CO/Pt(111): GGA density functional study of site preference for adsorption

M. Alaei,[1,2] H. Akbarzadeh,[1] H. Gholizadeh,[1] and S. de Gironcoli[2]

[1]*Department of Physics, Isfahan University of Technology, Isfahan 84156, Iran*

[2]*International School for Advanced Studies (S.I.S.S.A.) and CNR-INFM DEMOCRITOS National Simulation Center, Via Beirut 2-4, 34014 Trieste, Italy*

Based on density functional formalism, we investigate the site preference for the adsorption of CO on Cu, Rh, Ag, Pt, and Au(111) surfaces. The exchange-correlation term was approximated by BLYP, a functional within the generalized gradient approximation (GGA) family that combines Becke's exchange functional with the Lee-Yang-Parr correlation functional. Our study shows that BLYP, although not a hybrid functional, can correctly predict the adsorption site for CO. This invalidate the general belief that only hybrid functionals are able to predict the correct site preference. We analyze our results by repeating all calculations using another well-known GGA functional, Perdew-Burke-Ernzerhof, which could trace back the origin of the success of BLYP to the different behavior of the two GGA funcionals at large values of the reduced density gradients, $s \propto \frac{|\nabla n|}{n^{3/4}}$. This is a region where different functionals in the GGA family may legitimately behave very differently as it is poorly constrained on physical ground. Our present observation points to the possibility of further improving the accuracy of exchange-correlation functionals in the GGA family by properly constraining the remaining flexibility in the exchange-correlation kernel in this underdetermined region so as to reproduce known results in simple but critically important systems like the one studied here.

I. INTRODUCTION

The chemisorption of carbon monoxide on transition metals (TMs) has been extensively studied both theoretically and experimentally. The simplicity of the adsorption mechanism makes CO on metal surfaces a prototypical system for small molecule chemisorption on surfaces. Despite of this simplicity, intensive recent studies have shown that prevalent density functional theory approximations, i.e., local density approximation (LDA) and generalized gradient approximation (GGA), are not able to properly predict the CO/Pt(111) site preference.[1] Experimental investigations by different methods and at different temperatures (4–160 K) identify the top site as the most stable location,[2–7] while within GGA and LDA calculations, the hollow sites are preferred. The top site stability has only been confirmed by B3LYP[8,9] and recently also by some Perdew-Burke-Ernzerhof (PBE0) calculations,[12] (two hybrid functionals[10,11]) as well as Hartree-Fock plus Møller-Plesset perturbation theory method.[13] Similar erroneous site determination has also been observed in CO/Cu(111) and CO/Rh(111) systems.[1,14] Furthermore, two other cases, CO/Ag(111) and CO/Au(111), show in theoretical studies[14] a degenerate site preference which is not consistent with experimental data.

There is a general belief that the shortcoming originates from the exchange-correlation functionals. A widely accepted belief is that hybrid functionals are more successful in describing chemisorption of CO molecules on TM surfaces, although even this idea seems controversial for PBE0 hybrid functional.[12,15] Technical issues make hybrid-functional calculations extremely expensive[16] in periodic extended systems, and thus, a proper assessment of these results is still difficult.

It has been suggested that a GGA+U-type functional[17] could be an alternative solution. In this approach, the Hubbard-type repulsion is implemented on CO molecular orbitals. The disadvantage of this method is, however, that the U parameter needs to be adjusted for each case.

For these reasons, it is very attractive to further verify whether some appropriate GGA functionals could be able to correctly predict the adsorption site, especially for small molecules such as CO. Among the several GGA funcionals, BLYP [which combines Becke's exchange functional[18] with the correlation functional of Lee, Yang, and Parr (LYP)[19]] seems to be more successful at atomic energy level compared to other GGA functionals[20] and hence worth to be tested.

We therefore adopted the BLYP functional to study the adsorption-site preference in three paradigmatic problematic cases: CO/Pt(111), CO/Rh(111), and CO/Cu(111). We additionally examined CO/Ag(111) and CO/Au(111), where PBE erroneously predicts near degeneracy in adsorption energy.

II. COMPUTATIONAL DETAILS

In this research, we used two density functional theory (DFT) based packages; most calculations have been performed using the plane-wave-pseudopotential code PWSCF in the QUANTUM-ESPRESSO[22] distribution. In these calculations, ultrasoft pseudopotentials were used to describe electron-ion interactions. kinetic energy cutoffs of 40 and 250 Ry were used in the plane-wave expansion of wave functions and charge density, respectively. The surface Brillouin zone was sampled according to a grid of $8 \times 8 \times 1$ k points, and the smearing method, with a broadening of 0.01 Ry, was used in order to deal with the metallic character of the slabs. The distance between the periodically repeated slabs was set to 13 Å. For the calculation of the d-band center, we used 16-

TABLE I. Parameters of the FP-LAPW calculations for CO/Cu(111): cut off for the plane-wave representation (expansion) of the wave functions (E^{wf}) and potential (E^{pot}); cut off for the spherical harmonics representation (l_{max}) and the muffin-tin radii (R^{MT}).

Parameter	Value
E^{wf}	18.8 Ry
E^{pot}	625 Ry
l_{max}^{wf} (sph)	12
l_{max}^{wf} (nonsph)	6
l_{max}^{pot}	6
R^{MT} (Cu)	1.8 (a.u.)
R^{MT} (C)	0.9 (a.u.)
R^{MT} (O)	0.8 (a.u.)

layer unrelaxed slab with $16 \times 16 \times 1$ k-point sampling. A vacuum region between repeated slabs corresponding to eight atomic layers was chosen in this case.

The full potential linearized augmented plane-wave WIEN2K[23] code is considered as one of the most accurate packages for electronic structure calculations. Hence, in order to validate the accuracy of our home-made pseudopotentials, a number of WIEN2K calculations have been performed to compare the bulk properties obtained by the two methods. Additionally, the calculation for CO/Cu(111) was repeated with this package using both PBE and BLYP functionals. We used the most efficient method within full potential linearized augmented plan wave (FP-LAPW) approach, namely, APW+LO, to find accurate energy eigenvalues. All numerical parameters in our calculations were carefully optimized. We used a $7 \times 7 \times 1$ k-point sampling and a 18.8 Ry cutoff energy for plane-wave expansion. We considered a vacuum region of 12.6 Å thickness between slabs. Other numerical parameters are shown in Table I. In comparison to previous work by Feibelman *et al.*,[1] a more accurate set of parameters was used.

For all simulations of CO/TM(111), we used five-layer metallic slabs with a $\sqrt{3} \times \sqrt{3}$ in-plane periodicity resulting in $\frac{1}{3}$ coverage of CO molecules. The two topmost layers as well as carbon and oxygen atoms were allowed to relax. For simplicity, we only compared two sites: fcc, as representative of a hollow site, and the top site.

TABLE II. PBE bulk properties: a_0 is lattice parameter and B_0 is bulk module; experimental data have been taken from Ref. 34.

| Transitian metal | PBE (ESPRESSO) | | PBE (WIEN2K) | | Expt | |
	a_0 (a.u.)	B_0 (GPa)	a_0 (a.u.)	B_0 (GPa)	a_0 (a.u.)	B_0 (GPa)
Cu	6.86	139	6.83	149	6.83	140
Rh	7.32	250	7.25	250	7.19	380
Ag	7.87	91	7.80	102	7.72	100
Pt	7.53	247	7.48	258	7.42	230
Au	7.84	141	7.81	131	7.71	220

TABLE III. BLYP bulk properties: a_0 is lattice parameter and B_0 is bulk module; experimental data have been taken from Ref. 34.

| Transitian metal | BLYP (ESPRESSO) | | BLYP (WIEN2K) | | Expt. | |
	a_0 (a.u.)	B_0 (GPa)	a_0 (a.u.)	B_0 (GPa)	a_0 (a.u.)	B_0 (GPa)
Cu	7.00	115	7.00	116	6.83	140
Rh	7.36	221	7.38	221	7.19	380
Ag	8.04	70	7.99	80	7.72	100
Pt	7.68	203	7.64	206	7.42	230
Au	8.01	105	8.06	110	7.71	220

III. RESULTS AND DISCUSSION

A. Test of pseudopotentials

As a first step, in order to validate the accuracy of our home-made pseudopotentials and to check the effect of PBE and BLYP functionals on the structural properties, we compared the lattice parameter and bulk modulus of transition metals obtained by PWSCF and WIEN2K codes using PBE and BLYP functionals (Tables II and III).

It is clearly seen that the structural properties calculated by the two methods are very close to each other and in reasonable agreement with the corresponding experimental data. The lattice parameters predicted by BLYP functional for all metals are, however, larger than the corresponding values obtained by PBE. The error in the theoretical lattice parameter obtained using BLYP is large (about 3%, Table III), while PBE gives small errors for the lattice parameter (less than 1%, Table II).

B. Adsorption energy

According to the site-energy difference (ΔE_{t-h}) calculated by PWSCF and shown in Table IV, BLYP functional is clearly successful in the correct prediction of the site preference for all studied samples, while PBE gives the wrong answer for CO/Cu, CO/Rh, and CO/Pt systems. As a matter of fact, the BLYP functional improves the energy difference of fcc and top site by about 0.2 eV with respect to PBE.

The calculated adsorption energies are compared with the corresponding experimental values in Table V. The absolute value of the CO binding energy to the surfaces is generally

TABLE IV. The difference of total energy on top and hollow sites for BLYP and PBE functionals ($\Delta E_{t-h} = E_{top} - E_{fcc}$).

Transition metal	BLYP E_{t-h} (eV)	PBE E_{t-h} (eV)
Cu	−0.07	0.15
Rh	−0.18	0.07
Ag	−0.24	−0.06
Pt	−0.10	0.14
Au	−0.29	−0.03

TABLE V. Adsorption energy (E_{ads}); the experimental data have been taken from Abild-Pedersen and Andersson (Ref. [26]).

Transition metal	BLYP E_{ads} (eV)	PBE E_{ads} (eV)	Expt E_{ads} (eV)
Cu	−0.31	−0.72	−0.50 ± 0.05
Rh	−1.50	−1.83	−1.45 ± 0.14
Ag	−0.10	−0.17	−0.28
Pt	−1.20	−1.67	−1.48 ± 0.09
Au	−0.10	−0.26	−0.4

reduced, thus improving in many cases the agreement with the experimental results. This is at variance with the hybrid-functional case[12,15] where the correct site preference is obtained at the expense of a further increase in the molecule-surface binding energies with respect to the already too large PBE results. Calculations performed for CO/Cu(111) by WIEN2K are in good agreement with the pseudopotential results: PBE predicts a wrong site preference, while according to BLYP functional, top site is more stable by 0.1 eV (Cu was chosen for this test as, being the lightest element among sampled TM elements, the FP-LAPW calculation is less time consuming).

In order to understand why a simple GGA functional such as BLYP, in spite of its poor performance in the bulk structural properties, can predict the correct adsorption-site preference, we analyzed in detail the effect of BLYP on the TM surface and the CO molecule.

C. Effect of BLYP on transition metal surfaces

A difference between BLYP and PBE is a noticeable shift in the density of state of TM surfaces. To quantify this difference exactly, we calculated the center of d-band orbitals from the lowest energy up to the Fermi energy. The result is that BLYP shifts the center of d band of transition metals toward the Fermi energy (Table [VI]) by 0.1–0.2 eV depending on the particular system. Does this upward shift of d center toward the Fermi energy obtained by BLYP has any role in the correct site preference predicted by this functional? To answer this question, we exploited the fact that this feature can be modified, and thus its actual importance

TABLE VI. The center of d orbital calculated by BLYP and PBE functionals for (111) surface of transition metals.

Transition metal	BLYP d center (eV)	PBE d center (eV)
Pt	−2.51	−2.79
Rh	−2.42	−2.49
Cu	−2.56	−2.64
Ag	−4.05	−4.18
Au	−3.45	−3.68

TABLE VII. The effect of center of d orbital (d_c) on $\Delta E_{t\text{-}h} = E_{top} - E_{fcc}$. The calculations have been done without any surface relaxation, so the results are a little bit different from Table [IV]. The exchange-correlation functional is PBE. a_0 is optimum lattice parameter.

Transitian metal	a_0 (a.u.)	d_c (eV)	$\Delta E_{t\text{-}h}$ (eV)	$a_0 - 0.2$ (a.u.)	d_c (eV)	$\Delta E_{t\text{-}h}$ (eV)
Pt	7.53	−2.8	0.17	7.33	−3.2	0.12
Rh	7.32	−2.5	0.16	7.12	−2.8	0.11
Cu	6.86	−2.6	0.16	6.66	−2.8	0.12
Ag	7.84	−4.2	0.04	7.64	−4.4	−0.06
Au	7.87	−3.7	−0.01	7.67	−4.0	−0.08

analyzed, by strain:[24] by decreasing the lattice parameter of a transition metal, the center of its d band moves downward in energy. We therefore calculated the d-center position as well as the energy difference of the two adsorption sites ($E_{top} - E_{fcc}$) at two different lattice parameters: the equilibrium lattice parameter (a_0) and a second one of 0.2 bohr smaller. To make the comparison safe, we prevented the metal layers to relax (otherwise, the layers which were allowed to relax would expand so as to approximately maintain the atomic volume unchanged, somehow masking the effect). The results are compared in Table [VII]. It is clearly seen that the downward shift of d center produced by a lattice parameter reduction improves $\Delta E_{t\text{-}h}$, hence the upward shift caused by BLYP actually worsen the situation. We also checked for an upward shift of d center for Pt and indeed found out that $E_{top} - E_{fcc} = 0.23$ eV.

D. Effect of BLYP on CO molecule

A commonly accepted approach to study the effect of different exchange-correlation functionals on the chemisorption of CO on transition metals is to calculate the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap or its more meaningful equivalent, singlet-triplet excitation energy. Although DFT within the Kohn-Sham formalism is inherently not capable to predict the accurate value of this gap, the direct application of the gap in the well-known Blyholder model[25] makes it of special interest. The Blyholder model is, in fact, the most widely used framework to study the CO adsorption on TM surfaces. In this model, charge donation and backdonation are considered as the two most important factors and it is believed that CO 5σ orbital (HOMO) donates charge to the metal d orbital, and conversely, to compensate their charge transfer, there is a charge backdonation from d orbital to the originally empty molecular CO $2\pi^*$ orbital (LUMO). Therefore, according to this model, the HOMO-LUMO gap and the position of HOMO and LUMO orbitals with respect to the Fermi energy are the quantities that are significant in predicting the correct site preference.[27–29] The underestimation of the gap which is common in DFT causes the LUMO orbital to shift to a lower energy, and as a result, charge backdonation is enhanced. Based on this argument, the fcc site, with
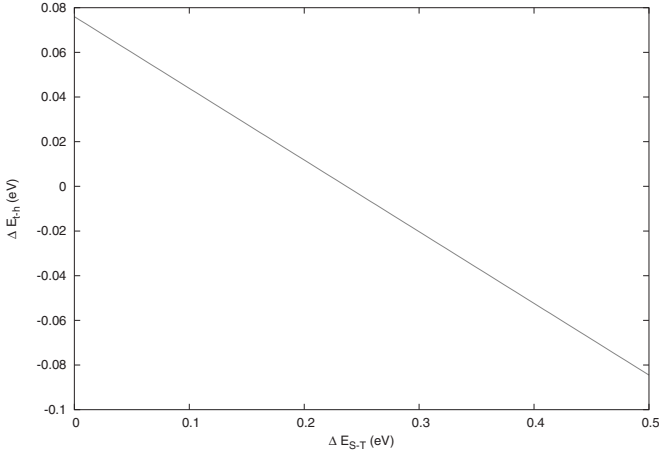
FIG. 1. $\Delta E_{t\text{-h}}$ (eV) for CO on Pt(111) versus $\Delta E_{\text{S-T}}$ (eV). The origin of horizontal axes is taken according to $\Delta E_{\text{S-T}}^{\text{GGA}}$ in Ref. 30

FIG. 2. (Color online) The enhancement factor $F_{\text{xc}}^{\text{GGA}}$ calculated by B88-, BLYP-, and PBE-GGA functionals in terms of the dimensionless reduced density gradient $s = \frac{|\nabla n|}{2(3\pi^2)^{1/3} n^{4/3}}$ and $r_s = \left(\frac{3}{4\pi n}\right)^{1/3}$.

its higher coordination (three TM atoms interact with CO molecule), compared to top (one TM atom interact with CO molecule), is expected to be more stable (the backdonation favors hollow sites[17] and this quantity is more likely to increase at hollow sites because of more access of d orbitals to LUMO orbital of CO). It has also been shown that there is a linear relationship between adsorption energy and HOMO-LUMO gap[17] similar to the linear dependence that exists between adsorption energy and singlet-triplet excitation energy.[30] These two relations are interconnected to each other due to the linear dependency of HOMO-LUMO gap and singlet-triplet excitation energy. Since, unlike the HOMO-LUMO gap, the CO singlet-triplet excitation energy is rigorously well defined in DFT, we focus on this quantity. The slope of linear regressions of chemisorption energy versus singlet-triplet splitting energy was estimated in Ref. 30 for top, bridge, and hcp hollow sites. By using these data, we plotted $\Delta E_{t\text{-h}}$ versus singlet-triplet excitation energy in Fig. 1. In order to increase $\Delta E_{t\text{-h}}$ by -0.1 eV, as needed to reproduce the $\Delta E_{t\text{-h}}$ calculated by BLYP in CO/Pt(111), Table IV, we would need about 0.55 eV increase in the singlet-triplet excitation energy (Fig. 1). However, the values for the singlet-triplet splitting that we have obtained by using BLYP and PBE functionals are $\Delta E_{\text{S-T}}^{\text{BLYP}} = 5.52$ eV and $\Delta E_{\text{S-T}}^{\text{PBE}} = 5.48$ eV, respectively.[31] This means that the singlet-triplet excitation energy shift obtained going from PBE to BLYP functional can only cause a 0.01 eV decrease in the adsorption energy difference, a value that is not sufficient to change the site preference. Thus, it seems that the traditional reasoning is not able to offer a convincing argument for the correct site preference predicted by BLYP. Hence, in order to explain our calculated results, the two functionals need to be studied more in depth.

E. Large reduced density gradient and its effect on the puzzle

We therefore compared the characteristics of the two used functionals, BLYP and PBE, and, in particular, we look at their differences in the more rapidly varying density regions. A basic comparison between GGA functionals is to compare
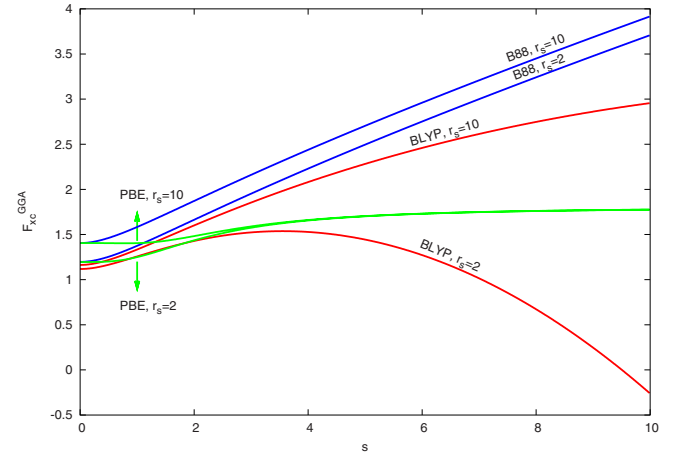
their enhancement factor F_{xc}, which can be defined as follows:[21]

$$E_{\text{xc}}^{\text{GGA}}[n^{\uparrow}, n^{\downarrow}] = \int d^3 r n \epsilon_{\text{x}}^{\text{LDA}}(n) F_{\text{xc}}(r_s, \zeta, s), \qquad (1)$$

where $E_{\text{xc}}^{\text{GGA}}$ is the exchange-correlation energy, $n^{\uparrow}$ and $n^{\downarrow}$ are spin densities, $\epsilon_{\text{x}}^{\text{LDA}}(n)$ is the LDA exchange density $[\epsilon_{\text{x}}^{\text{LDA}}(n) = -3(3\pi^2 n^{1/3} / (4\pi)]$, $r_s = \left(\frac{3}{4\pi n}\right)^{1/3}$, s is the reduced density gradient $\left(s = \frac{|\nabla n|}{2(3\pi^2)^{1/3} n^{4/3}}\right)$, and $\zeta = (n^{\uparrow} - n^{\downarrow})/n$. As our system is not spin polarized, the enhancement factor does not depend on ζ. In Fig. 2, we compare the behavior of $F_{\text{xc}}(r_s, s)$ with respect to s calculated for BLYP and PBE at two extreme densities; $r_s = 2$ and $r_s = 10$. It can clearly be seen that the enhancement factor of PBE goes asymptotically to a constant value at large s, while BLYP has no such behavior at this range and increases monotonically with respect to s at low density ($r_s = 10$).

Hence, for conventional extended bulk systems with small density-gradient contribution, different GGA formalisms are expected to give rather similar results, while for systems with high value of s (large density gradient) and low density (large r_s) such as the free surface of a solid or the area around a molecule, where the electron density falls off rapidly and the reduced density gradient diverges, the two GGA functionals, BLYP and PBE, are *not* expected to yield similar results. When a CO molecule is adsorbed on a Pt surface, the total free surface of the whole system decreases with respect to a clean Pt surface plus a gas phase CO molecule. Figure 3 which has been adapted from Ref. 32 clearly shows the modification of free surfaces occurring for hollow site adsorption. A similar graph could be depicted for a top site adsorption. The shaded area shown in the graph indicates the fact that, once a chemisorption bond between the Pt surface and CO molecule is formed, the free surface area with large reduced density gradient s will decrease. The loss of free surface, as shown in Fig. 3, appears in the region between the Pt surface and the CO molecule; a region with high value of
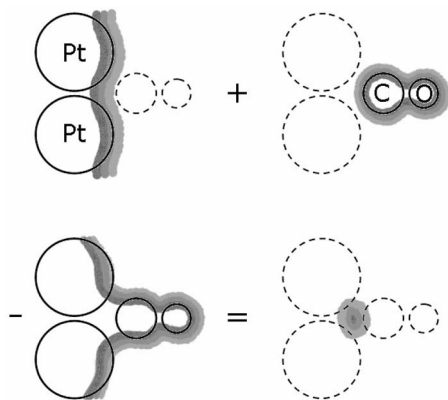
FIG. 3. Outside a solid surface, e.g., Pt, and all round a molecule, e.g., CO, the electron density falls off. These regions of "surface," here shown shaded, have large reduced density gradients, $s \propto \frac{|\nabla n|}{n^{4/3}}$. Once a chemisorption bond between the solid surface and the molecule is formed, less surface results. The loss of surface appears in the region between the solid surface and the chemisorbed molecule. We mimicked this schematic drawing from Ref. 32

s. The first noticeable point is that the lost surface is not identical for top and hollow sites, and as a result of that, the chemisorption energy, which depends on it, is not the same for the two sites. Second, the difference in chemisorption energy for top and hollow sites calculated by BLYP and PBE is also not identical due to the fact that the two functionals behave differently for large values of s.

In order to quantify the effect of large s area in the chemisorption energy calculated by different GGA functionals, we follow the procedure suggested in Ref. 32 and define the gradient-dependent contributions in the GGA to the chemisorption energy as follows:[32]

$$\Delta e_{\text{chem,GGA}}(\mathbf{r}) = \sum_{i=A,M,AM} p_i n_i(\mathbf{r})[\epsilon_{i,\text{GGA}}(\mathbf{r}) - \epsilon_{i,\text{LDA}}(\mathbf{r})],$$

$$(2)$$

where $n_i(\mathbf{r})\epsilon_{i,\text{xc}}(\mathbf{r})$ is the exchange-correlation energy density at $\mathbf{r}$ for each of the systems, $i=A,M,AM$ [A, M, and AM stand for the isolated adsorbate (CO), the isolated metal (Pt), and the full system (CO on Pt surface), respectively], $p_{AM} = 1$, and $p_A = p_M = -1$. To compare gradient-dependent contributions from different sites, we have integrated $\Delta e_{\text{chem,GGA}}(\mathbf{r})$ over the cell area A parallel to the Pt(111) surface,[32]

$$\Delta e_{\text{chem,GGA}}(z) = \int_A \Delta e_{\text{chem,GGA}}(\mathbf{r})dxdy. \quad (3)$$

We plotted this new quantity as a function of the distance from the outermost layer of Pt atoms (z) for two functionals, BLYP and PBE, for the two different sites, fcc and top in Figs. 4 and 5. It is clearly seen that the change in the chemisorption energy is mainly caused by gradient-dependent contribution located in a region between Pt surface and C atom close to C (as a result of a loss of surface area due to adsorption). Furthermore, the effects of BLYP and PBE on the fcc site are slightly larger than their effect on the top site. This is
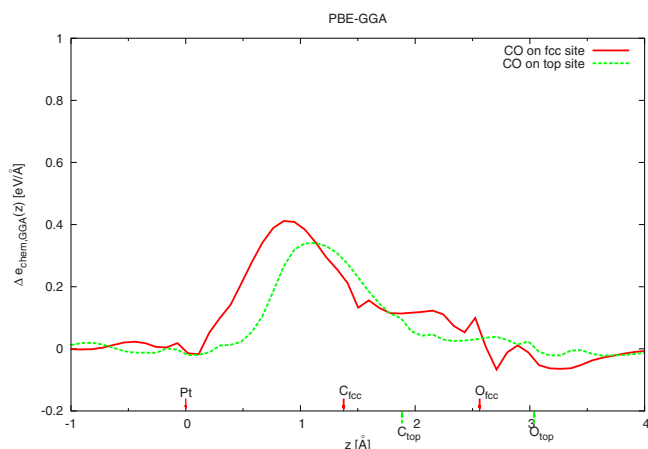

FIG. 4. (Color online) The GGA contribution of PBE in chemisorption energy for two different sites, top and fcc sites, according to Eq. (3). The positions of atoms have been shown by arrows.

due to the fact that the loss in surface area is bigger for fcc site compared to the top site. In order to quantify this difference, we need to calculate the total effect of the nonlocal exchange correlation on the chemical energy by integrating over the whole range of z value. The value that we obtained for the gradient-dependent contribution to the chemical energy with BLYP is a factor of 2 larger than the corresponding value calculated with PBE, and this is the main reason causing the fcc site to become less favorable than the top site. This happens because of larger enhancement factor of BLYP with respect to PBE at large values of s and r_s. In order to provide more evidences to support our argument, we repeated our calculation by using B88,[18] a functional with larger enhancement factor than BLYP over the whole range of r_s (Fig. 1). The differences of total energy at top and fcc sites calculated by B88 for different metallic surfaces were as follows: Pt: $E_{\text{top}} - E_{\text{fcc}} = -0.23$ eV, Rh: $E_{\text{top}} - E_{\text{fcc}} = -0.34$ eV, and Cu: $E_{\text{top}} - E_{\text{fcc}} = -0.26$ eV, so, as expected, B88 further enhances the site preference toward top site with respect to BLYP.
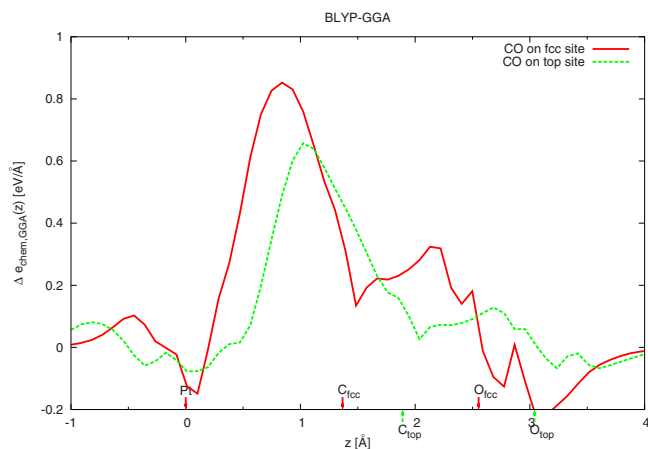

FIG. 5. (Color online) The GGA contribution of BLYP in chemisorption energy for two different sites, top and fcc sites, according to Eq. (3). The positions of atoms have been shown by arrows.

Furthermore, in order to clarify whether the correct results of BLYP originate from Becke B exchange or LYP correlation functional, we repeated the calculation by using a combination of B exchange and PBE correlation functions (BPBE). The results are as follows: Pt: $E_{\text{top}} - E_{\text{fcc}} = 0.07$ eV, Rh: $E_{\text{top}} - E_{\text{fcc}} = -0.03$ eV, and Cu: $E_{\text{top}} - E_{\text{fcc}} = 0.01$ eV. It is clearly seen that although the B exchange improves the results of BPBE compared to PBE, however, such improvement is not sufficient to correctly predicts the top site preference for Pt and Cu surfaces. An alternative functional which is worth to test is the revised PBE.[33] The results of our calculation for revised PBE are Pt: $E_{\text{top}} - E_{\text{fcc}} = 0.04$ eV, Rh: $E_{\text{top}} - E_{\text{fcc}} = -0.06$ eV, and Cu: $E_{\text{top}} - E_{\text{fcc}} = 0.02$ eV. These results indicate that revised PBE, similar to BPBE, is unable to give lower energy for top site in Pt and Cu cases. Finally, we calculated the exchange-correlation enhancement factors of BPBE and revised PBE at large r_s and found out that the results fall somewhere between PBE and BLYP.

IV. CONCLUSION

Numerous computational investigations of CO/Pt(111) puzzle have contributed to build the expectation that DFT/GGA method cannot correctly predict the most stable adsorption-site preference, thus concluding that the method is not qualitatively reliable and much more expensive hybrid functionals should be explored. We have here shown that a GGA functional such as BLYP can correctly give the site preference. In our study, we employed two different exchange-correlation functionals: PBE, a popular exchange correlation in the physics community and BLYP, the one which is more extensively used by chemists. The results obtained by BLYP can successfully predict the correct site preference for three challenging cases: CO/Pt(111), CO/Rh(111), and CO/Cu(111). We found out that, contrary to arguments that have been often used to address the present issue,[17,30] a difference in HOMO-LUMO gap in CO molecule calculated by different functionals cannot explain our results. Our findings can be understood, instead, in terms of the different behavior, going from PBE to BLYP, in the large reduced-density-gradient enhancement factor in the exchange-correlation kernels adopted. This is the functional part that is the least constrained on-physical ground in the, nowadays predominant, PBE functional, and modifications in this part[32,33] have already been shown to improve in many cases the interaction energy of surface-molecule systems. The success of our BLYP calculation in the simple, yet difficult, problem of CO adsorption of transition metal (111) surfaces shows that there might still be room for improvement in the ability of GGA functionals to describe accurately energetics of complex systems if, in addition to satisfy all the physically relevant limits and constraints, which mostly apply to the small reduced-density-gradient region, the remaining large functional flexibility could be fixed by properly training these functionals on a set of relevant problematic cases such as the one studied here.

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