

## Performance of correlation functionals in *ab initio* chemisorption cluster-model calculations: Alkali metals on Si(111)

A. Clotet and J. M. Ricart

*Departament de Química, Facultat de Química, Universitat Rovira i Virgili, Pl. Imperial Tàrraco 1, 43005 Tarragona, Spain*

J. Rubio and F. Illas

*Departament de Química Física, Facultat de Química, Universitat de Barcelona, C/Martí i Franquès, 1, 08028 Barcelona, Spain*

E. San Fabián and F. Moscardó

*Departamento de Química Física, Universidad de Alicante, Apartado 99, 03080 Alicante, Spain*

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The performance of different correlation functionals has been tested for alkali metals, Li to Cs, interacting with cluster models simulating different active sites of the Si(111) surface. In all cases, the *ab initio* Hartree-Fock density has been obtained and used as a starting point. The electronic correlation energy is then introduced as an *a posteriori* correction to the Hartree-Fock energy using different correlation functionals. By making use of the ionic nature of the interaction and of different dissociation limits we have been able to prove that all functionals tested introduce the right correlation energy, although to a different extent. Hence, correlation functionals appear as an effective and easy way to introduce electronic correlation in the *ab initio* Hartree-Fock description of the chemisorption bond in complex systems where conventional configuration interaction techniques cannot be used. However, the calculated energies may differ by some tens of eV. Therefore, these methods can be employed to get a qualitative idea of how important correlation effects are, but they have some limitations if accurate binding energies are to be obtained.

### I. INTRODUCTION

The *ab initio* Hartree-Fock cluster-model approach provides a simple and efficient tool for investigating many important aspects of surface-science-related phenomena.<sup>1-4</sup> Of course, only those processes which are dominated by local interactions can be adequately described through the cluster-model approach. Adsorbate geometries, vibrational frequencies, the origin of core-level binding-energy shifts, and the mechanism of chemical bonding are examples of local properties, while interaction energies may be more cluster-size dependent.<sup>5</sup> In some special cases it is possible to obtain interaction energies that are converged with respect to the cluster size, if the interaction energy is computed not from the electronic ground state but by using an appropriate excited state.<sup>6-10</sup> However, we must point out that the nature of the bond arising from two different electronic states might be very similar. The differences between the two states can be ascribed to the limited cluster representation of the surface conduction band. An important consequence of this limitation is that great care must be used to obtain estimates of the chemisorption bond energy.<sup>11</sup>

However, there are many key surface-science questions that are directly related to the interaction energy. The determination of the active site, the influence of promoters or inhibitors, and the activation energy for a given surface reaction are examples where the interaction energy is a very important property. Therefore, and within the limitations above described, it is convenient to

be able to compute rather accurately the interaction energy between a cluster model and a given adsorbate. Many of the cluster-model investigations rely on the use of *ab initio* self-consistent-field molecular-orbital Hartree-Fock (HF-SCF) wave functions in which the molecular orbitals (MO's) are expressed as a linear combination of atomic orbitals (LCAO's) (see Refs. 1-4). However, while this approach is able to provide useful information about the mechanism of the adsorbate-surface bond and reliable structural parameters, it usually leads to very poor interaction energies. Except for the possible cluster-model artifacts, these limitations are due to the so-called electronic correlation effects or the instantaneous electron-electron interactions, which are neglected at the Hartree-Fock level of theory. Better results can be achieved if electronic correlation effects are explicitly taken into account in the energy calculation. There are several possible choices for efficiently including these electronic correlation effects in an *ab initio* way. These include the use of configuration interaction or many-body perturbation theory (MBPT) techniques (see Refs. 3 and 4). However, all these techniques are computationally expensive and cannot be applied to medium or large cluster models. An alternative approach, also widely employed to study surface-science problems using cluster models, is the use of density-functional theory (DFT) methods such as the local spin density (LSD) approach and its various gradient corrected versions (see, for instance, Refs. 12-15 and references therein). However, in the DFT-based methods exchange and correlation effects are introduced through appropriate functionals. The limitations of the

DFT approaches are mainly due to the approximate nature of the various functionals and to the fact that there is no way to systematically improve the results. On the other hand, in the HF-SCF-based methods the results can be systematically improved by using larger and larger basis sets, and improving the description of the instantaneous electron-electron interactions either by considering larger configuration-interaction expansions or higher orders of the MBPT. This is one of the main advantages of the *ab initio* molecular-orbital cluster model; it allows the use of more sophisticated theoretical approaches without any modification in the model itself.<sup>6–10,16–20</sup>

In order to understand the physical origin of the electronic correlation, Ricart and co-workers have studied several adsorbate systems using uncorrelated and correlated *ab initio* wave functions.<sup>21,22</sup> Based on different theoretical techniques, these authors concluded that the qualitative picture of the chemisorption bond is essentially the same in both approaches. According to the results of Ricart and co-workers the HF-SCF electronic density of a given adsorbate-surface system is essentially correct. This fact opens the possibility of including the electronic correlation energy as an *a posteriori* correction using any of the recently developed electronic correlation functionals. This is a very attractive possibility because it starts from a suitable well-defined electronic density, because of its low computational cost, and because, in contrast to the standard DFT approaches, the exchange interactions are obtained without any approximation other than the use of a finite basis set.

In this work we will be concerned with the performance of a series of correlation functionals to properly describe the interaction of an alkali atom above several active sites of the Si(111) surface. The choice of this particular set of systems is not fortuitous. In a recent work Clotet *et al.*<sup>23</sup> have shown that, at low coverage, the bonding of alkali atoms to Si(111) can be regarded as essentially ionic. For an ionic bond it is well known that the failure of the HF-SCF approach arises from the poor description of the ions that are interacting at the equilibrium distance, compared to the better description at infinite separation when both interacting units are neutral. It is also known that, because in an ionic system the physical situation at large and short distances is equally badly described at the HF-SCF level of theory, this poor description can be corrected by simply using the ionic dissociation limit. Therefore, these kinds of systems provide a unique situation for testing the different correlation functionals in complex systems where no experimental data are available.

## II. SURFACE-CLUSTER MODELS

In order to make use of the aforementioned results reported by Clotet *et al.*<sup>23</sup> we have also chosen the unreconstructed Si(111) surface and explicitly considered the main adsorption sites. These are the onefold atop site ( $T_1$ ) where the adsorption takes place directly above a Si surface atom, and the threefold eclipsed ( $T_4$ ) and open ( $H_3$ ) sites, where the adatom interacts with three surface dangling bonds with or without a second layer Si atom

below the considered site (see Fig. 1 in Ref. 23). Moreover, we have considered the adsorption of a single alkali atom.

The cluster models are a simplified representation of the adsorption site. Ideally, one should use a cluster as large as possible; in practice the cluster size is limited because of the computational facilities. In the case of surface models simulating a silicon surface, there is an additional problem due to the cluster edge atoms, which introduce undesired dangling bonds. The easiest way to overcome this difficulty is to saturate the free valences with hydrogen atoms; this has been, indeed, the common strategy in the literature.<sup>24–37</sup> Accordingly, we have decided to saturate the free valences of the cluster silicon edge atoms with atomic hydrogen atoms placed at the usual Si-H distance. For specific details concerning these embedding hydrogen atoms and related approaches see Refs. 23 and 37.

To represent the atop interaction, i.e., the  $T_1$  site of the Si(111) surface, we use a  $\text{Si}_{10}\text{H}_{15}$  cluster model having four silicon layers and with the edge atoms saturated with hydrogen atoms. A four-layer cluster is also used to simulate the  $H_3$  open site, the resulting model may be written as  $\text{Si}_{10}\text{H}_{13}$ . Finally, the threefold  $T_4$  eclipsed site has been represented by a  $\text{Si}_5\text{H}_9$  cluster model. Results for the isolated clusters have already been reported in Refs. 33, 34, and 37. Here, we will only add the electronic ground state of the different cluster models using the irreducible representations of the  $C_{3v}$  point group. For  $\text{Si}_{10}\text{H}_{15}$  the electronic ground state is a  $^2A_1$ , which upon interaction with an alkali-metal atom leads to a closed shell  $^1A_1$ , whereas for both,  $\text{Si}_{10}\text{H}_{13}$  and  $\text{Si}_5\text{H}_9$ , the ground state is  $^4A_2$ , leading to a  $^3A_2$  after interaction with the adsorbate. Further details about the cluster models can be found in Ref. 23.

## III. COMPUTATIONAL DETAILS

In this work we have obtained *ab initio* HF-SCF wave functions for all alkali- $\text{Si}_n\text{H}_m$  cluster models previously described. The electronic wave function has been obtained in the well-known LCAO-MO framework, where the MO's are expressed in terms of a given basis set. Here we use the same nonempirical pseudopotentials and basis sets as in the work of Clotet *et al.*<sup>23</sup> For the nonsurface-Si-cluster atoms these basis sets are of double- $\zeta$  or  $(4s4p/2s2p)$  quality, whereas the basis set used to describe the cluster surface atoms directly interacting with the adsorbate includes also a single  $d$  polarization and the final basis set is  $(4s4p1d/2s2p1d)$ . For the embedding hydrogen atoms we use a  $(4s/2s)$  double- $\zeta$  basis set. Finally, for the alkali-metal atoms the Contracted Gaussian-type orbital basis set is as follows: for the Li atom we use the  $(11s5p/4s3p)$  basis set of Krishnan *et al.*,<sup>38</sup> whereas for atoms going from Na to Cs we have used the basis sets reported in Ref. 39, which all are of triple- or quadruple- $\zeta$  quality for the valence shell and for the most external nonvalence shell, and minimal to describe the other core electrons. Final basis sets for Na to Cs are Na  $(9s4p/7s4p)$ , K  $(12s7p/8s5p)$ , Rb  $(15s9p3d/9s5p1d)$ , and Cs  $(18s12p6d/10s6p2d)$ .

Using the basis sets just described we have obtained HF-SCF wave functions for the interaction of each alkali metal above each active site. Following the usual strategy, calculations have been carried out at several distances of the adsorbate to the surface, and from the potential energy curves we have obtained the equilibrium distance above the surface,  $r_e$ , the vibrational frequency of the adsorbate for the normal mode perpendicular to the surface ( $\nu_e$ ) and the interaction energy (BE). In this work we have computed different values of BE depending on the asymptote used. First, we have the interaction energy with respect to both neutral isolated fragments defined as

$$\text{BE1} = -\{E(\text{Si}_n\text{H}_m\text{M}) - E(\text{M}) - E(\text{Si}_n\text{H}_m)\}. \quad (1)$$

Here we must point out that a detailed description of the interaction has shown that, in all cases, the bonding is essentially ionic.<sup>23</sup> For an ionic bond a better approximation to the interaction energy than that above described is to use the ionic limits. This is because correlation effects, neglected at the HF-SCF level, are very important for a proper description of the ionization potential and the electron affinity of the charged systems at either equilibrium of infinite separation (see Ref. 40). However, these effects are essentially of atomic origin and will be nearly constant along the potential-energy curve. Using the ionic limits permits us to take advantage of an error cancellation, the origin of which is perfectly known. Therefore, we consider the interaction energy which corresponds to the charged,  $\text{Si}_n\text{H}_m - \text{M}^+$  ( $\text{M} = \text{Li} - \text{Cs}$ ), isolated systems:

$$\text{BE2} = -\{E(\text{Si}_n\text{H}_m\text{M}^+) - E(\text{M}^+) - E(\text{Si}_n\text{H}_m^-)\}. \quad (2)$$

To recover the interaction energy with respect to the neutral limits, we simply correct BE2 by using the experimental alkali-metal ionization potential (IP) and the Si(111) surface work function (4.6 eV):

$$\text{BE3} = -\{E(\text{Si}_n\text{H}_m\text{M}^+) - E(\text{M}^+) - E(\text{Si}_n\text{H}_m^-) - \text{IP}(\text{M}) + \Phi_{\text{Si}(111)}\}. \quad (3)$$

Moreover, the choice of the experimental surface work function instead of the cluster electron affinity permits an approximate correction to the limited cluster size.<sup>41</sup>

The contribution of electronic correlation to the interaction energy has been computed in the framework of the *a posteriori* Hartree-Fock density-functional theory. The precise theoretical approach used in this work corresponds to the Kohn-Sham equations with exact exchange usually also referred to as Hartree-Fock-Kohn-Sham equations:<sup>42</sup>

$$\left[ \hat{F} + \frac{\delta E_c[\rho]}{\delta \rho} \right] \Psi_i = \varepsilon_i \Psi_i, \quad (4)$$

where  $\hat{F}$  is the Fock operator of the Hartree-Fock theory. To obtain the total energy from this form of the Kohn-Sham equations, we will use a simple but very accurate approximation. This approach due to Stöll, Pavlidou, and Preuss<sup>43</sup> assumes that the correlation term in Eq. (4)

is small and has very little effect on the Fock operator, so the Kohn-Sham orbitals are nearly equal to the Hartree-Fock orbital and the resulting electronic densities will be almost the same. If  $\rho_{\text{KS}}$  and  $\rho_{\text{HF}}$  represent the Kohn-Sham and Hartree-Fock densities, the above approach can just be written as

$$\rho_{\text{KS}}(r) = \rho_{\text{HF}}(r). \quad (5)$$

In this case it is easy to prove that the Kohn-Sham functional for the total,  $E_{\text{KS}}[\rho_{\text{KS}}]$ , and correlation energy,  $E_c[\rho_{\text{KS}}]$ , can be approximated by

$$E_{\text{KS}}[\rho_{\text{KS}}] \approx E_{\text{KS}}[\rho_{\text{HF}}] = E_{\text{HF}} + E_c[\rho_{\text{HF}}], \quad (6)$$

where  $E_{\text{HF}}$  is the Hartree-Fock, or HF-SCF, energy (see Ref. 44). The above assumptions have been successfully tested for atoms and small molecules for currently used functionals. Furthermore, it has been seen that some currently used  $E_c[\rho]$  functionals are quite insensitive to changes in the density, including basis-set improvements or the use of more accurate density instead of the Hartree-Fock one (see Ref. 44 and references therein). As pointed out elsewhere, the computational simplicity of Eq. (6), where exchange is explicitly treated permits us to study different approximations to the correlation functional in their purest form, that is, without contamination from an approximate exchange functional.

The total energy in Eq. (6) has been computed using a variety of different functionals. These include the LSD approximation,<sup>45,46</sup> using the expressions suggested by Vosko, Wilk, and Nusair,<sup>47</sup> VWN-LSD, and its self-interaction correction version developed by Stoll, Pavlidou, and Preuss<sup>48</sup> VWN-SIC; we also have considered the SIC procedure suggested by Perdew and Zunger<sup>49</sup> hereafter referred to as PZ-SIC. In order to take into account gradient corrections to LSD we use the approach due to Becke,<sup>50</sup> here referred to as B-GC. Finally, we have considered methods which are derived from the correlation factor method and depend not only on the first-order density. Here we consider the methods proposed by Colle and Salvetti<sup>51</sup> (CS), by Moscardó and San-Fabián<sup>52</sup> (MSF), and by Lie and Clementi<sup>53</sup> (LC).

To investigate the effect of electronic correlation in the HF-SCF calculated values, the structural parameters,  $r_e$  and  $\nu_e$ , and the interaction energies BE1, BE2, and BE3 have been also computed using the seven correlation functionals mentioned above.

#### IV. RESULTS AND DISCUSSION

First, we will briefly comment on the electronic correlation effects on the internuclear equilibrium distance  $r_e$ , and the vibrational frequency  $\nu_e$ , for the normal mode perpendicular to the surface. For the  $r_e$  values the different functionals always lead to distances which are shorter than the HF-SCF values. In all cases, different active sites and different adsorbates, the largest correction occurs for the B-GC functional while the smaller one usually occurs for the LC one. The difference with respect to the HF-SCF value ranges from 0.28 bohr for Li on the  $\text{Si}_{10}\text{H}_{13}$  cluster modeling the  $\text{H}_3$  site of 0.5 bohr for

Cs above the  $\text{Si}_5\text{H}_9$  model of the  $T_4$  site. In relative terms, the correlation correction to  $r_e$  is as much as 5–8 % depending on the functional. Among different functionals the differences range from 0.07 bohr for  $\text{LiSi}_{10}\text{H}_{15}$  to 0.4 bohr for  $\text{CsSi}_5\text{H}_9$ . Hence, while all functionals predict an equilibrium distance shorter than the HF-SCF one, the magnitude of the correction itself is of the order of the uncertainty of the HF-SCF value. We can conclude this discussion by stating that the HF-SCF distances are too long by a factor of about 2%. For ionic bonds, as is the case here, the main effect of the electronic correlation on the equilibrium distance must be due to a reduction of the Pauli repulsion resulting in a shorter distance. This is well predicted by the different functionals, but with an average uncertainty of about 0.15 bohr.

For the vibrational frequency, changes with respect to the calculated HF-SCF values are even smaller than those on the equilibrium distance. Overall, the deviation is smaller than 1%. This is not surprising, because for an ionic bond the electronic correlation will shift the HF-SCF potential-energy curve without affecting its curvature.

Now we will turn our attention to the calculated interaction energies where electronic correlation effects are expected to be very important. To avoid huge tables with seven functionals, five adsorbates, three active sites, and, for each case, three values of the interaction energy as given by Eqs. (1)–(3), we will restrict the main discussion to the case of K above the atop and open active sites discussed above. We must point out that this choice is arbitrary but it is representative of the whole series of calculations. The analysis that we will present for K on Si(111) does also hold for the remaining adsorbates and active sites; the whole series of results being available upon request to the authors. In Tables I and II we report the electron affinity (EA) of the  $\text{Si}_{10}\text{H}_{15}$  and  $\text{Si}_{10}\text{H}_{13}$  surface-cluster models calculated at the HF-SCF level and after including the electronic correlation effects using the seven correlation functionals mentioned above. Here we must point out that, although the surface work function does not distinguish the case where an electron is

TABLE I. Ionization potential of K, electron affinity (EA) of the atop  $\text{Si}_{10}\text{H}_{15}$  cluster model of Si(111), and the interaction energy of K above this model computed with respect to neutral (BE1), ionic (BE2), and ionic corrected to neutral (BE3) limits. Values, in eV, have been obtained from Hartree-Fock (HF-SCF) and from the different correlation functionals described in Sec. III.

Method	IP	EA	BE1	BE2	BE3
HF-SCF	4.01	1.12	1.00	3.89	4.16
VWN-LSD	4.47	2.46	1.90	3.91	4.17
VWN-SIC	4.12	1.91	1.70	3.90	4.16
PZ-SIC	4.11	1.94	1.73	3.90	4.16
B-GC	4.25	2.08	1.91	4.08	4.34
CS	4.27	1.98	1.76	4.05	4.31
MSF	4.21	2.12	1.90	3.98	4.24
LC	4.10	1.73	1.53	3.90	4.16
Expt.	4.34				

TABLE II. Ionization potential of K, electron affinity (EA) of the open  $\text{Si}_{10}\text{H}_{13}$  cluster model of Si(111), and the interaction energy of K above this model computed with respect to neutral (BE1), ionic (BE2), and ionic corrected to neutral (BE3) limits. Values, in eV, have been obtained from Hartree-Fock (HF-SCF) and from the different correlation functionals described in Sec. III.

Method	IP	EA	BE1	BE2	BE3
HF-SCF	4.01	0.16	0.03	3.88	4.15
VWN-LSD	4.47	1.65	1.02	3.84	4.10
VWN-SIC	4.12	1.15	0.90	3.86	4.12
PZ-SIC	4.11	1.19	0.94	3.86	4.12
B-GC	4.25	1.37	1.25	4.13	4.39
CS	4.27	1.18	0.96	4.05	4.31
MSF	4.21	1.41	1.14	3.94	4.20
LC	4.10	0.73	0.49	3.86	4.12

added from that where an electron is taken, in a surface-cluster model the situation is very different. For  $\text{Si}_{10}\text{H}_{15}$ , the Hartree-Fock IP is 7.68 eV,<sup>37</sup> but the EA is only 1.12 eV. Therefore, the EA in Tables I and II corresponds to the cluster work function to be used when there is a cationic adsorbate, as is the case here. Notice that even after correcting the HF-SCF electron affinity of  $\text{Si}_{10}\text{H}_{15}$ , by means of correlation functionals, the cluster EA lies between 1.7 and 2.5 eV, still far from the Si(111) work function which is 4.6 eV. Therefore, there are two sources of error in the calculation of the interaction energies of ionic adsorbates on a surface-cluster model. One is due to the neglect of electronic correlation and can be corrected by explicitly introducing it in the energy calculation; the other one is due to the limited cluster size. The first deficiency can be approximately corrected by using the ionic limit BE2. The second one is more difficult to deal with, but, according to Russier and co-workers,<sup>54,55</sup> it is possible to get a rough empirical estimate by using the experimental work function in the calculation of the interaction energy. A similar approach was used by Torras *et al.*<sup>41</sup> in the study of O chemisorption above Cu(111) and Ag(111), where the interaction is also largely ionic. Therefore, we have computed the interaction energy with respect to the ionic limit and by correcting to the neutral limit using the experimental surface work function, i.e., BE3 or Eq. (3). Therefore, in Tables I and II, we report the interaction energies with respect to the neutral (BE1) ionic (BE2) and ionic corrected (BE3) asymptotes [cf. Eqs. (1)–(3)]. The K ionization potential calculated at different levels has also been included in the tables in order to allow the reader to compute BE2 or BE3 from BE1.

The first point to comment on is the large improvement of the surface cluster EA after including the electronic correlation, which results in a much larger interaction energy with respect to the neutral isolated fragments; this is simply because the cost of forming a cation above the surface model is compensated by the energetic gain of the surface. For an infinite surface the gain is equal to the surface work function, but in the case of a

finite cluster model the gain is given simply by the cluster EA.<sup>23</sup> For the atop site the HF-SCF value for the cluster EA is  $\approx 1.12$  eV, whereas all correlation functionals predict EA values ranging from  $\approx 1.73$  to 2.46 eV. Hence, the improvement on the cluster EA is responsible for the improvement of the HF-SCF interaction energy with respect to the neutral limits, BE1. In fact, the correlated values of BE1 range from 1.53 to 1.91 eV, while the HF-SCF value is 1.00 eV only. Similarly, for the open site the improvement in EA leads to an improved BE1 value that ranges from 0.49 to 1.25 eV. In order to test the reliability of the different correlation functionals we analyze the results corresponding to BE2 (or BE3). Since the interaction is mainly ionic the HF-SCF value for BE2 will be correct, because the same error is made at short and large (ionic limit) distances. Results for BE2 corresponding to the different correlation functionals are remarkably close to the HF-SCF value. This may indicate that the different functionals do in fact introduce the proper electronic correlation correction to the cluster EA and to the adsorbate IP at short and large distances. For atomic species it is well known that this is the case (see Ref. 44 and references therein). Here, an error cancellation similar to that occurring at the HF-SCF level is also possible. To prove that this is not the case we point out that, because of the ionic nature of the chemical bond exhibited by these systems, the interaction energy BE1 for the

different functionals can be obtained approximately (by an average error of  $\approx 0.2$  eV) by simply correcting the HF-SCF value by the HF-SCF error in the cluster EA and the alkali-metal IP; this is, simply,

$$\text{BE1(DFT)} \approx \text{BE1(HF)} + [\text{EA(DFT)} - \text{EA(HF)}] - [\text{IP(DFT)} - \text{IP(HF)}]. \quad (7)$$

The relation in Eq. (7) simply means that one can obtain the correlation-corrected value by simply carrying out the density-functional calculation on the isolated cluster without having to compute the correlation energy for the cluster-adsorbate supersystem. Also, Eq. (7) shows that all correlation functionals used in the present work introduce the physically correct correlation effects, although to a different extent as indicated by the different values of the cluster EA. Also, we have to point out that for the alkali metals the correlation correction to the IP is fairly small. Accordingly, the correlation-corrected BE1 values appearing in Tables I and II can almost be obtained using the Hartree-Fock value and the calculated EA data reported in these tables. According to the present results all but the LC functionals lead to interaction energies that agree within 0.2–0.3 eV. Finally, we notice that results concerning BE3 at the HF-SCF level and for the different functionals are again in good agreement and may be regarded as a reasonable estimate of the interac-

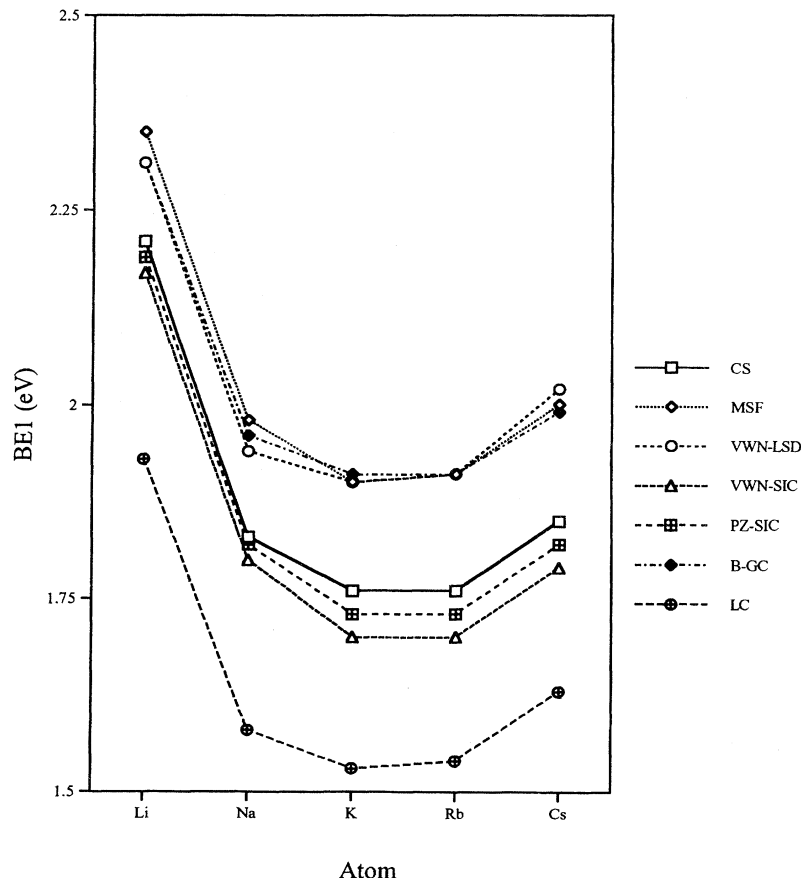


FIG. 1. Interaction energies with respect to neutral limits (BE1) for Li to Cs above the  $\text{Si}_{10}\text{H}_{15}$  cluster model as obtained from several correlation functionals.

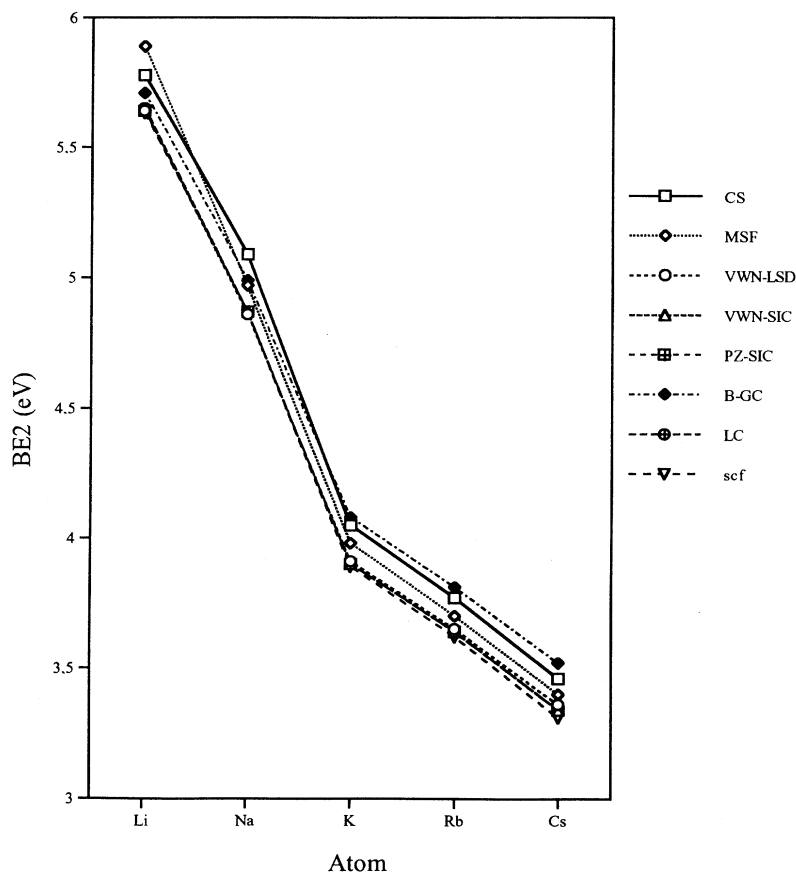


FIG. 2. Interaction energies with respect to ionic limits (BE2) for Li to Cs above the  $\text{Si}_{10}\text{H}_{15}$  cluster model as obtained from Hartree-Fock and from several correlation functionals.

tion energy of K above the different sites of Si(111), provided the EA value has been corrected with respect to the experimental surface work function and, hence, a correction for the cluster size is indeed indirectly included (see Refs. 23 and 41).

The above discussion was carried out for K on the  $T_1$  and  $H_3$  sites only. To show that the overall situation is the same for the different adsorbates, we plot the BE1 and BE2 values for the different adsorbates Li to Cs above the  $\text{Si}_{10}\text{H}_{15}$  model (Figs. 1 and 2, respectively). Similar plots (not shown) exist for Li to Cs above the  $\text{Si}_{10}\text{H}_{13}$  and  $\text{Si}_5\text{H}_9$  models. The analysis of the data on Fig. 1 reveals that different correlation functionals behave rather similarly, but again with uncertainties of  $\approx 0.3$  eV in the calculated binding energies. Also, Fig. 2 shows that when we refer to the ionic limit all the different functionals behave in the same way. As expected from the ionic nature of the interaction, the correlation-corrected values for BE2 are very similar to those obtained at the Hartree-Fock level. As indicated above, this is because all methods, HF and the different correlation functionals, make the same error at short and large distances. However, the absolute error is much smaller when using the correlation functionals, and the BE1 values are much better when correlation is explicitly included.

## V. CONCLUSIONS

The performance of different correlation functionals has been investigated for cluster models simulating the interaction of alkali metals above different active sites of the Si(111) surface. The ionic nature of the interaction facilitates largely the analysis of the results arising from different functionals, because its physical origin is known. By using different dissociation limits we have been able to show that all functionals are capable of introducing the proper correlation energy, although to different extents.

The effects of the electronic correlation on the equilibrium distance are noticeable but small. Overall, the distances are reduced from the HF value by about 3–5%. The effect on the vibrational frequencies is even smaller.

As a final comment we must point out that, while the different correlation functionals investigated in the present work introduce the correct correlation energy, the different values have a marked dispersion. For a given adsorbate at a given site, and apart from the LC functional, which always leads to the most different results, the calculated binding energies with respect to the neutral fragments show uncertainties of  $\approx 0.2$ – $0.4$  eV; the values with respect to the ionic limits show a smaller dispersion, but due to error cancellation. Therefore, we may conclude that the use of correlation functionals is a

useful and easy way to explicitly include correlation effects in complicated systems. Hence, our results support the strategy recently reported by Causà and Zupan,<sup>56</sup> which permits the inclusion of correlation effects as an *a posteriori* correction to periodic Hartree-Fock calculations. However, we must point out the final energies exhibit uncertainties of some tens of eV. Consequently, DFT correlation-corrected energies are doubtlessly an improvement over the HF ones, but for quantitative purposes results have to be handled with caution.

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