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Theory of Field Adsorption of Hydrogen

by

Xiaoming Ye and H. J. Kreuzer and D. R. Salahub

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Department of Physics, Dalhousie University
Halifax, Nova Scotia, Canada B3H 3J5

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Theory of Field Adsorption of Hydrogen

Xiaoming Ye and H.J. Kreuzer

Department of Physics, Dalhousie University

Halifax, N.S. B3H 3J5, Canada

and

D.R. Salahub

Département de Chimie, *Université* de *Montréal*

C.P. 6128, Succ. A, *Montréal*, Que. H3C 3J7, Canada

Abstract

Field effects on the adsorption characteristics of H, H_2 and H_3 on metals are calculated using density functional theory for a jellium metal and for small metal clusters. New dissociation channels are explored and a mechanism for the formation of a field-stabilized linear H_3 species is proposed.

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1. Introduction

Hydrogen adsorbs on metal and semiconductor surfaces in either atomic or molecular form in on top, bridge and multicoordinated hollow sites. Adsorption energies for atomic hydrogen range from 2 to 4 eV; molecular hydrogen, on the other hand is weakly physisorbed with less than 0.5 eV.[1]

Electric fields of the order of volts per angstrom, i.e. of the same order of magnitude as intra-atomic fields, dramatically effect the electronic properties of the surface layers of metals and semiconductors.[2,3] For instance, on clean metals electric fields reduce the activation barrier of evaporation, eventually to zero at the evaporation field strength. Electric fields also change the binding characteristics of adsorbates. For instance, the binding energies of rare gases, weakly physisorbed in the field-free case, increase by at least an order of magnitude due to field-induced chemisorption. Likewise, for adsorbed molecules dissociation may become enhanced or inhibited as the field is increased changing reaction pathways. Hydrogen is no exception to this scenario. Two effects in particular have so far defied a detailed theoretical explanation: (*i*) the reduction of the evaporation field strength in the presence of an electric field, and (*ii*) the appearance of a H_3^+ species in the field ion mass spectrum[4-9].

In this paper, we will report theoretical studies of the adsorption characteristics of atomic and molecular hydrogen as a function of electric field strength. Two quite general field effects simplify our task: (*i*) Electric fields are always enhanced at kink sites, terraces and in front of single atoms on closed packed planes. We can therefore restrict our calculations to on top sites. (*ii*) Molecules are usually alligned along the field direction; we will therefore only consider such geometries.

We will see that the binding energy of atomic hydrogen, H, is reduced as the field is increased, whereas H_2 is bound more strongly. As a result, dissociative adsorption and associative desorption are modified considerably. Within our theoretical framework we will also be able to propose a reaction pathway for the formation of a linear H_3 species at metal surfaces in high electric fields. A detailed analysis of experimental data in the light of the present theoretical results will be given elsewhere.[10]

2. Theoretical Models

Electric fields at metal surfaces are greatly enhanced around kink sites and around single metal atoms on flat crystal planes. These local electric fields of the order of $V/\mathring{A}$ arise, via Poisson's equation, from local enhancements of the surface electron density. The field distribution around isolated atoms on an otherwise flat jellium surface have recently been calculated selfconsistently within the framework of the local density approximation of density functional theory.[11] A field enhancement by a factor 1.5 to 2 is found some 1-2$\mathring{A}$ above an adsorbed metal atom. Calculated evaporation field strengths, e.g. $3.0V/\mathring{A}$ for Ti and $3.5V/\mathring{A}$ for Nb, agree very well with experimental data.

To understand field adsorption of molecules, one would like to calculate the electronic structure of an adsorbed molecule in the local field at kink sites or around single atoms on densely packed planes of transition metals. Unfortunately, such a complete calculation is not available at the present time. We will therefore resort to two approaches, both of which are based on density functional theory to determine the electronic structure and the local electric field selfconsistently, namely the jellium model to describe field adsorption of atomic hydrogen and a cluster model for field adsorption

of the mocelular species.

For the field adsorption of atomic hydrogen we will use the jellium model to represent a densely packed metal surface on which we will study the chemisorption of atomic hydrogen as a function of applied field using local density functional theory.[12,13] One assumes that the ionic lattice can be smoothed into a uniform positive charge density n_+ that drops to zero abruptly half a lattice constant above the topmost layer of ion cores. In front of this jellium metal we add a hydrogen atom[14] around which we will study the local electron and field distribution within the framework of density functional theory. The latter determines the exact ground-state electron density as the self-consistent solution of *a* Schrödinger-like equation and of Poisson's equation. The local density approximation is invoked.[12] To include an external electric field, one adds an excess surface charge whose spatial distribution is then determined selfconsistently.

To account for the local lattice effects for adsorption around isolated atoms on densely packed surfaces or at kink sites, we will, in a second set of calculations, use a finite cluster model based on spin density functional theory. Because the number of metal atoms is rather small in such calculations for practical reasons, long range metallic effects such as image forces are poorly described by such a model. The inclusion of electric fields is also no longer staightforward. If we do this by adding charges to the cluster, they will distribute themselves over its surface. By choosing an appropriate geometry, e.g. *a* pyramidal shape, we can ensure that most of the extra charge resides on the top atom of the cluster and a strong electric field is generated in its vicinity. This field will fall off rather rapidly like r^{-3} a few angstroms away, rather than approach a constant as it does in front of a single metal atom on top of an extended metal surface.

Still, one can generate fields of about $1V/\mathring{A}$ one or two angstroms away from the top atom in the cluster, i.e. at the position where atomic hydrogen will adsorb. In earlier cluster calculations[15-17] based on the semi-empirical ASED-MO method[18] the electric field distribution as calculated for a flat jellium surfaces was imposed on the cluster. This method successfully explained field-induced chemisorption of rare gases[15,17] and field evaporation of metals[16]. For the cluster calculations reported here we employ a different, and simpler scheme to include field effects. Because we are interested in field adsorption around single metal atoms on top of closed packed surfaces or around kink sites, we take a cluster consisting of a single metal atom and the adsorbing atom or molecule. This cluster is then put into a constant external field which is supposed to arise from the flat metal surface beneath it. The induced field will then lead to a net field expulsion over the volume of the metal atom and to a field enhancement in front of it where field adsorption of the additional atoms or molecules takes place.

To set up the cluster model, we again start from the one-electron equations of density functional theory and add the potential energy of a constant electric field, F_0, i.e. $V_F(z) = -eF_0z$ to the effective potential. For the exchange and correlation part of the effective potential we employ both local and nonlocal approximations. To allow for more flexibility we divide the total electron density $n(r)$ into spin-up and spin-down components.[19]

3. Results

3.1. H, H_2, H_3 and their Ions

To assess the reliability of the local and nonlocal spin density approximations (LSDA and NLSDA), we have compiled, in Table 1, bond lengths, total

electronic energies, binding energies, and ionization energies for the various hydrogen species and their ions. In the basis set for hydrogen we included $1s$, $2s$, and $2p$-type gaussian orbitals. For atomic hydrogen LSDA is not too reliable yielding an ionization energy of 13.02 eV instead of the exact value of 13.59 eV; a similar discrepancy exists for the ionization energy of H_2. For the molecular species bond lengths calculated in LSDA are typically too long by as much as 0.1 $\mathring{A}$. Ionization energies for linear and triangular H_3 are in good agreement with CI calculations.[20,21] The latter, being specifically designed for H_3, employ much larger basis sets and ought to be more reliable. We also note that CI calculations based on the Gauss' 90 package[22] give rather poor results as does an approach based on a basis of floating spherical Gaussian orbitals.[23] Proceeding to the NLSDA we note a significant overall improvement.

As a first step towards the understanding of field effects on hydrogen we calculate the electronic properties of H_2 in a constant electric field using LSDA. In Fig.1 we show the energy difference, $\Delta E = E(H_2,F) - 2E(H,F=0)$ as a function of the H-H distance for various field strengths. We note a steady decrease in the minimum of the total energy, with the bond length increasing slightly. The Schottky barrier of dissociation disappears at 5.14 $V/\mathring{A}$. The earlier FSGO calculation put the dissociation field strength between 5.6 and 6.0 $V/\mathring{A}$.[22] To assess the reliability of our method we have also calculated the field dependence of the activation energy of dissociation for H_2^+. According to Hiskes [24] it dissapears for fields larger than $2V/\mathring{A}$ whereas we find $1.8V/\mathring{A}$.

3.2 Field Adsorption of H

For the field adsorption of atomic hydrogen we present results modeling the

metal by (*i*) a jellium and (*ii*) a small cluster of metal atoms. In Fig. 2 we show the potential energy curves of H on jellium with r_s=2.0 for various field strengths. As the field is increased, the position of the binding minimum remains essentially unchanged at 0.25Å above the jellium edge, i.e. about 1 - 1.5 Å above the topmost ion cores. The activation energy for field desorption is, however, decreasing continuously, suggesting that atomic hydrogen can no longer be field adsorbed at field strengths beyond 5V/Å. Slight changes occur when one takes r_s=3.0 confirming earlier results in the field free case which found that the total energy has a flat plateau for r_s between 2 and 4.[25,26]

To get an idea for the importance of the localized *p*- and *d*-electrons of transition metals and of the lattice structure we now report the results of LSDA cluster calculations for Rh. In a first calculation we have mimicked the (111) surface of *Rh* by a tetrahedral cluster of 4 *Rh* atoms with a *H* atom on its apex. It is known that atomic hydrogen adsorbs preferentially at multi-coordinated sites in the field-free case. Nevertheless we have used the on top geometry because in the presence of a field, adsorption is preferrable at on top sites, i.e. at kinks and steps. In the absence of a field we find the binding energy for H on Rh_4 to be 2.36 *eV* (compared to 1.6eV on jellium with r_s=3 bohr and 2.0 *eV* for r_s=2 bohr) with H located 1.5 Å from the top *Rh* atom (compared with 1.6Å on jellium if we assume that the first lattice plane is half a lattice constant, i.e. 1.35Å below the jellium edge). In a third calculation, also based on LSDA, we look at the *Rh-H* dimer. We find a binding energy of 3.3eV at a distance of 1.5 Å, i.e. somewhat stronger binding at shorter distances for the dimer than for the cluster because the single *Rh* in the dimer has more electrons available for binding to hydrogen. The further reduction in binding as one goes to jellium is largely due to the

lack of localized p- and d-electrons.

Within the dimer model we next include field effects by placing the dimer in a uniform external field. This overestimates the field effect on Rh, because of the absence of the field expulsion by conduction electrons in an extended metal cluster. Nevertheless, the calculation has its merits as an estimate. In Fig.3 we plot the potential energy curves for the Rh-H dimer as a function of the separation for various field strengths. It suggests that for F_0 of the order of 3.0-3.5$V/\mathring{A}$ the dimer no longer exists. This is indeed the range above which field adsorption of hydrogen on metals can no longer be observed. The fact that a dimer model yields good answers confirms a long held belief[27,28] that the local fields and thus the local electronic structure around adsorption sites (kink sites, steps etc.) are more important than long range metallic effects for the understanding of field adsorption. It is at first sight surprising that the jellium model predicts too large maximum field strengths for hydrogen field adsorption, i.e. of the order of 5-6$V/\mathring{A}$ instead of 3-3.5$V/\mathring{A}$, considering the fact that similar calculations for field evaporation of metal atoms yielded good agreement with experiment.[11] However, we should bear in mind that hydrogen adsorption takes place at very short distances from the topmost ion core of the metal, i.e. in the region of the classical image plane where the local field varies rapidly. The local structure must therefore be known rather accurately, a task that the jellium model of a metal cannot provide. The geometries and energies of field-free adsorption are summarized in fig.4 with field effects displayed in fig.5.

3.3 Field adsorption of H_2

We have used the LSDA method to calculate the binding energy of a linear Rh-

H-H species and of H_2 linearly adsorbed on top of a tetrahedron of Rh. Such a geometry is of course very unlikely in the absence of a field. However, as soon as a field is applied, it will align the molecular dipole moment, i.e. the molecular axis along it. We will therefore only study field effects for this geometry.

In the absence of a field we find a binding energy in LSDA of 0.66 and 0.54eV on a single *Rh* atom and on a Rh_4 tetrahedron respectively, i.e. too much binding for a weakly physisorbed species. Using NLSDA the binding of H_2 on a single *Rh* atom decreases to a more realistic value of 0.065eV. Unfortunately, we could not do the calculation for H_2 on a Rh_4 cluster due to rstictions in computer size. In the LSDA calculations the first hydrogen is a distance of 1.88 (1.90) $\mathring{A}$ from the top *Rh* atom and the second *H* a further 0.79 $\mathring{A}$ away, roughly the bonding distance in the free H_2 molecule, see fig.4. These numbers indicate physisorption for molecular hydrogen. The weakening of the *Rh-H* bond as one goes form a single *Rh* to a Rh_4 cluster is again the result of a small charge transfer into the internal *Rh* bonds. The reduction of the binding energy as one employs the NLSDA is also reflected by the fact that the binding distance increases to 2.17$\mathring{A}$.

We next look at the effect of a uniform electric field on the binding characteristics of a linear *Rh-H-H* species. As the field is increased, the distance between *Rh* and the inner *H* shrinks and the *H-H* separation increases enhancing the binding between the *Rh* and the H_2 but diminishing the *H-H* binding energy. For fields of the order of $3V/\mathring{A}$ the activation barrier for H_2 dissociation (in a direction normal to the surface) dissappears. Some relevant numbers can be found in fig.5. We should stress that this is a new, field-induced dissociation channel for an upright H_2 species leading to only one *H* atom adsorbed rather than two as a result of the stretching of an H_2

molecule physisorbed parallel to the surface.

3.4 Field Adsorption of H_3

The bond lengths and binding energies for field-free adsorption of a linear H_3 molecule on either a Rh_4 cluster or on a single Rh atom are given in fig.4. This suggests to interpret H_3 adsorption as chemisorption of a H atom on Rh with a H_2 molecule physisorbed on top of it. Dissociation energies support this, i.e. 0.1 eV for Rh-H plus H_2 and 3.28 eV for Rh plus H_3. Clearly this is not the lowest energy state for the adsorption of 3 hydrogen atoms on a metal surface.

What we want to show next is that the linear H_3 configuration in an on top position will be stabilized in the presence of an electric field. We therefore put the Rh-H-H-H cluster into a uniform electric field of $2V/\mathring{A}$ and calculate the binding energy as a function of the Rh-H_3 distance keeping the H-H distance at its field-free value. The minimum remains at the same distance but the activation barrier against thermal field desorption is reduced to less than 1eV. If we vary next the distance between the first and the second H atoms we find that a substantial contraction occurs with a significant increase in the corresponding H-H bond strength implying a field stabilisation of the linear H_3 molecule. The relevant bond lengths and binding energies are summarized in Figs. 4 and 5.

4. Summary

The main conclusions of this study are as follows:

(i) Adsorption of atomic hydrogen on metal surfaces is weakened in the presence of electric fields. The maximum field strength of the order of 3 $V/\mathring{A}$ is reproduced by a simple dimer model whereas field effects on adsorbed

hydrogen are underestimated on a jellium surface.

(*ii*) H_2 linearly adsorbed in an on top position will be dissociated in fields of the order of $3V/\mathring{A}$.

(iii) H_3 linearly adsorbed will be stabilized in fields of the order of $2V/\mathring{A}$.

In fields of less than $3V/\mathring{A}$ we therefore have present on the surface (*i*) chemisorbed, i.e. immobile atomic hydrogen, and (*ii*) weakly, field-stabilized chemisorbed H_2, most likely mobile even at temperatures of the order of 50K. The H_2 molecule will then migrate up the field gradient along the metal tip. If it encounters a chemisorbed H atom, it might hop on top forming a field-stabilized linear H_3 species which can be field desorbed as H_3^+.

We hope to do further calculations for hydrogen field adsorption in three-fold hollow sites. In addition, we will check the influence of the metal cluster size on the field adsorption characteristics.

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Table 1 Binding characteristics of H_2, linear and triangular H_3 and their ions.

	H_2	H_2^+	H_3 (*li*)	H_3^+ (*li*)	H_3 (tr)	H_3^+ (tr)
Bond length (Å)						
exact	0.74	1.06				
CI (SL)			0.93		1.11	
CI (CKP)				0.81		0.88
FSGO	0.70	1.00				0.83
CI (Gauss' 90)	0.75		0.94	0.81		
LSDA	0.78	1.16	0.95	0.87	1.1	0.94
NLSDA	0.77	1.15	0.95	0.86	1.10	0.94
E_{total} (*eV*)						
exact	-31.94	-16.38				
CI (SL)	-31.92		-45.08		-42.78	
CI (CKP)	-31.88			-34.72		-36.44
FSGO	-27.84	-13.73				-31.64
CI (Gauss' 90)	-31.32		-44.23	-34.11		
LSDA	-30.85	-15.89	-44.00	-33.70	-41.87	-35.28
NLSDA	-32.00	-16.60	-45.61	-34.88	-43.36	-36.45
$E_{binding}$ (*eV*)						
exact	4.75	2.79				
CI (SL)	4.74		-0.44		-2.74	
CI (CKP)	4.70			2.84		4.56
FSGO	4.75					3.80
CI (Gauss' 90)	4.13		-0.67	2.79		
LSDA	4.82	2.875	-0.14	2.85	-1.99	4.43
NLSDA	4.72	2.95	-0.03	2.87	-2.28	4.45
$E_{ionization}$ (*eV*)						
exact	15.43					
CI			10.36		6.34	
CI (Gauss' 90)			10.12			
LSDA	14.96		10.29		6.59	
NLSDA	15.40		10.73		6.91	

Figure Captions

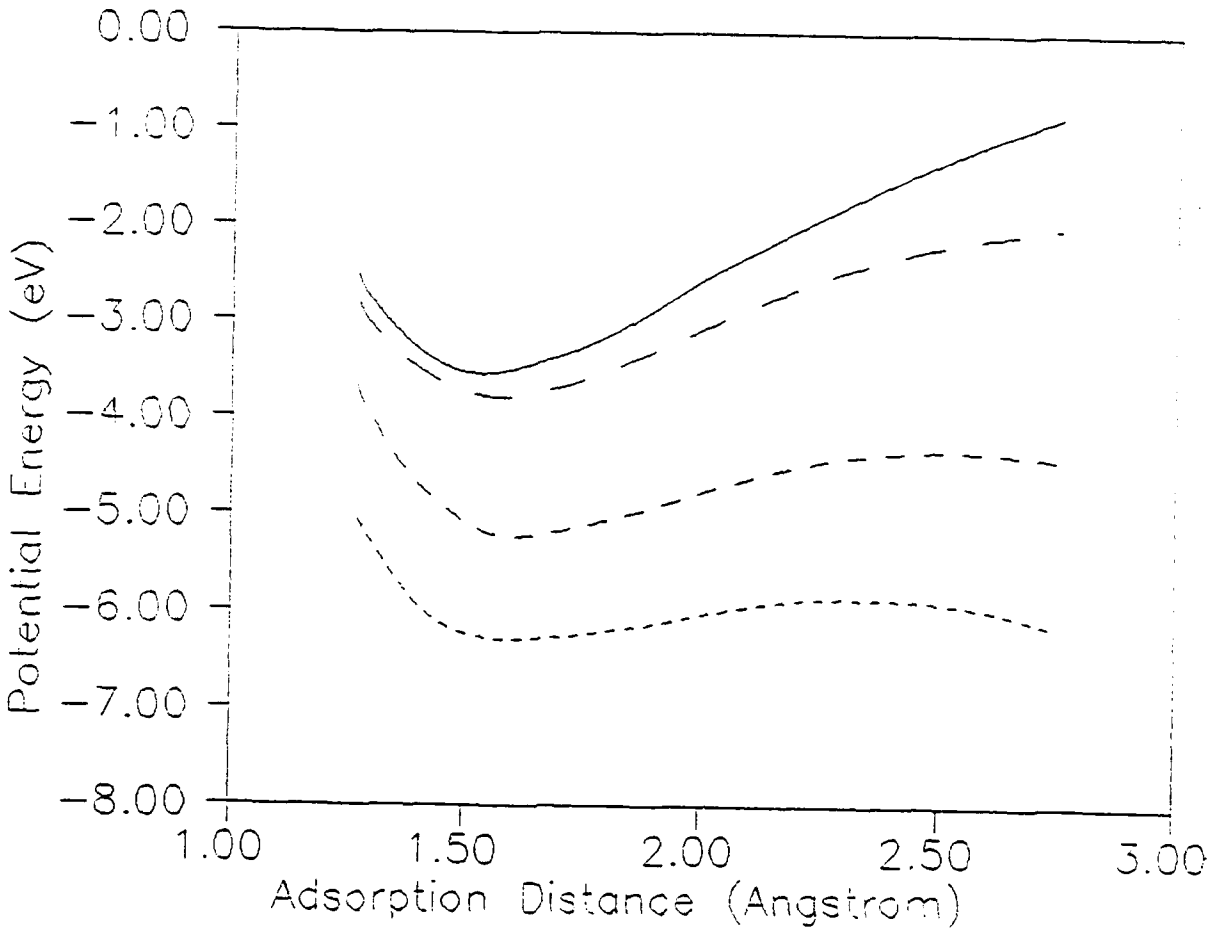
Fig.1: Total energy of H_2 in a uniform electric field, F_0, as a function of the H-H distance. From top to bottom, the field strengths are 0.0, 3.0, 4.5, 5.14 $V/\mathring{A}$.

Fig.2: Field adsorption of atomic hydrogen on a jellium metal with r_s=2.0. From top to bottom, the field strengths (at the minimum) are 3.0, 5.0, 6.0, 0.0 $V/\mathring{A}$.

Fig.3: Total energy of the Rh-H dimer in a constant electric field, F_0. From top to bottom, the field strengths are 0.0, 2.0, 3.0, 3.5 $V/\mathring{A}$.

Fig.4: Field-free adsorption of hydrogen on jellium, a single Rh atom and a tetrahedron Rh_4. Internuclear distances are in angstroms and energies in eV. The cluster calculations are based on LSDA.

Fig.5: Field adsorption of hydrogen on a Rh atom, using NLSDA.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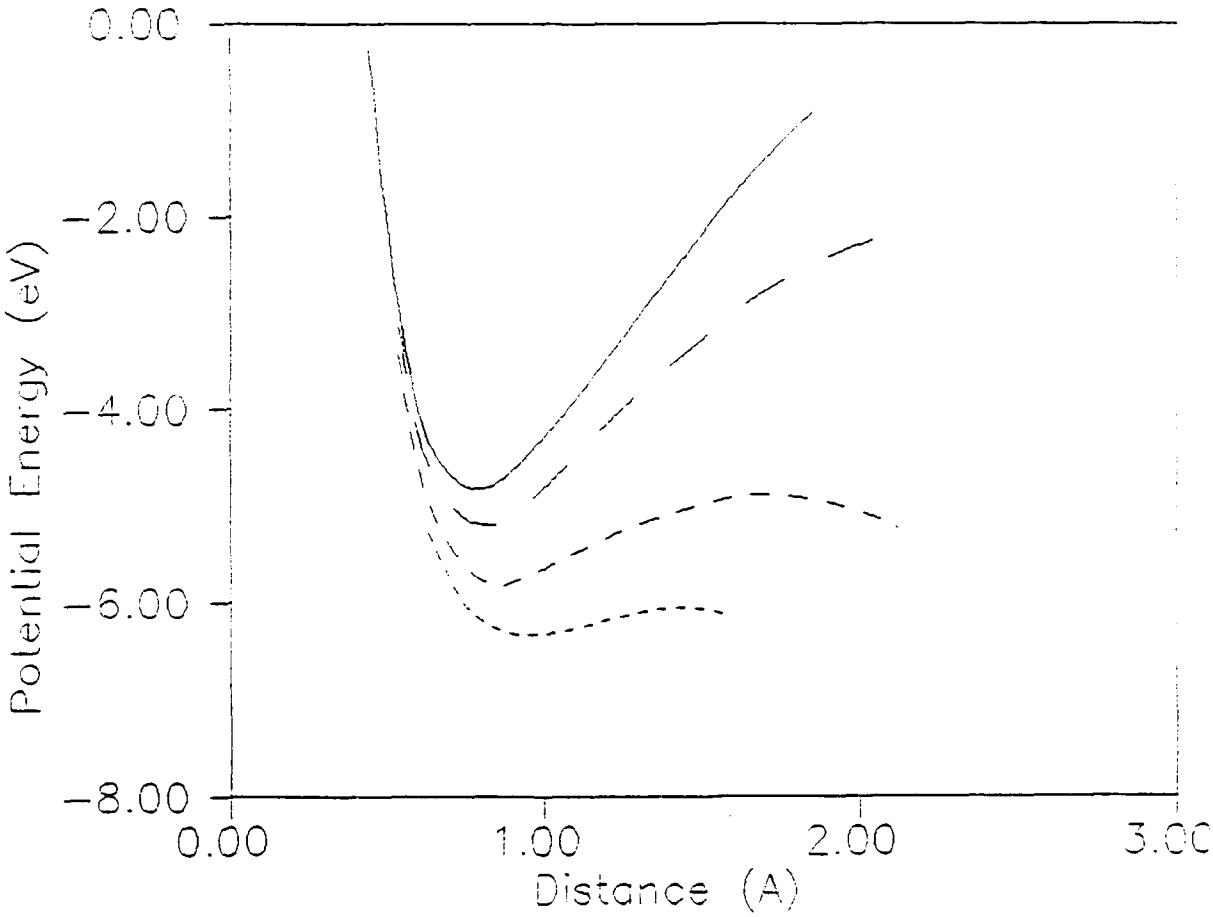
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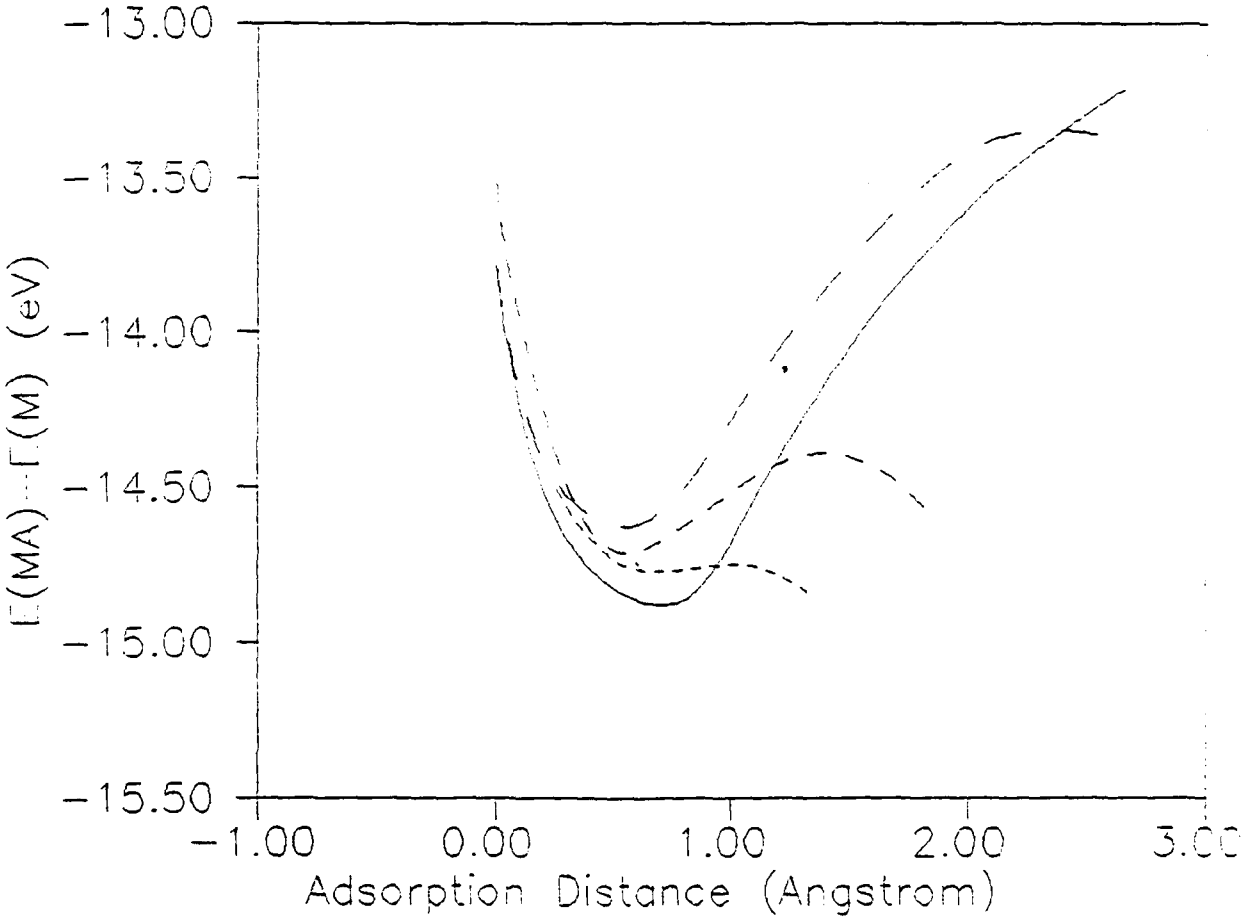
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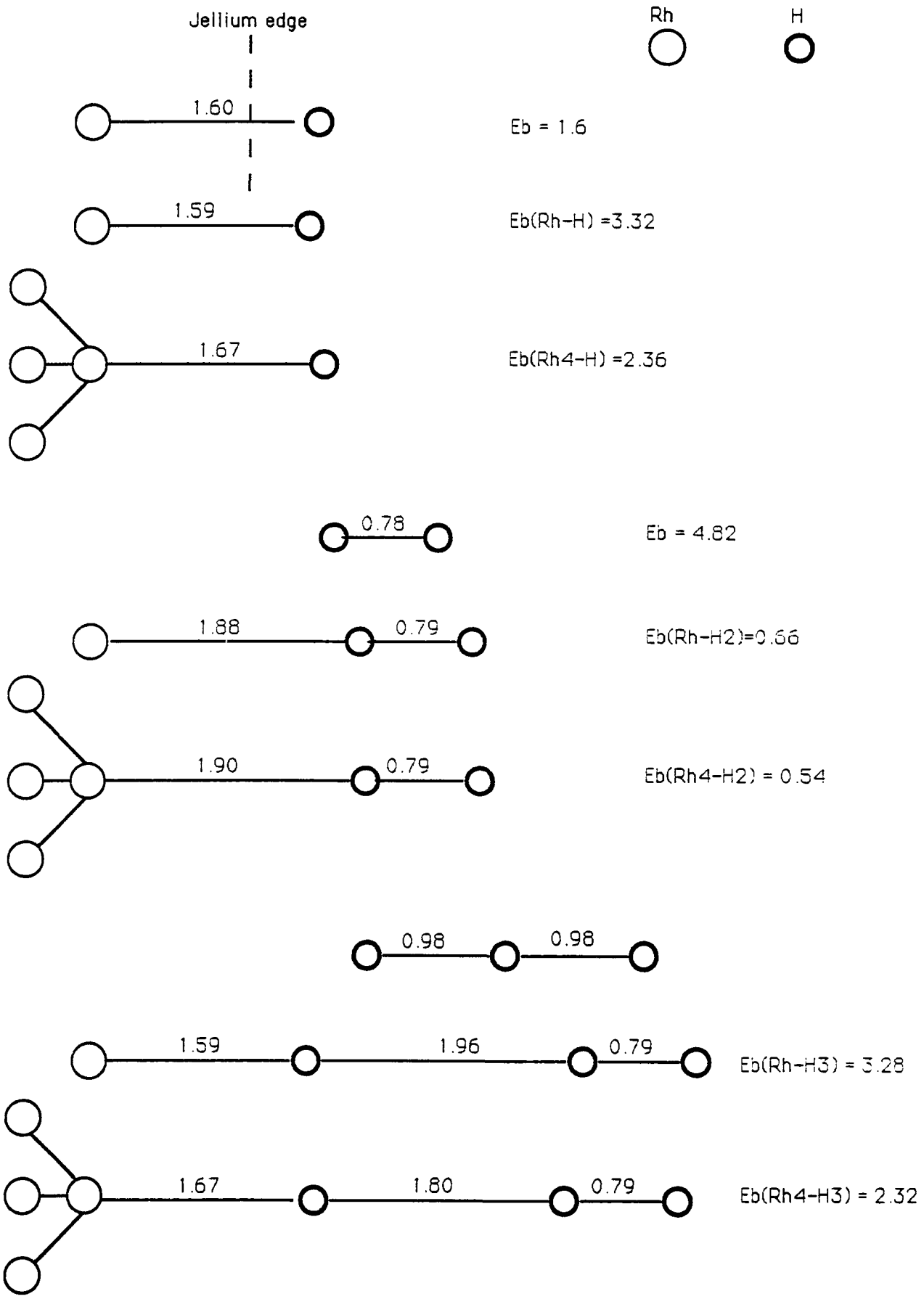
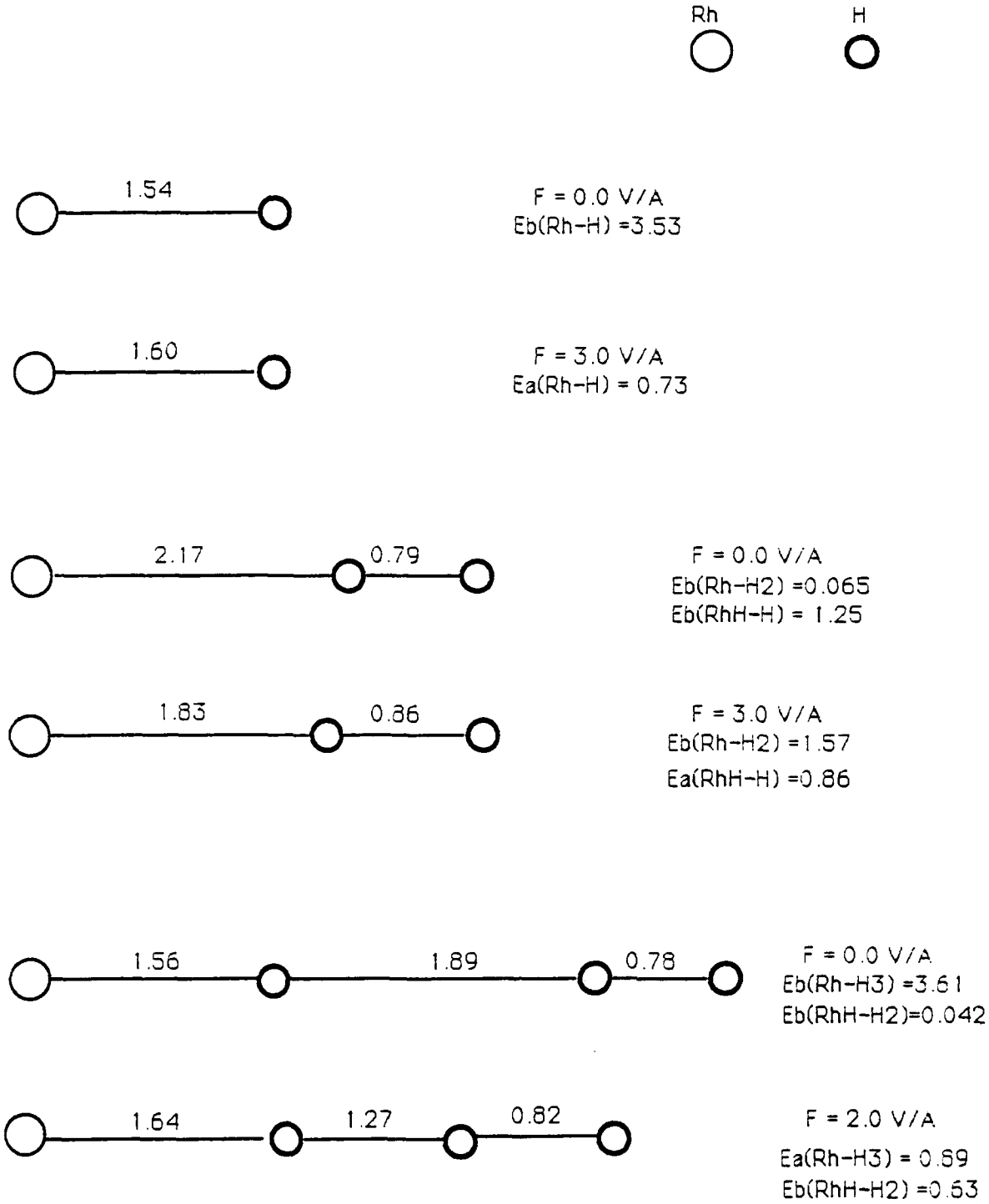

Jellium edge
Rh
H
1.60
Eb = 1.6
1.59
Eb(Rh-H) =3.32
1.67
Eb(Rh4-H) =2.36
0.78
Eb = 4.82
1.88
0.79
Eb(Rh-H2)=0.66
1.90
0.79
Eb(Rh4-H2) = 0.54
0.98
0.98
1.59
1.96
0.79
Eb(Rh-H3) = 3.28
1.67
1.80
0.79
Eb(Rh4-H3) = 2.32


Rh
H
1.54
F = 0.0 V/A
Eb(Rh-H) =3.53
1.60
F = 3.0 V/A
Ea(Rh-H) = 0.73
2.17
0.79
F = 0.0 V/A
Eb(Rh-H2) =0.065
Eb(RhH-H) = 1.25
1.83
0.86
F = 3.0 V/A
Eb(Rh-H2) =1.57
Ea(RhH-H) =0.86
1.56
1.89
0.78
F = 0.0 V/A
Eb(Rh-H3) =3.61
Eb(RhH-H2)=0.042
1.64
1.27
0.82
F = 2.0 V/A
Ea(Rh-H3) = 0.69
Eb(RhH-H2) =0.53