

Analysis of the Reactivity of Small Cobalt Clusters

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The electronic structures of small cobalt clusters have been calculated within the local spin density approximation using the LCAO method. The calculations were done for simple geometries with the optimized number of interatomic bonds, and both for the bond length of the cobalt dimer and the bulk metal. The Fermi energy is found to be smaller for Co_N clusters with $N=3, 4, 5$ and $N>10$ than for the other ones. The variation of the Fermi energy with the cluster size correlates in a striking way with the observed H_2 tendency for chemisorption as found for cobalt clusters in a supersonic beam. Furthermore, the magnetic moments are somewhat smaller for these active clusters. In addition the lowest unoccupied levels of majority spin appear close to the highest occupied levels of minority spin which is not the case for the inert clusters.

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I. Introduction

Over the past decades extensive experimental and theoretical research in heterogeneous catalysis have been focused on the understanding of the microscopic behaviour of catalytic reactions [1–7]. In the experiments metal catalysts are dispersed on amorphous carriers or prepared in a form of well defined surfaces or surfaces with different types of defects as kinks, steps, terraces etc. Knowing, the structure of the substrate further studies in surface reaction dynamics have given information about the adsorption and desorption processes of reactants, and the physics behind the formation of intermediate species and final reaction products [8]. The theoretical treatments have been focused on the electronic structures of the substrate and particularly the adsorbate. One of the main objectives in this field has also been the calculation of potential energy surfaces of the combined system and in such a way get the possibility to map out the kinetics and dynamics of catalytic reactions [9–10]. However, without access to theoretical potential energy surfaces knowledge of charge transfer processes close to the Fermi level give useful information about catalytic activity. For example the adsorption

of CO on transition metals have to a large extent been analyzed in terms of σ donation and 2π back donation [11–13].

The electronic structures of the solid metal catalysts are strongly related to the catalytic behaviour of small metal clusters [14] and particularly to the activity of a few atom metal clusters as recently observed by a few groups [15–19]. In these experiments metal cluster beams were produced in a supersonic beam and seeded with reactants such as H_2 , D_2 , O_2 , H_2S or CH_4 . The Cu_N clusters were found to be quite inert to H_2 , while the activity for hydrogen chemisorption changed quite drastically as a function of the number of atoms for cluster beams of Co_N and Nb_N [18]. In the present work calculations of the electronic structure for some of these small cobalt clusters will be used for the analysis of the difference in reactivity for hydrogen chemisorption. The emphasis of the calculations has been to analyze trends of parameters as a function of cluster size such as the Fermi energy, one-electron levels at the Fermi level, magnetic moments, $3d$ - and $4s$ - contributions to the electronic structure and the energy difference between the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO).

A short summary of our computational procedure is presented in Sect. II with the results and discussion in Sect. III.

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II. Computational Procedure

The electronic structures of the small Co_N -clusters presented in this work were calculated within the local-density approximation [20, 21] in spin-polarized form with the exchange correlation potential by von Barth and Hedin [22]. A variational method is used to find the molecular wave functions which are determined within the LCAO method with numerical basis functions. The one-electron equations are solved within the self-consistent multipolar (SCM) method [23] as used in other applications of metal clusters [24–26]. The basis functions have been generated from a free atom $\text{Co } 3d^8 4s 4p^0$ configuration with the addition of $3d$, $4s$ and $4p$ wave functions generated from a free ion $\text{Co}^{4+} 3d^5 4s^0 4p^0$ configuration. The calculations for all the clusters were performed for two different bond-distances: $d(\text{Co}-\text{Co}) = 4.2$ a.u. and 4.7 a.u. corresponding to the bond-distance in the Co dimer [27] and bulk [28], respectively. The conformation or the geometry for the clusters bigger than the dimer is not known. Extended X-ray absorption fine structure (EXAFS) measurements for big copper particles have shown a linear decrease of the bond distance from the bulk value for smaller clusters [29]. Calculations for bond distances of the two extremes are therefore expected to show the general trends of the electronic structure for these cobalt clusters. We have done the calculations for clusters with optimum number of bonds of equal length, which can be done within the same symmetry group C_{3v} . Optimization of the geometry by minimization of the total energy as done in other works [25, 30–32] would be highly desirable. However, that would lead to too extensive calculations for the series of clusters treated in this work.

Co_3 is in our calculations treated as a triangle with extension to a pyramid and double pyramid for Co_4 and Co_5 , respectively. Co_6 has been calculated as a double pyramid with four atoms in a plane, one below and one above the plane which geometry can also be oriented to C_{3v} symmetry. This geometry has then been extended to the bigger clusters up to Co_7 and Co_8 , and finally geometries approaching the *fcc* structure were used for Co_{10} and Co_{13} . The levels close to the Fermi level have been occupied with a Fermi-Dirac distribution corresponding to a temperature of about 160 K or a thermal energy of about 14 meV.

III. Results and Discussion

The trends in hydrogen chemisorption on transition metal surfaces have recently been analyzed by Scillard

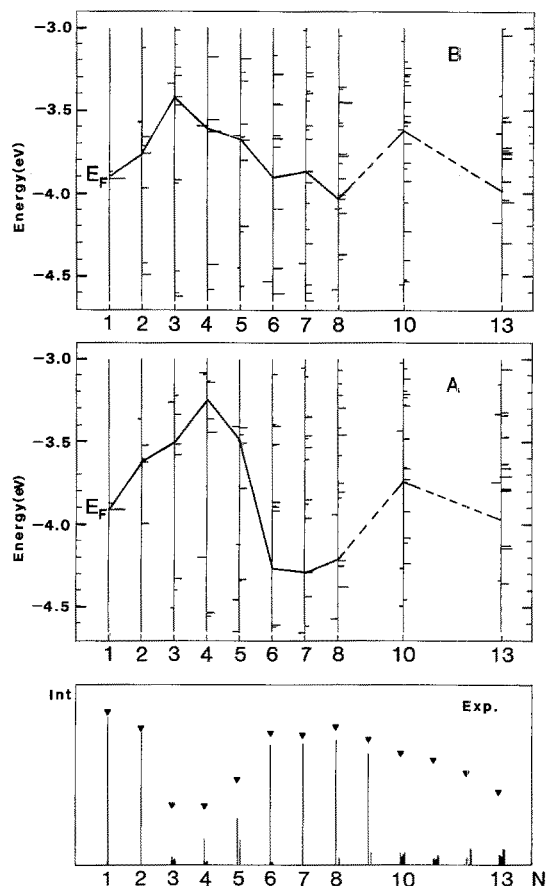


Fig. 1. Energy level diagram of the molecular one-electron levels in the Co_N clusters calculated with the bond distance for the dimer denoted by A and for the bulk denoted by B. The levels to the left for each cluster are those with majority up-spin, while those to the right are those with minority down-spin. As a comparison experimental photoionization spectra for pure cobalt clusters denoted by a black triangle and clusters reacted with D_2 are displayed with vertical lines [18]. The difference between these experimental spectra shows the reactivity of cobalt clusters

and Hoffmann [33] and calculated applying the effective medium theory by Nordlander et al. [34]. These results show that the chemisorption of hydrogen is due to *sd*-hybridization with a reduced occupancy of anti-bonding metal/hydrogen orbitals for the lighter substrate elements. The experimentally found activity of H_2 chemisorption on Co_N metal clusters and inertness for Cu_N clusters follows therefore the general theoretical and experimental trends of H_2 chemisorption on transition metal surfaces. The difference in chemisorption of H_2 on Cu and Ni surfaces have also recently been analyzed by Harris and Andersson [10].

A view of the photoionization mass spectra for Co_N metal clusters without and with seeded D_2 [18] is displayed in the lowest panel of Fig. 1. The most interesting result of this experiment is that clusters with $N=3, 4, 5$ and $N>10$ were very active for chemi-

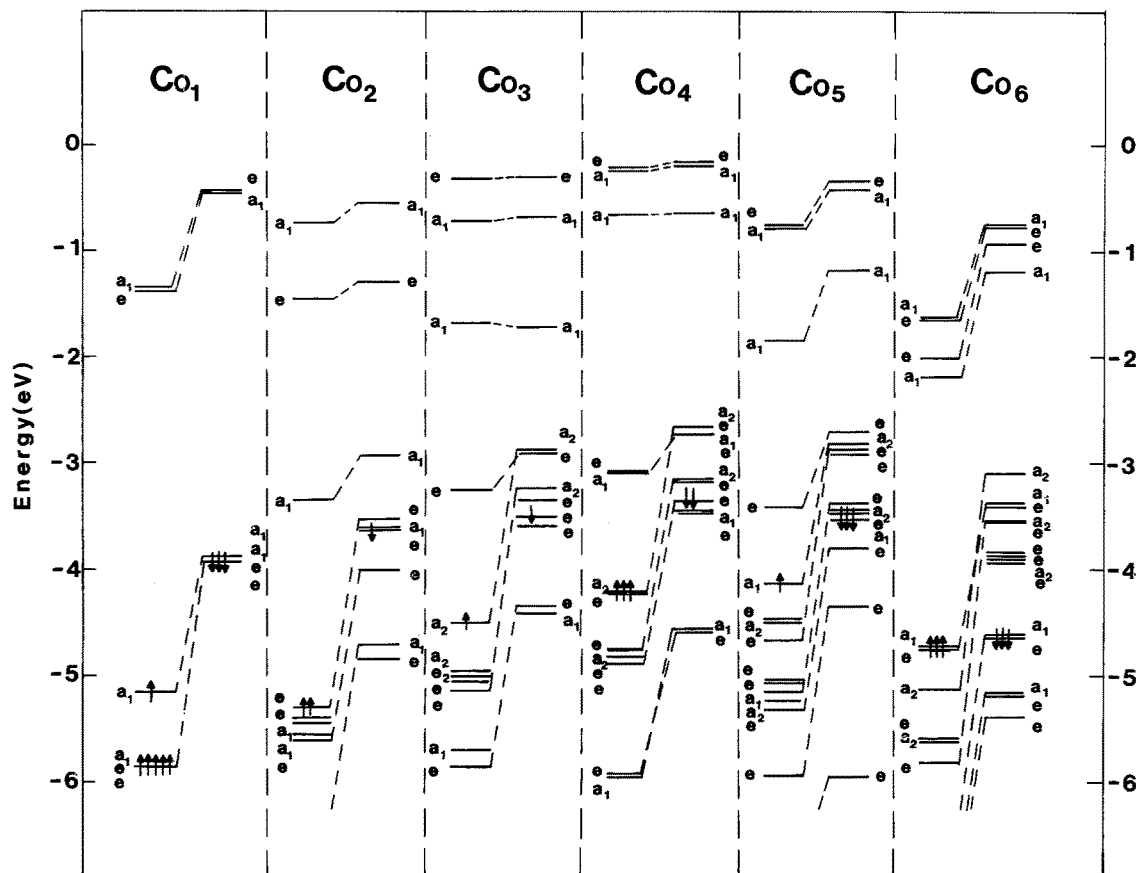


Fig. 2. Energy level diagram of the molecular one-electron levels in the Co_N clusters for $N=1-6$ calculated for the bond distance of the dimer. The labeling of the levels refer to the C_{3v} symmetry representation. The levels to the left are those with majority up-spin while those to the right are those minority down-spin. Occupancies of the last occupied levels are marked with arrows

sorption dissociation of H_2 while the clusters of other sizes were rather inert. The question is if this variation in reactivity with cluster size correlates with the cluster ionization energy as found experimentally for the Fe_N clusters [19]. The results for the Fermi level and the molecular levels close to the Fermi level for two series of our calculations are presented, denoted A and B for the dimer and bulk bond distance, respectively. The calculations show the same qualitative behaviour for the two bond distances as function of cluster size, although the results for the dimer bond distance are more pronounced. We notice a comparatively big change in the position of the Fermi level as a function of cluster size when going from Co_2 to Co_3 and from Co_5 to Co_6 and from Co_8 to Co_{10} , respectively. The value of the Fermi energy is significantly smaller for the reactive clusters and correlate in a striking way with the activity for hydrogen chemisorption of the Co_N clusters.

A more detailed view of the electronic structure for the Co_N clusters with $N=1-6$ calculated with the dimer bond distance is presented in Fig. 2. We notice how the spin-polarized calculations allow the majori-

ty up-spin to become stabilized and the minority down-spin to be destabilized relative to their common origin in a spin restricted calculation. The resulting difference in one-electron energies identified as the orbital exchange energy amounts to about 2 and 1.5 eV for the cobalt atom and the dimer, respectively. This exchange splitting is further reduced to less than 1 eV for the Co_3 , Co_4 and Co_5 clusters with an increase to 1.5 eV for Co_6 . Further examination of the molecular one-electron levels shows how the LUMO levels of majority up-spin are rather close in energy with the HOMO levels of minority down-spin for Co_N with $N=2-5$. This behaviour is changed drastically for the Co_6 cluster for which the energy difference between the same LUMO and HOMO levels is about 2 eV. A similar behaviour exist also for the Co_7 and Co_8 cluster as seen in Fig. 1. Another interesting feature for the Co_6 cluster is that HOMO levels of majority and minority spin from different one electron levels are close in energy. For detailed analysis of the relative importance of the HOMO and LUMO levels spin polarized calculations for clusters with adsorbed H_2 would be desirable. The relative

Table 1. Mulliken orbital and spin populations evaluated for the Co_N clusters. Values are given for calculations with the bond distance of the dimer (first line) and the bulk (second line) denoted by A and B in Fig. 1

	Orbital			Spin diff.			μ_{eff}
	3d	4s	4p	3d	4s	4p	
1	7.91	1.09	0.00	2.09	0.91	0.00	3.0
2	7.94	1.00	0.07	2.02	-0.01	-0.01	2.0
	7.94	1.01	0.06	2.03	-0.02	-0.01	2.0
3	7.99	0.83	0.19	1.87	-0.14	-0.06	1.7
	8.00	0.86	0.15	1.88	-0.17	-0.00	1.7
4	8.01	0.69	0.32	1.75	-0.15	-0.11	1.5
	7.95	0.80	0.28	1.89	0.03	0.01	1.9
5	7.94	0.77	0.34	1.83	-0.01	-0.02	1.9
	7.90	0.83	0.29	1.94	0.04	0.01	2.0
6	7.82	0.82	0.39	2.04	0.25	0.05	2.3
	7.81	0.87	0.34	2.08	0.21	0.04	2.3
7	7.86	0.81	0.36	1.97	0.15	0.02	2.1
	7.55	0.86	0.32	2.01	0.11	0.01	2.2
8	7.89	0.79	0.34	1.88	0.09	0.02	2.0
	7.81	0.89	0.32	2.05	0.15	0.04	2.2
10	7.94	0.80	0.26	1.80	0.03	-0.03	1.9
	7.90	0.85	0.25	1.91	0.06	-0.01	2.0
13*	8.04	0.88	0.29	0.90	-0.04	0.04	
	7.87	0.66	0.55	1.76	-0.07	-0.37	1.6
**	7.95	0.72	0.32	1.76	-0.04	-0.04	2.1
	7.87	0.82	0.31	1.95	0.15	0.04	

* Central atom in the cluster

** Outer atoms in the cluster

importance of metal-hydrogen interaction and the σ - and σ^* -bonding within the adsorbed H_2 molecule will then determine the dissociation or adsorption of H_2 .

A commonly discussed feature for the transition elements is the relative importance of 3d and 4s electrons [35]. Generally, the atomic ground state configuration for the transition elements is $nd^N(n+1)s^2$ except for a few elements as Cr, Ru, Rh, Mo, Pt for which $nd^{N+1}(n+1)s^1$ appears as the ground state configuration [36]. The configuration for metals is normally closer to $nd^{N+1}(n+1)s^1$ [37], which is also the configuration used in the generation of our basis set. Examination of the molecular orbitals through a Mulliken orbital- and spin-analysis in terms of our basis functions is presented in Table 1. We notice how the $3d^8 4s$ configuration for the cobalt atom and the dimer is changed for the bigger clusters with redistribution of the 4s to the 3d and 4p occupancy. The most striking effect is the orbital contribution to the spin difference i.e. the difference between the value of up (majority) and down (minority) spins for the reactive clusters with a zero and even negative value for clusters with $N=3, 4, 5, 10, 13$. Summation of the spins gives magnetic moments presented in the last column in Table 1. These values should be compared with the total magnetic moment of $1.72 \mu_B$ for

the metal of which $1.59 \mu_B$ represents the spin part [38, 39].

To summarize, there is a striking correlation between the cluster size dependence of the Fermi energy, HOMO/LUMO electronic structure, magnetic moments etc to the experimentally observed reactivity for hydrogen chemisorption. Further work is now in progress for calculations of Nb_N clusters and for the combined system of a Co_N cluster and a H_2 molecule. One of the goals is to analyze the importance of symmetry rules [40] in chemisorption which has been used particularly in the analysis of CO chemisorption [11, 12, 41].

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