Size effects on adsorption energies of complex atoms and diatomic molecules on metal surfaces from small-cluster calculations

LETTER TO THE EDITOR

Size effects on adsorption energies of complex atoms and diatomic molecules on metal surfaces from small-cluster calculations

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Abstract. We present a new method for calculating binding energies of atoms and diatomic molecules chemisorbed on transition metal surfaces from cluster models. Our method relies on the separation between electronic and ionic contributions, by partitioning the desorption process into three steps. This allows us to remove the size effects due to the electronic relaxation by introducing the work function of the bare metal instead of the ionization potential of the cluster.

A current model of the chemisorption of atoms and molecules on transition metal surfaces is based on small clusters of metal atoms, in the presence or absence of the adsorbate [1–6]. Such a model is attractive in the sense that one can then use accurate quantum chemistry methods and, therefore, expect precision as regards the quantum chemical level used. For example, numerous cluster calculations are done using a linear combination of Gaussian-type orbitals (LCGTO) and model potentials (MP) for the inner core electrons of the metal atoms in the framework of the local spin density (LSD) approximation [2]. However, even though the geometrical structure and vibrational frequencies (or force constants) are well reproduced using this description, this is not the case for both the work function, approximated by the ionization potential of the cluster, and the binding energies of the chemisorbed species, which are generally over-estimated [3]. This discrepancy is mainly due to the effect of the finite size of the cluster used in the calculation. Some authors [4, 5] analyse this discrepancy as an effect of the electronic configuration of small clusters which, in some cases, would not be suitable for comparison with an infinite metal surface. They are then led to look for rules that the cluster electronic states must satisfy in order to be used in the chemisorption modelling. Such rules do not appear to us convincing. For instance, Upton and Goddard [6] suggest that the ionization potential of the bare cluster must be similar to that of the infinite system. Unfortunately, this rule can be satisfied only for very large clusters. Indeed the importance of the cluster size effect is clearly confirmed by the experimental results for the ionization potential of Ni clusters [7, 8], these experimental results being well reproduced by the LSD approximation [9]. Recently we proposed a method for reducing the size effects in the cluster-like calculation for both the electronic work function and the binding energy of the hydrogen atom on a transition metal surface [9]. In this work,

the H desorption was decomposed into three steps: the extraction of the electron, then the desorption of the proton and finally the recombination of the H atom far away from the surface. The energy change associated with the first step is the ionization potential W_i of the cluster and becomes, in the limit of a macroscopically large system, the work function Φ of the bare metal surface at the zero-coverage limit. Our correction was to replace the energy change of this step by the work function; this relies on the assumption that the binding energy of the proton is only weakly dependent on size. The work function was determined from the opposite of the (DFT) Fermi level of the cluster [10–12], which was found to be nearly independent of the cluster size and to reproduce the experimental polycrystalline work function very well. The final result for the binding energy of the H atom was significantly improved when compared with the result of the direct calculation. Thus the important size effect was analysed as being due to the change of the total number of electrons included in the cluster.

In the present work we generalize the method of [9] for complex atoms or diatomic molecules. Let us consider the case of an atom, say A, adsorbed on an n-metal-atom cluster M_n. The binding energy is

$$E_{M\text{-}A}^{(n)} = E(M_n) + E(A) - E(M_n A). \tag{1}$$

We still consider the desorption as being decomposed into the three steps outlined above. The important difference is that now the number of electrons extracted in the first step, say x, and accordingly the charge of the ion to be desorbed in the second step, is a continuous variable. The energy change of the first step is, in the finite-cluster case, the ionization potential of the cluster corresponding to x electrons, $W_i(x) = E((M_n A)^{x+}) - E(M_n A)$, in the presence of the atom A (notice that $W_i^{(0)}(x)$, corresponding to the bare cluster, is nearly equal to $W_i(x)$). We can rewrite (1) as follows:

$$E_{M\text{-}A}^{(n)} = W_i(x) + W(A^{x+}) + (E(A) - E(A^{x+})). \tag{2}$$

Here, $(E(A) - E(A^{x+}))$ is the opposite of the ionization energy of A for x electrons, and $W(A^{x+})$ is the binding energy of the ion A^{x+},

$$W(A^{x+}) = E(M_n) + E(A^{x+}) - E((M_n A)^{x+}). \tag{3}$$

As in [9] we replace $W_i(x)$ by its infinite-case counterpart, namely $x\Phi$. This is the first step of our method and it is of great importance. Indeed it is well known, at the experimental level, that small metallic clusters are characterized by a first ionization potential $W_i(x = 1)$ significantly higher [7, 8], or an electronic affinity $W_i(x = -1)$ significantly smaller [13], than the infinite metal work function. Therefore we define a modified binding energy, $E_{M\text{-}A}^{*(n)}(x)$ according to

$$E_{M\text{-}A}^{*(n)}(x) = x\Phi + W(A^{x+}) + (E(A) - E(A^{x+})). \tag{4}$$

It is important to notice first that $E_{M\text{-}A}^{*(n)}(x = 0) = E_{M\text{-}A}^{(n)}$ and, secondly, that at the limit of a macroscopically large system $E_{M\text{-}A}^{*\infty}(x)$ is independent of x (since then $W_i(x) = x\Phi$) and coincides with $E_{M\text{-}A}$. In (4) the only term that formally depends on the size of M_n is the binding energy of the ion A^{x+}, $W(A^{x+})$.

Now, and this is the second step of our method, we exploit the flexibility we get in defining $E_{M\text{-}A}^{*(n)}(x)$. We consider the variable x as an optimization variable: we choose x such that $E_{M\text{-}A}^{*(n)}(x)$ depends as little as possible on the size of the system. Doing this we state that the cluster approximation, which lies on the assumption that the adsorbate–substrate interaction is very localized, can be much more accurate for a charged species.

This means that the modification of the metal surface when one adds the ion A^{x+} is strongly localized and thus the electronic density induced by this adsorption is non-negligible only for a small region Ω_A around the adsorption site, which does not extend over the whole cluster. We emphasize that the ion A^{x+} should not be confused with an actual ion since its charge x does not necessarily take an integer value. Nevertheless, the use of a fractional value for x is quite justified in the framework of the density functional theory [14].

Thus our method consists, in principle, of calculating $E_{M\text{-}A}^{*(n)}(x)$ for a set of small clusters in a reasonable range of values of x and to choose that value, x_0, for which $E_{M\text{-}A}^{*(n)}(x)$ exhibits the smallest variations over the clusters set. A strictly constant value for $E_{M\text{-}A}^{*(n)}(x_0)$ when the cluster size is changed is hardly conceivable since, except for very large clusters, the number n of atoms included in the cluster cannot be considered as a continuous variable. Moreover, when the cluster size is changed, the structure of the cluster is also modified. We expect that the result, $E_{M\text{-}A}^{*(n)}(x_0)$, averaged on the clusters set considered, is a good approximation for the value $E_{M\text{-}A}^{\infty}$ corresponding to the infinite substrate within the approximation one uses for the electronic calculations of the total energies of the clusters.

From a practical point of view, we note that the smaller the cluster size, the more $E_{M\text{-}A}^{*(n)}(x)$ varies. Therefore, the optimization of x is more efficient when it is done on a set of small clusters rather than on a set of large ones. This allows us to simplify the preceding scheme by using only two small clusters of different sizes: we simply impose the condition that $E_{M\text{-}A}^{*(n)}(x)$ takes the same value on the two clusters. Since we are in the zone of a maximum variation of $E_{M\text{-}A}^{*(n)}(x)$ with the cluster size we expect to find a reasonable approximation for the optimum value of x.

Now we outline the feasibility of our scheme. Let x be positive, the generalization to $x < 0$ being straightforward We consider the expression $E_{M\text{-}A}^{*(n)}(x) = E_{M\text{-}A}^{(n)} + x\Phi - W_i(x)$. $E_{M\text{-}A}^{*(n)}(x)$ decreases with x because the ionization potential $W_i(x)$ increases much more rapidly with x than $x\Phi$, except for very small clusters and especially in the case of Ni [7, 8]. On the other hand, when the size 'n' of the cluster increases, this behaviour is less pronounced (at the limit of a very large n, $E_{M\text{-}A}^{*(n)}(x)$ is independent of x). Then, if we consider two clusters characterized by n_1 and n_2, with $n_1 < n_2$, and since we have quite generally $E_{M\text{-}A}^{*(n_1)}(x = 0) > E_{M\text{-}A}^{*(n_2)}(x = 0)$, there exists $x = x_0$ for which $E_{M\text{-}A}^{*(n_1)}(x_0) = E_{M\text{-}A}^{*(n_2)}(x_0)$. The function $x\Phi - W_i(x)$ can be expanded in powers of x and the linear term is nearly negligible since $W_i(x)$ does not differ much from $W_i^{(0)}(x)$ for which the linear term is $x\Phi$. Therefore, the quadratic term is dominant (corresponding to second-order terms in the total energy) and in a first approximation it seems equivalent to consider either a positive or a negative value for x_0. However, the terms with odd powers of x must be considered, and we have to decide the sign of x_0 on the basis of a more precise physical picture. Our criterion for choosing the sign of x_0 is to make the delocalized part of the adatom-induced electronic density in the cluster as small as possible. To this end we consider the effect of the so-called orthogonalization hole of the pseudopotential formalism used for bulk metals [15, 16]. Following the chemisorption of the atom A the valence states of the metal, which are delocalized over the whole system, must be orthogonalized to the electronic states of the atom, and this creates a depletion hole in the delocalized part of the electronic density. In an infinite system this extra charge will be smeared in the surface region, leading to a vanishingly small surface charge, which means that the electronic density in the interior of the metal must be unchanged. On the other hand there is no such flexibility in a finite cluster. The delocalized part of the electronic density will be modified over the whole cluster, and in (1)
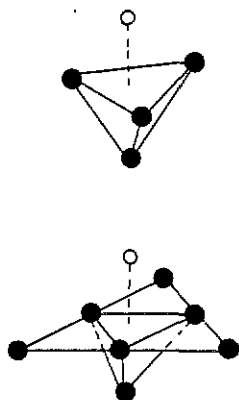
Figure 1. Clusters used in the calculations. Full circles: Pd atoms; open circles: chemisorbed atoms. In the case of CO we consider the C atom towards the metal and the C–O bond normal to the surface.
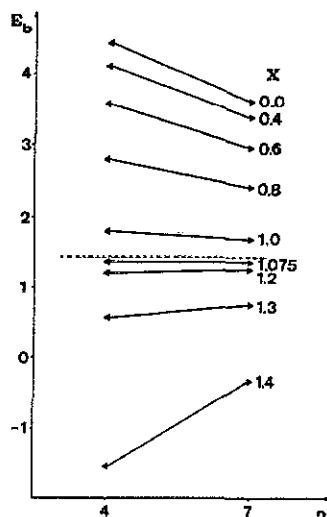

Figure 2. Binding energy $E_b = E_{M-CO}^{*(n)}(x)$, in eV, of CO calculated for Pd$_4$ and Pd$_7$, for different values of x. $x_0 = 1.075$ corresponds to the case for which the binding energy of CO is equal on both clusters. The broken line indicates the experimental value of E_{M-CO}.

Table 1. Binding energies, in eV, resulting from the direct calculation ($E_{M-A}^{*(n)}(x = 0)$); from H$^+$, C$^+$, O$^+$, CO$^+$, $E_{M-A}^{*(n)}(x = 1)$; and from the optimized calculation ($E_{M-A}^{*(n)}(x = x_0)$).

	$E_{M-A}^{*(n)}(x)$						
	$x = 0$		$x = 1$		x_0	$x = x_0$	Exp.
Adsorbate	Pd$_4$	Pd$_7$	Pd$_4$	Pd$_7$			
H	5.047	4.585	2.486	2.667	0.855	3.21	2.7 [20]
C	9.996	9.294	7.378	7.219	1.135	6.61	(Ni: 6.90) [21]
O	5.360	5.229	2.936	3.093	0.820	3.79	3.75 [22]
CO	4.487	3.629	1.811	1.698	1.075	1.38	1.55 [23]

the energy difference between the first and the third terms will correspond to metallic clusters of different delocalized electron densities. We see that the error (due to the finite size of the cluster) corresponding to this orthogonalization hole scheme is similar in nature to the difference between the ionization potential of a cluster and the work function. Moreover, by using a positively charged cluster (see (2)) we decrease the electronic density corresponding to the delocalized electrons in the cluster and thus we reduce the orthogonalization hole type of error.

The calculations are done by using the LCGTO scheme [17] in the framework of the LSD approximation [18]; the exchange–correlation energy functional used is the VWN [19] one and model potentials are used for the metal atoms. Further details can be found in the literature [9]. Our results concern the chemisorption of H, C, O and CO on Pd. We use in each case the Pd$_4$ and Pd$_7$ clusters shown in figure 1, corresponding to the

threefold hollow site above the tetrahedral interstice. The Pd–Pd distance is that of the bulk metal, $d = 5.185$ au. We present $E_{M-A}^{*(n)}(x)$ calculated by using $x = x_0$, the value optimized as described above from the Pd_4 and Pd_7 clusters, in table 1. The case corresponding to $x = 1$ is given in table 1. It is interesting to note that in all the cases studied here x_0 is rather close to 1, and thus we can propose the approximation $E_{M-A} = E_{M-A}^{*(n)}(x = 1)$.

We point out that the size effect is very much affected by the value of x used in the calculation of $E_{M-A}^{*(n)}(x)$ and this is the main result of the present work. This is shown in figure 2 where we plot $E_{M-CO}^{*(n)}(x)$ calculated for Pd_4 and Pd_7, for different values of x. Therefore the assumption on which the cluster model for chemisorption energies relies is satisfied only for a particular value of x, which is not $x = 0$. As we can see in the tables, our scheme leads to results for E_{M-A} much improved over the usual direct calculation result ($x = 0$). Thus we can conclude that an important part of the error one gets for E_{M-A} in the cluster-like calculations within the LSD approximation is due to size effects. Nevertheless, we do not rule out some other sources of error, such as basis set expansions, structure effects (lattice relaxation, surface reconstruction, . . .) and non-local corrections. Finally, we emphasize that the variation of the adsorbate–cluster interaction energy with respect to the surface–adsorbate distance does not depend on x (for reasonable values of x) and therefore in our description we finally find accurate results for both energies and force constants (equilibrium positions and frequency vibrations).

In this work, starting from the comparison between the ionization potential of finite clusters and the work function of infinite metals, we have removed the significant size effect due to the electronic relaxation involved in binding energies of atoms and small molecules on transition metal surfaces, as calculated from cluster models.

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