined by

TABLE I. The atomization energy (A. E.) and the energy gain in adding an H atom  $\Delta E_H$  for  $\text{Fe}_n\text{H}_m$  clusters.

Cluster	A. E. (eV)	$\Delta E_H$ (eV)
FeH	2.15	2.15
FeH <sub>2</sub>	4.89	2.74
Fe <sub>2</sub>	2.48	-
Fe <sub>2</sub> H	4.58	2.10
Fe <sub>2</sub> H <sub>2</sub>	7.58	3.00
Fe <sub>3</sub>	5.00	-
Fe <sub>3</sub> H	7.94	2.94
Fe <sub>3</sub> H <sub>2</sub>	11.11	3.17
Fe <sub>4</sub>	8.22	-
Fe <sub>4</sub> H	11.29	3.06
Fe <sub>4</sub> H <sub>2</sub>	14.35	3.07

$$\Delta E_H = -[E(\text{Fe}_n\text{H}_x) - E(\text{Fe}_n\text{H}_{x-1}) - E(\text{H})]. \quad (2)$$

For pure clusters the binding energy  $\Delta E$  is defined as

$$\Delta E = -[E(\text{Fe}_n) - nE(\text{Fe})]. \quad (3)$$

Note that the hydrogen binding energies increase with clusters size and vary from 2.15 eV to 3.06 eV.

Figure 2 shows the corresponding results on bare and hydrogenated  $\text{Co}_n$  clusters. There are significant differences in the nature of adsorption. As opposed to  $\text{FeH}_2$  that has a linear structure, the ground state of  $\text{CoH}_2$  is a bent structure. For  $\text{Co}_2\text{H}$ , the H atom is bound to only one Co atom while for  $\text{Co}_2\text{H}_2$ , the ground state corresponds to a  $\text{H}_2$  molecule bound to  $\text{Co}_2$ . The situation for  $\text{Co}_3$  and  $\text{Co}_4$  is similar to that for the corresponding  $\text{Fe}_n$  clusters. The H is absorbed in bridge positions. Table II gives the atomization energy of the pure  $\text{Co}_n$  clusters as well as the energy gain in adding the subsequent H atoms to the clusters. The hydrogen binding energies vary from 2.42 to 3.07 eV.

The focus of the current work is the changes in magnetic moment upon adsorption of H. For Fe, Fe<sub>2</sub>, Fe<sub>3</sub>, and Co<sub>2</sub>, the successive H atoms lead to an oscillatory change in the magnetic moment while in the remaining clusters the magnetic moment decreases upon adsorption of H. The oscillatory behavior implies that in certain clusters, the addition of H can increase the magnetic moment. This is contrary to the case on surfaces where the H adsorption reduces the magnetic moment.<sup>19</sup> This shows that the behavior of small particles can be very different from larger clusters,<sup>4</sup> thin layers, or bulk. We now show that the progressions of the magnetic moment can be understood within a simple model<sup>20</sup> we had earlier proposed for hydrogen around  $\text{Ni}_n$  clusters.<sup>10</sup> Consider a filled orbital of parent cluster (before the addition of hydrogen) with a pair of electrons interacting with the H 1s state of the adsorbed atom. The interaction leads to the formation of a low-lying bonding and a high-energy antibonding molecular orbital. Of the three electrons involved in the process, the two occupy the bonding orbital. The third electron goes to the LUMO of parent orbital. The change in moment is thus related to the location of the lowest unoccu-

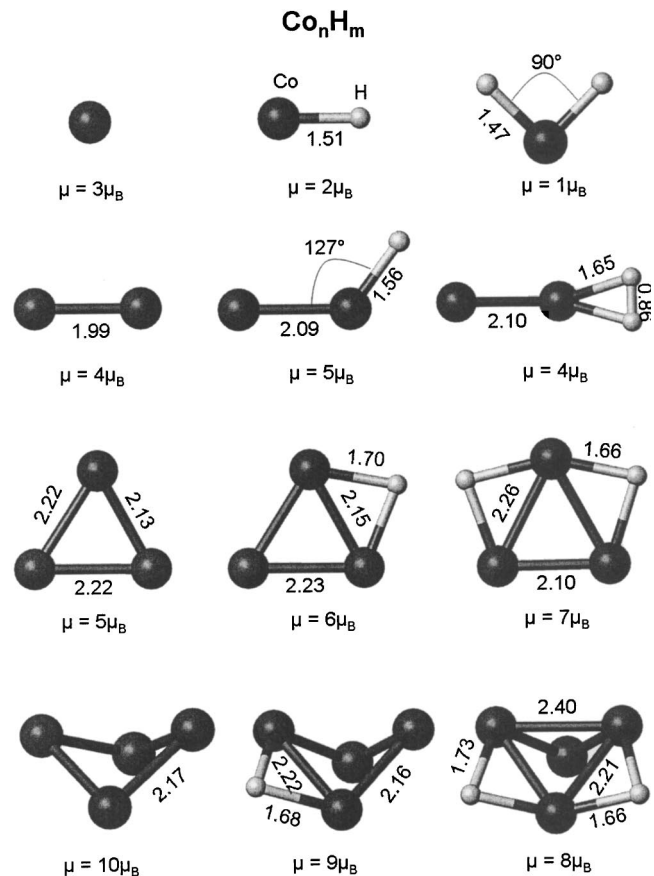


FIG. 2. Ground-state geometries of  $\text{Co}_n\text{H}_m$  clusters. The large circles are the Co atoms while the small circles are the H atoms. All distances are in Å.

piated orbital of the preceding cluster. This can also be arrived from another point. 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 transition metal atom. These considerations may not hold when the LUMO of the majority and minority spin states are close in energy. This is because

TABLE II. The atomization energy (A. E.) and the energy gain in adding an H atom  $\Delta E_H$  for  $\text{Co}_n\text{H}_m$  clusters.

Cluster	A. E. (eV)	$\Delta E_H$ (eV)
CoH	2.63	2.63
CoH <sub>2</sub>	5.05	2.42
Co <sub>2</sub>	2.57	-
Co <sub>2</sub> H	4.93	2.36
Co <sub>2</sub> H <sub>2</sub>	7.50	2.57
Co <sub>3</sub>	4.90	-
Co <sub>3</sub> H	7.97	3.07
Co <sub>3</sub> H <sub>2</sub>	10.93	2.96
Co <sub>4</sub>	8.20	-
Co <sub>4</sub> H	11.14	2.94
Co <sub>4</sub> H <sub>2</sub>	14.13	2.98

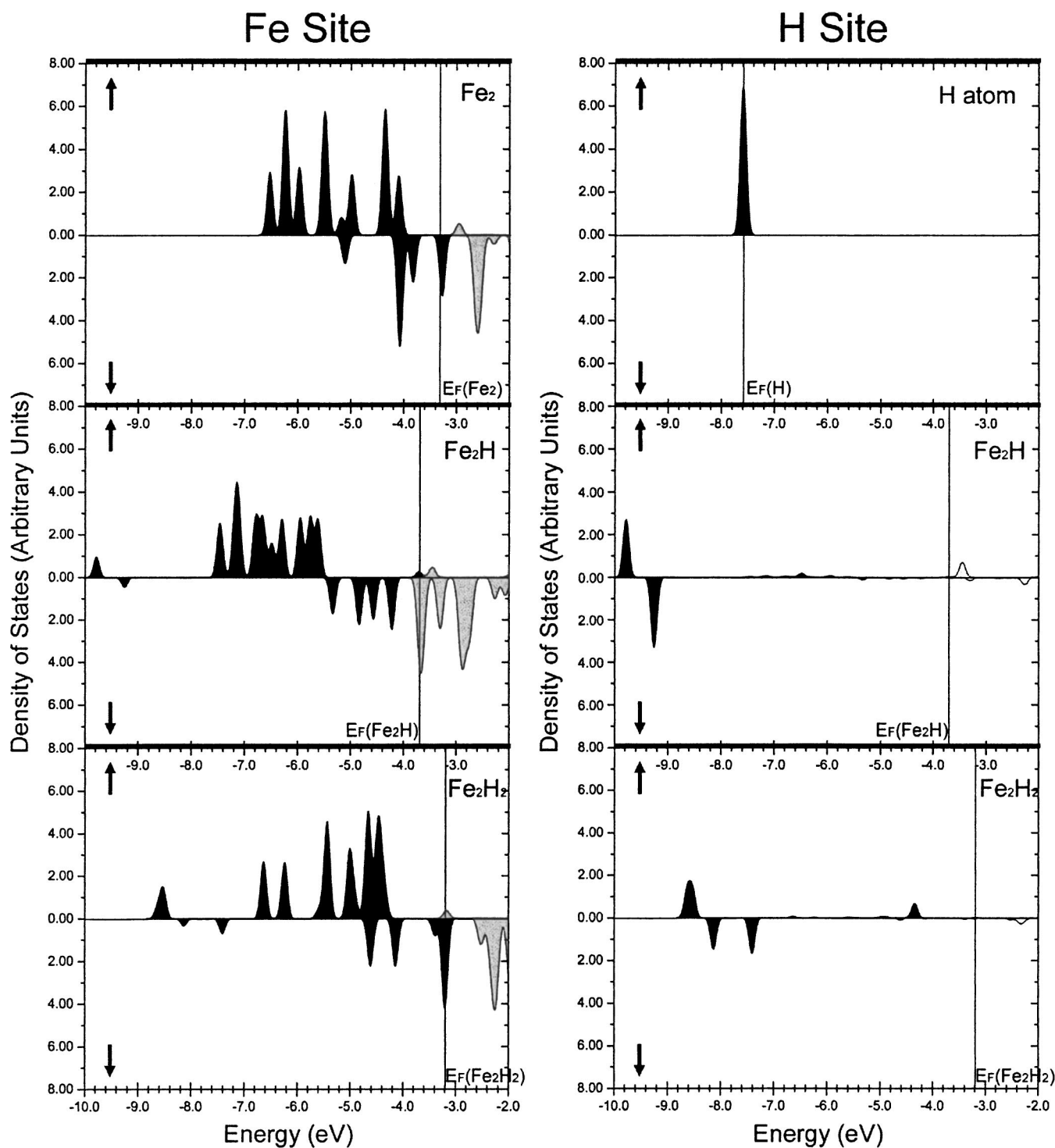


FIG. 3. Density of states in  $Fe_2H_m$  clusters. The dark regions correspond to the filled states while the lightly shaded region corresponds to the unfilled states.

if the LUMO of the preceding cluster belongs to the minority manifold and the LUMO of majority 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 that this simple model does apply to real clusters, we show in Fig. 3 the local density of states<sup>9</sup> at the Fe and H sites in  $Fe_2H$  and  $Fe_2H_2$  clusters. Also shown is the density of states in pure  $Fe_2$  and H atom. The blue region corresponds to the filled states while the red region corresponds to the empty states. Let us start with the addition of H



TABLE III. The net spin  $S$  (difference between spin-up and spin-down electrons, multiplicity= $S+1$ ), HOMO and LUMO levels (hartrees) of the majority and minority spin states and  $\delta E$  (eV) in  $\text{Fe}_n$  and  $\text{Fe}_n\text{H}_m$  clusters.

Cluster	$S$	Majority		Minority		$\delta E$
		HOMO	LUMO	HOMO	LUMO	
Fe	4	-0.179 944	-0.052 019	-0.139 796	-0.131 764	-2.17
FeH	3	-0.162 907	-0.091 554	-0.113 823	-0.096 705	-0.14
FeH <sub>2</sub>	4	-0.232 789	-0.057 118	-0.203 967	-0.181 582	-3.39
Fe <sub>2</sub>	6	-0.151 474	-0.108 926	-0.120 924	-0.097 150	0.32
Fe <sub>2</sub> H	7	-0.135 991	-0.126 842	-0.155 026	-0.135 469	-0.23
Fe <sub>2</sub> H <sub>2</sub>	6	-0.159 490	-0.116 515	-0.117 524	-0.092 557	0.65
Fe <sub>3</sub>	10	-0.135 009	-0.124 616	-0.138 878	-0.120 599	0.11
Fe <sub>3</sub> H	9	-0.156 114	-0.122 212	-0.131 600	-0.115 216	0.19
Fe <sub>3</sub> H <sub>2</sub>	10	-0.152 203	-0.089 234	-0.154 845	-0.137 683	-1.32
Fe <sub>4</sub>	14	-0.144 854	-0.138 154	-0.154 319	-0.136 833	0.04
Fe <sub>4</sub> H	13	-0.140 862	-0.133 420	-0.145 607	-0.122 908	0.29
Fe <sub>4</sub> H <sub>2</sub>	12	-0.153 154	-0.127 651	-0.139 506	-0.113 730	0.38

to Fe<sub>2</sub>. As the first panel shows, the 1s state of hydrogen is deep in energy. Upon interaction with Fe<sub>2</sub>, the H induces deep spin-up and spin-down bonding states formed from the interaction between the 1s orbital of the H and the Fe states. The corresponding antibonding states are above the highest occupied molecular orbital (HOMO) of the parent cluster. Note that the LUMO of the Fe<sub>2</sub> gets filled upon the addition of the H atom. The same situation occurs in going from Fe<sub>2</sub>H to Fe<sub>2</sub>H<sub>2</sub> where the empty red state of the Fe<sub>2</sub>H gets occupied. To further show that these simple considerations do have some validity, we list in Tables III and IV, the HOMO and LUMO of all the clusters. It is gratifying that the simple rule is obeyed in almost all cases. In particular, when  $\delta E$  is

less than  $-0.40$  eV, the spin magnetic moment does decrease upon addition of H.

The above simple model brings out an interesting point. For the cases, where the magnitude of  $\delta E$  is large, the effect of adding hydrogen should be similar to adding an electron. To investigate this, we calculated the spin magnetic moments of Fe<sup>-</sup>, Fe<sub>2</sub><sup>-</sup>, Co<sup>-</sup>, and Co<sub>4</sub><sup>-</sup> where  $\delta E$  is large. For Fe<sup>-</sup> and Co<sup>-</sup>, the spin multiplicity of the anionic clusters were 4 and 3, respectively, as in case of FeH and CoH (Tables III and IV). For Fe<sub>2</sub><sup>-</sup> and Co<sub>4</sub><sup>-</sup>, the spin multiplicities were 8 and 10, respectively, again matching those of Fe<sub>2</sub>H and Co<sub>2</sub>H. These agreements provide further evidence for the validity of the above simple model.

TABLE IV. The net spin  $S$  (difference between spin-up and spin-down electrons, multiplicity= $S+1$ ), HOMO and LUMO levels (hartrees) of the majority and minority spin states and  $\delta E$  (eV) in  $\text{Co}_n$  and  $\text{Co}_n\text{H}_m$  clusters.

Cluster	$S$	Majority		Minority		$\delta E$
		HOMO	LUMO	HOMO	LUMO	
Co	3	-0.173 727	-0.040 531	-0.140 880	-0.131 632	-2.47
CoH	2	-0.166 856	-0.095 300	-0.134 036	-0.144 988	-0.54
CoH <sub>2</sub>	1	-0.171 549	-0.107 954	-0.154 575	-0.117 048	-0.27
Co <sub>2</sub>	4	-0.158 471	-0.109 005	-0.118 447	-0.105 491	0.09
Co <sub>2</sub> H	5	-0.182 340	-0.096 558	-0.185 038	-0.154 336	-1.57
Co <sub>2</sub> H <sub>2</sub>	4	-0.183 003	-0.083 674	-0.151 826	-0.121 490	-1.03
Co <sub>3</sub>	5	-0.150 435	-0.109 867	-0.113 129	-0.102 233	0.21
Co <sub>3</sub> H	6	-0.161 682	-0.123 111	-0.135 256	-0.121 966	0.07
Co <sub>3</sub> H <sub>2</sub>	7	-0.155 817	-0.081 884	-0.159 553	-0.152 129	-2.10
Co <sub>4</sub>	10	-0.156 897	-0.114 585	-0.160 880	-0.143 870	-0.81
Co <sub>4</sub> H	9	-0.148 860	-0.117 933	-0.151 036	-0.131 550	-0.38
Co <sub>4</sub> H <sub>2</sub>	8	-0.169 110	-0.115 405	-0.138 197	-0.124 492	-0.25

TABLE V. Magnetic anisotropy energy of  $\text{Fe}_n\text{H}_m$  and  $\text{Co}_n\text{H}_m$  clusters. The energies are expressed in kelvins (K).

Cluster	MAE (K)	MAE/atom (K)
CoH	1.07	0.53
CoH <sub>2</sub>	10.70	3.57
Co <sub>2</sub>	9.25	4.63
Co <sub>2</sub> H	12.66	4.22
Co <sub>2</sub> H <sub>2</sub>	16.52	4.13
Co <sub>3</sub>	18.04	6.01
Co <sub>3</sub> H	27.77	6.94
Co <sub>3</sub> H <sub>2</sub>	75.88	15.18
Co <sub>4</sub>	22.00	5.50
Co <sub>4</sub> H	27.65	5.53
Co <sub>4</sub> H <sub>2</sub>	25.83	4.31
FeH	43.10	21.55
FeH <sub>2</sub>	16.49	5.50
Fe <sub>2</sub>	5.44	2.72
Fe <sub>2</sub> H	15.15	5.05
Fe <sub>2</sub> H <sub>2</sub>	15.94	3.99
Fe <sub>3</sub>	26.59	8.86
Fe <sub>3</sub> H	5.41	1.35
Fe <sub>3</sub> H <sub>2</sub>	11.72	2.34
Fe <sub>4</sub>	32.20	8.05
Fe <sub>4</sub> H	9.59	1.92
Fe <sub>4</sub> H <sub>2</sub>	4.82	0.80

Figure 3 also shows that the variations in the moment also lead to variations in the exchange splitting between the majority and minority manifolds. A direct outcome of the changes in the electronic structure is the magnetic anisotropy energy. Using the procedure outlined above, we calculated the magnetic anisotropy in all the clusters. Table V gives the results of our calculations for  $\text{Fe}_n\text{H}_m$  and  $\text{Co}_n\text{H}_m$  clusters. Note that the addition of H can significantly alter the mag-

netic anisotropy. In particular,  $\text{Co}_3\text{H}_2$  has a magnetic anisotropy energy of 76 K. Note that this is unusually high considering the fact that even  $\text{Mn}_{12}\text{O}_{12}$  nanomagnet consisting of 24 atom  $\text{Mn}_{12}\text{O}_{12}$  unit has only an anisotropy energy of around 50 K. The reason for this large anisotropy lies in the electronic spectrum. As pointed out in our previous papers<sup>11–13</sup> the anisotropy energy depends on the matrix elements and the energy difference between the majority filled and minority unfilled states near the HOMO. What is more important is to note that the addition of H can have significant effect on magnetic anisotropy.

#### IV. CONCLUSIONS

To summarize, the present studies show that the effect of hydrogen adsorption in small clusters can be significantly different than in bulk. For the bulk surfaces, H invariably leads to a quenching of the magnetic moment. In clusters, however, the moment can also increase upon adsorption. It is shown that the progressions in the magnetic moment can be understood within a simple model involving the unoccupied electronic states in the parent cluster. The effect of adding H can effectively be looked upon as adding an electron to the unfilled states of the parent cluster. In addition to the spin magnetic moment, the changes in the electronic structure can result in large variations in the magnetic anisotropy. In particular, some of the hydrogenated clusters have magnetic anisotropies that are larger than in any of the known nanomagnets. We hope that the present investigations would inspire experiments to probe these interesting effects.

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<sup>1</sup>H. Zhang, B. K. Rao, S. N. Khanna, and P. Jena, Phys. Rev. B **55**, 4174 (1997).

<sup>2</sup>S. N. Khanna and S. Linderorth, Phys. Rev. Lett. **67**, 742 (1991).

<sup>3</sup>R. L. Whetten, D. M. Cox, D. J. Trevor, and A. Kaldor, Phys. Rev. Lett. **54**, 1494 (1985).

<sup>4</sup>M. B. Knickelbein, G. M. Koretsky, K. A. Jackson, M. R. Pederson, and Z. Hajnal, J. Chem. Phys. **109**, 10692 (1998); M. B. Knickelbein, Annu. Rev. Phys. Chem. **50**, 79 (1999).

<sup>5</sup>G. J. Mankey, M. T. Kief, F. Huang, and R. F. Willis, J. Vac. Sci. Technol. A **11**, 2034 (1993).

<sup>6</sup>W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

<sup>7</sup>M. R. Pederson and K. A. Jackson, Phys. Rev. B **41**, 7453 (1990); K. A. Jackson and M. R. Pederson, *ibid.* **42**, 3276

(1990); D. V. Porezag and M. R. Pederson, Phys. Rev. A **60**, 2840 (1999).

<sup>8</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

<sup>9</sup>M. R. Pederson and S. N. Khanna, Phys. Rev. B **60**, 9566 (1999).

<sup>10</sup>C. Ashman, S. N. Khanna, and M. R. Pederson, Chem. Phys. Lett. **368**, 257 (2003).

<sup>11</sup>J. Kortus, T. Baruah, M. R. Pederson, C. Ashman, and S. N. Khanna, Appl. Phys. Lett. **80**, 4193 (2002).

<sup>12</sup>M. R. Pederson, J. Kortus, and S. N. Khanna, J. Appl. Phys. **91**, 7149 (2002).

<sup>13</sup>M. R. Pederson, D. V. Porezag, J. Kortus, and S. N. Khanna, J. Appl. Phys. **87**, 5487 (2000).

<sup>14</sup>M. Castro, C. Jamorski, and D. R. Salahub, Chem. Phys. Lett. **271**, 133 (1997); G. L. Gutsev, S. N. Khanna, and P. Jena, Phys. Rev. B **62**, 1604 (2000).

- <sup>15</sup>R. E. S. Clegg and D. L. Lambert, *Astrophys. J.* **226**, 931 (1978).
- <sup>16</sup>C. W. Bauschlicher Jr. and S. R. Langhoff, *Chem. Phys. Lett.* **145**, 205 (1988); S. R. Langhoff and C. W. Bauschlicher Jr., *J. Mol. Spectrosc.* **141**, 243 (1990).
- <sup>17</sup>S. P. Beaton, K. M. Evenson, T. Nelis, and J. M. Brown, *J. Chem. Phys.* **89**, 4446 (1988); A. E. Stevens, C. S. Feigerle, and W. C. Lineberger, *ibid.* **78**, 5420 (1983).
- <sup>18</sup>H. Körsen, W. Urban, and J. M. Brown, *J. Chem. Phys.* **110**, 3861 (1999).
- <sup>19</sup>P. E. M. Siegbahn, M. R. A. Blomberg, and C. W. Bauschlicher, Jr., *J. Chem. Phys.* **81**, 1373 (1984); G. Granucci and M. Perisco, *Chem. Phys.* **167**, 121 (1992).
- <sup>20</sup>R. Fournier and D. R. Salahub, *Surf. Sci.* **238**, 330 (1990).