

Cluster Calculations for H₂ Dissociation on Cu and Ni

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Abstract

Self-consistent cluster calculations have been carried out for hydrogen dissociation on Cu and Ni clusters using local-density theory and the LCAO-DVM expansion. We find physisorption, chemisorption and dissociation minima in the resulting two-dimensional potential energy surfaces, and for the Ni cluster, also an indication of the associative molecular chemisorption state. For Cu we find a considerable barrier at the seam separating the molecular chemisorption and dissociative minima. The analysis of one-electron levels supports the picture of Harris and Andersson that the *s* to *d* conversion present on Ni surfaces does not similarly lower the barrier on Cu surface.

1. Introduction

Despite the simplicity of molecular and atomic hydrogen, the physics and chemistry of that element on metal surfaces is amazingly rich and complex [1]. The various aspects of metal–H₂ interaction include coherent and incoherent scattering [2], physisorption [3] and both dissociative and associative [4] chemisorption. Once adsorbed, the quantal behaviour [5] of hydrogen leads to anomalies in its mobility [6] and excitations [7].

For all of the above, the adiabatic potential energy hypersurface forms the basis of understanding. Hydrogen dissociation, in particular, is expected to show important and interesting features in its potential energy diagram. Jellium calculations [8], most relevant for simple metal surfaces, indicate for H₂ on approach to the surface the presence of a physisorption well, a relatively large activation barrier, a molecular chemisorption state (the “*M* state”) and the final atomic chemisorption separated by a relatively low barrier.

Harris and Andersson [9] have recently investigated H₂ dissociation on Cu and Ni dimers to elucidate the role of *d*-electrons in the dissociation process. They find that the presence of *d*-holes in Ni reduces the Pauli repulsion for incoming H₂ (via *s* to *d* conversion) and substantially lowers the activation barrier. Moreover, they find the dissociation reaction to be endothermic on Cu and exothermic on Ni while desorption energies are similar for both. Finally, they find no evidence for the *M* state in either case. The purpose of the present paper is to extend the work of Harris and Andersson for larger clusters in order to find whether the features they observe are sensitive to cluster size. In addition, we discuss the effects of cluster–atom spacings and magnetism on dissociation reactions. These studies are part of a larger program where we aim at calculating numerically reli-

able potential energy hypersurfaces (within the local-density approximation) relevant for catalytic reactions on impurity alloyed surfaces and bimetallic surfaces.

The organisation of the paper is as follows. In Section 2, we describe the computational aspects of our method, based on the DVM-LCAO techniques developed by Ellis, Rosén and coworkers [10, 11]. In Section 3 we discuss the results for the reaction systems H₂/Cu₄(111) and H₂/Ni₄(111). Section 4 contains a discussion and the conclusions.

2. The LCAO-DVM cluster method

The linear combination of atomic orbitals (LCAO) provides a simple but effective scheme of expansion for the electronic states of clusters. Combined with the local-density approximation (LDA) [12] it is efficient in computations for systems from small molecules to large clusters and solids. Our calculations are carried out using the discrete variational method (LCAO-DVM) [10, 11] which gives one freedom to compromise between basis functions, cluster geometries and computational accuracy. Hence, we are able to use a natural and efficient basis set collected from free atom and free ion one-electron functions in a numerical form. The symmetry of the cluster does not impose essential restrictions, although we can derive benefit from the symmetry properties. Neither do we restrict us to the muffin-tin nor to the frozen-core approximation.

The self-consistent multipolar (SCM) extension [10] in solving the Poisson equation of the charge density has increased the accuracy of the LCAO-DVM method to the level where evaluation of the total energy is becoming feasible [11, 13]. The LCAO-DVM procedure which we use here was tested against the potential energy curves of diatomic molecules CO and N₂ [11], and it was found to be able to yield results both qualitatively and quantitatively comparable to the results from other methods tailored for small systems.

In order to treat open *d*-shell atoms we modified the computational procedure to include spin-polarisation by rewriting the equations in Ref. 11. The one-electron hamiltonian is written now

$$h^{\sigma}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + v_{\text{eff}}^{\sigma}(\mathbf{r}), \quad (1)$$

where

$$v_{\text{eff}}^{\sigma}(\mathbf{r}) = -\sum_v \frac{Z_v}{|\mathbf{r} - \mathbf{R}_v|} + \int \frac{\varrho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\varrho^{\sigma}(\mathbf{r}), \varrho(\mathbf{r})) \quad (2)$$

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and σ stands for the spin. The contributions to the effective potential in eq. (2) are the nuclear Coulomb potential, the Coulomb potential of the electron density and the spin-dependent local-density exchange-correlation potential, respectively. The one-electron solutions are found self-consistently as follows. The hamiltonian and overlap matrices are computed using the DVM integration technique, the secular equation is solved for the eigenvalues, the eigenvectors are used to expand the wavefunctions and the electron density, and finally, the effective potential is recomputed. The total energy for the self-consistent system is then obtained from

$$E = \sum_{\sigma} \left[\left(\sum_i e_i^{\sigma} - \int q^{\sigma}(\mathbf{r}) v_{\text{eff}}^{\sigma}(\mathbf{r}) d\mathbf{r} \right) - \int q^{\sigma}(\mathbf{r}) \sum_v \frac{Z_v}{|\mathbf{r} - \mathbf{R}_v|} d\mathbf{r} \right. \\ \left. + \frac{1}{2} \iint q^{\sigma}(\mathbf{r}) \frac{q(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} + E_{\text{xc}}[q^{\sigma}, q] \right] \\ + \sum_{\mu < \nu} \frac{Z_{\mu} Z_{\nu}}{|\mathbf{R}_{\mu} - \mathbf{R}_{\nu}|}. \quad (3)$$

The potential energy (hyper)surface (PES), i.e., the total energy as a function of the cluster geometry, provides the starting point for the studies of reaction systems. It is the basis of energetics establishing the adiabatic reaction path with various minima separated by barriers. The driving force of the reaction and the adiabatic dynamics is also obtained from the PES. However, the PES from full *ab initio* electronic structure calculations have not been published in literature to a larger extent, reflecting the extensive efforts and high accuracy, which are required to achieve useful results.

We used the potential energy curve of a free H_2 molecule as the first test case, where simultaneously, the effect of the choice of the particular LDA was investigated. The basis functions were chosen to be $1s^1$ from the neutral H atom and $1s^0$, $2s^0$ and $2p^0$ from the H^+ ion. Molecular data were

Table I. Calculated molecular data of H_2

	d_e (Å)	D_e (eV)	ω_e (cm $^{-1}$)
spin-pol.	0.81	4.65	4355
spin-restr.	0.84	4.66	4234
exp. ^a	0.74	4.75 ^b	4395

^a Ref. 17.

^b $D_e = D_0 + \frac{1}{2}\hbar\omega_e = 4.48 \text{ eV} + 0.27 \text{ eV}$.

evaluated for both the spin-polarised and spin-restricted H_2 . The resulting potential curves are shown in Fig. 1 and the molecular data from a fit to the Morse potential is given in Table I. The fit to the spin-polarised data leads to somewhat better agreement with the experiments: the bond length of about 10% too large and the dissociation energy a few percent too small. The vibration frequency agrees very well with the experimental data. The use of von Barth–Hedin [14] formula for the LDA leads to a dissociation energy of about 0.5 eV smaller than the use of Vosko–Wilk–Nusair (VWN) [15] formula, which was chosen to be used for later work. This difference originates from the spin-polarised free atom reference energies, which are 13.02 eV and 13.28 eV for VWN and von Barth–Hedin, respectively.

3. H_2 on Cu_4 and Ni_4 surface clusters

Copper and nickel surfaces were chosen for investigation, because differences in the mechanism of H_2 dissociation are expected for these metals, where the role of d electrons is of particular interest [9]. The bridge site of the (111) surface of these fcc metals was chosen in order to keep the cluster size small enough and to be able to compare the results with those of Harris and Andersson [9].

The planar cluster model consists of four surface atoms forming two triangles, which become the three fold center sites of atomic adsorption after the H_2 dissociation (see the inset of Fig. 2). The bulk lattice constants 3.61 Å and 3.52 Å were used for Cu and Ni, respectively. These lead to the interatomic distances of 2.55 Å for Cu and 2.49 Å for Ni. Thus the two hydrogen atoms at the surface center sites are separated by 1.5 Å on Cu(111) and 1.4 Å on Ni(111), which can be compared to the initial H_2 bond length $d = 0.8$ Å from the free molecule calculation.

The atomic basis functions were chosen to be $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ from a free Cu atom and $3d^8 4s^0 4p^0 4d^0$ from a Cu^{3+} ion. For Ni the basis was $\dots 3p^6 3d^9 4s^1$ and $3d^7 4s^0 4p^0 4d^0$ from a free Ni atom and a Ni^{3+} ion, respectively. The Hartree–Fock ground state configuration of a free Ni atom is $3d^8 4s^2$, while the LDA free atom ground state is $3d^9 4s^1$, the latter one being probably closer to the metallic configuration. Some testing with different basis sets was done but the actual choice was not found to be crucial. Even inclusion of $4d$ functions was not found to be essential.

The number and extent of multipole functions used for fitting the charge density and solving the Poisson equation were carefully examined. A crucial problem appeared to be the fitting of open d -shells of Ni atoms, whereas the nearly spherical charge density of Cu was easier to expand with multipole functions. Therefore, six multipole functions of lowest order ($l = 0-2$) were included for each atom in the C_{2v} cluster symmetry. Seven radial functions for each symmetry

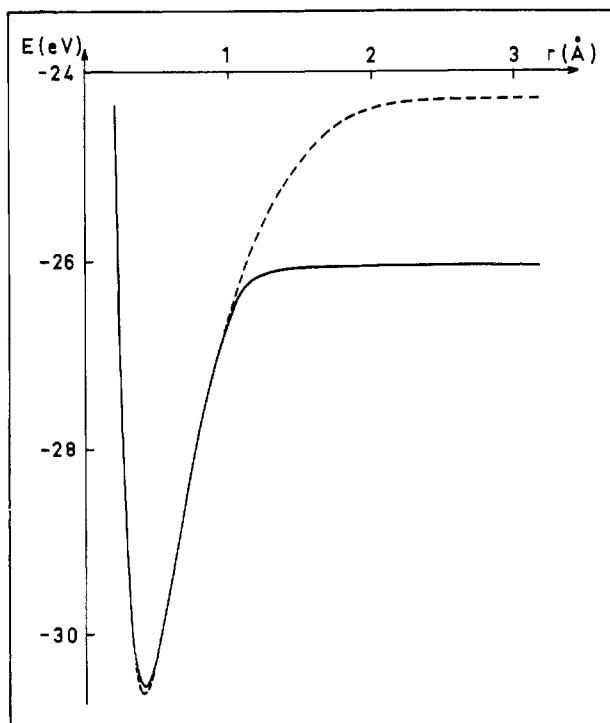


Fig. 1. The potential curve of an H_2 molecule from spin-polarised (full curve) and spin-restricted (dashed curve) calculations. Note that the variable r is half of the molecular bond length d , in order to be consistent with the notations in Fig. 2.

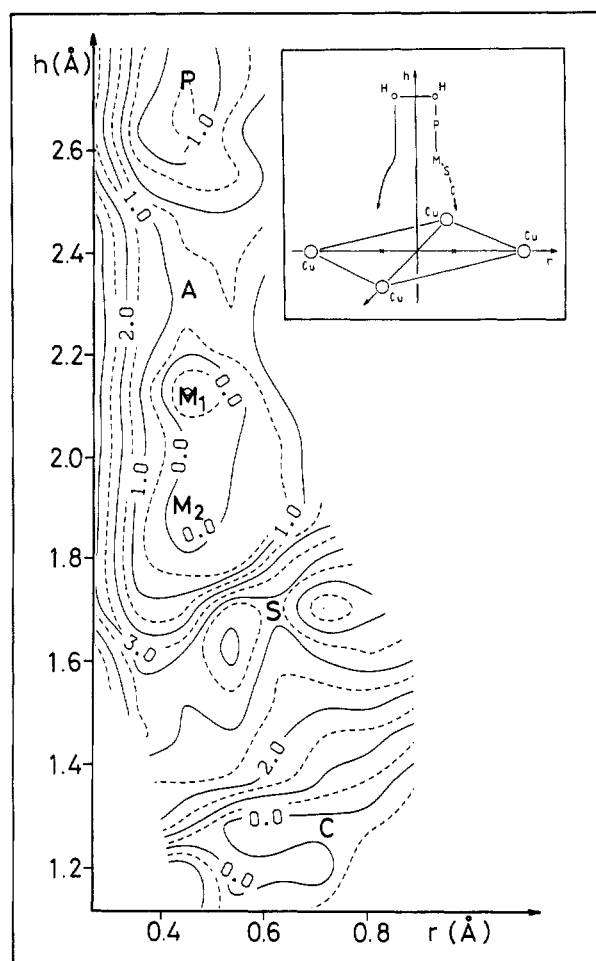


Fig. 2. The adiabatic potential energy surface of the H_2 dissociation on a bridge site of $Cu_4(111)$ cluster surface, with the geometry shown in the inset. Full curves are given in steps of 1 eV measured from an arbitrary zero level. For other notations see the text.

component were used, ranging from about 0.3 Å to 2 Å of radial distance from each nucleus.

The calculations were initially started with a DVM integration mesh of 6000 points for the $H_2/Ni_4(111)$ system, which was found, however, to be inadequate. Only 30 000 points or more made the computations accurate enough but too much time consuming to be carried out for the whole PES of $H_2/Ni_4(111)$ or $H_2/Cu_4(111)$ system. The final choice was then a distribution of 15 000 DVM points and a reduction to totaling of about 7000 points by using a Gauss-Legendre integration in the spheres with radii of 1 Å around the metal atoms.

To describe the coupling of one-electron levels of the cluster to the levels of an infinite substrate, the levels near the Fermi energy (ϵ_F) were broadened using the procedure of Ref. 16. This also stabilises the calculations due to the redistribution of the charge within the Ni d electrons leading to more spherical d -shells. The procedure probably describes better metallic Ni (as embedded cluster) and also makes it easier to fit the charge density using the multipole functions. However, we were forced to use broadening of 1.4 eV for the levels at ϵ_F to achieve adequate multipole fitting. This would correspond to the Fermi-Dirac distribution at the temperature of 6000 K for the occupation of the initial discrete levels. As a consequence, the total magnetic moment of the Ni cluster almost vanishes due to the considerable occupation of the minority spin levels above ϵ_F . Due to the washing out of

magnetism to obtain numerically stable total energies, our quantitative results for Ni do not answer the questions related to the role of magnetism in H_2 dissociation.

Let us first consider the H_2 dissociation on Cu ($H_2/Cu_4(111)$). Total energies for the cluster were computed for more than hundred different geometries and the resulting potential energy hypersurface (PES) is shown in Fig. 2. Firstly, the canonical structure of the entrance-channel activated reaction path is seen with the typical molecular and the dissociation regions separated by a seam barrier. The physisorption minimum (P) occurs at about $h = 2.7$ Å above the surface plane, and it seems to be deep enough to bind the molecule, at least in the geometry considered. The molecular chemisorption minimum shows a double structure (M_1 and M_2) at $h = 1.9$ Å–2.1 Å. An activation energy of about 3 eV is then required for dissociation through the saddle point (S) at $h = 1.7$ Å and $r = 0.6$ Å. Another path for dissociation can also be found via bond contraction before crossing the seam. Finally, above the three fold center site ($r = d/2 = 0.7$ Å) we find a shallow minimum of atomic chemisorption at $h = 1.3$ Å. The location of the calculated minimum may be disturbed by a numerical artifact arising from a change in the DVM integration mesh when moving the H atom in the region closer to the Cu atom. Inspection of the energetics according to the Fig. 2 leads to a conclusion that the H_2 dissociation is endothermic on Cu_4 cluster surface.

A comparison with the H_2/Cu_2 -PES of Harris and Andersson [9] can be made, but one should take into account the different geometry and the smaller size of the cluster they consider. Firstly, they do not find a molecular chemisorption minimum but a long and shallow structure representing rather physisorption. Secondly, their atomic chemisorption is closer to the Cu atoms than ours and is not localized above the (111)-surface triangle (which does not, on the other hand, exist in the geometry they use). Compared to the free HCu molecule bond length of 1.5 Å [17] their result for H-Cu distance is less than that but our calculations result in a H-Cu distance of about 1.9 Å from each of the three Cu atoms in the triangle. The seam occurs at the same region in our PES and theirs, although the height of the barrier is quite different, theirs being of about 1 eV and ours of about 3 eV. Our result must be considered as an upper limit, since we know that possibly remaining incompleteness in the charge density (multipole) fitting leads to an overestimation of the structures in PES.

The calculations for the $H_2/Ni_4(111)$ cluster were less successful due to the open d -shell structure, as explained above. Therefore, we comment these results only qualitatively. The observed features may reflect, however, the difference between these two substrates. Generally, the PES of $H_2/Ni_4(111)$ shows more structure at the molecular chemisorption region than that of $H_2/Cu_4(111)$. The existence of the associative molecular chemisorption (the M -state) is supported, with a location $h = 1.8$ Å and $r = d/2 = 0.3$ Å as a part of broadened M_2 structure, cf. Fig. 2.

In order to see the effects from different lattice constants of these two metals, we evaluated part of the $H_2/Cu_4(111)$ PES at the molecular chemisorption region with Cu atom spacings contracted by 2.5% to that of Ni metal. This resulted in a similar M_1 and broadened M_2 structure as that of $H_2/Ni_4(111)$. This suggests a conclusion that atom spacings barely may have strong influence on the chemisorption.

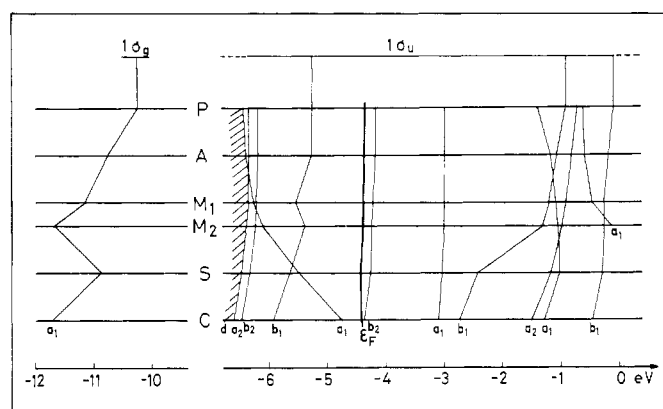


Fig. 3. The evolution of the one-electron levels of $\text{H}_2/\text{Cu}_4(111)$ along the reaction path shown in Fig. 2. The energy scale is referenced to the vacuum level. Symmetries of the levels are also indicated, and the H_2 derived levels are denoted by $1\sigma_g$ and $1\sigma_u$.

On the other hand, we want to remark that the level broadening procedure, which we use to describe embedding and to stabilize calculations, may lead to a less reliable description of the Ni surface.

Finally, we consider the H_2 dissociation mechanism in terms of the one-electron levels. This is nicely seen by following the evolution of the levels along the reaction path, shown for $\text{H}_2/\text{Cu}_4(111)$ in Fig. 3. The dissociation follows from the increase in occupation of the molecular antibonding $1\sigma_u$ derived levels of b_1 symmetry. These levels are seen to sink down in energy along the path from the molecular chemisorption state (M_2) to the dissociation minimum (C).

Simultaneously, on approach the molecular bonding $1\sigma_g$ level must be orthogonal to the Cu 4s derived levels, which results in a strong Pauli repulsion. As a consequence we can follow one particular a_1 level in Fig. 3, which is pushed up in energy close to the ϵ_F . This is the origin of the large barrier at the seam between the molecular and atomic chemisorption. This process is expected only for closed d -shell metals and not for Ni, for example. The number of d electrons per Cu atom in $\text{H}_2/\text{Cu}_4(111)$ remains constant 9.8 through the whole reaction path considered. But in the case of Ni the Pauli repulsion, instead of pushing up in energy, forces that particular s -like (a_1) level of Ni to convert to a d electron filling a hole in the open d -shell. Hence for Ni surface the barrier at the seam is expected to be much lower, in accord with the ideas of Harris and Andersson [9].

4. Conclusions

LCAO cluster calculations carried out for H_2 dissociation on a $\text{Cu}_4(111)$ surface cluster result in a potential energy surface with the canonical structure: physisorption, molecular chemisorption and dissociation to atomic chemisorption. Chemisorption appears to consist of a double minimum separated by a barrier from the physisorption. A larger barrier at the seam separates the dissociation or atomic

chemisorption. An interesting result is the appearance of two possible paths over the seam with about equal activation energies.

Our results for the chemisorption of H_2 on $\text{Ni}_4(111)$ support the existence of the associative molecular chemisorption, the M state. The same structure is found in the PES of $\text{H}_2/\text{Cu}_4(111)$ when the Cu atom spacings are contracted to that of Ni atoms, indicating the importance of the effects arising purely from the lattice constant. By the same token, the existence of such a state on real surfaces may not be definitely investigated by small cluster configurations, where the geometric effects are not accurately mimicked. Consequently, the final assignment of the experimental evidence for a precursor state [18] has to be postponed.

Inspection of the one-electron level evolution along the reaction path reveals the dissociation mechanism, and in particular, the origin of the large activation energy for H_2 dissociation on Cu with filled d shells. Similar activation energy is not expected for H_2 dissociation on Ni with open d shells [9].

Acknowledgments

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