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Significance of single-electron energies for the description of CO on Pt(111)

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Semilocal density functionals predict that the stable adsorption site of carbon monoxide (CO) on Pt(111) is the hollow fcc site, in disagreement with experimental studies which indicate that CO adsorbs on the top site at low coverage. This site preference depends on a subtle balance between the interaction of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) with the metal substrate. Local and semilocal functionals seem to overestimate the interaction of the LUMO with the metal substrate, in turn favoring the wrong site. It is argued that this error is related to the ‘‘gap’’ problem of present density functionals and might be cured by functionals that increase the HOMO-LUMO separation.

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Adsorption of carbon monoxide on metal surfaces is a prototypical system in surface science, with studies dating back at least 30 years. The Pt(111) substrate has recently attracted attention, as present density functionals seem to predict the wrong stable adsorption site.[1] Experiments indicate that CO adsorbs on the top site on the Pt (111) substrate at low coverage. The most important experimental data are the high CO stretch frequency ($2100\ \mathrm{cm}^{-1}$) observed for CO on Pt(111) at low coverage,[2,3] and diffuse low-energy electron diffraction data.[4] Furthermore, in a recent scanning tunneling microscopy study of CO on a Pt-Co surface alloy, CO molecules were observed exclusively on top of Pt atoms.[5] The theoretical studies, however, yield a different result. A recent investigation applying large clusters and local orbitals indicates that the hollow site is preferred over the top site for sufficiently large clusters and semilocal density functionals.[6] Another comprehensive study applying slabs and three different plane wave based approaches showed as well that CO prefers the hollow site.[1] Two of the density functional codes were based on ultrasoft pseudopotentials and the projector augmented-wave (PAW) method, whereas the third one used the linearized augmented plane-wave method (LAPW). All three programs have been applied to a vast number of adsorption problems before, are mature and highly reliable (at least within the boundaries established by DFT), and, additionally, the authors of the aforementioned study have done careful tests to obtain technically converged results. The conjecture is clear and not particularly ‘‘friendly’’: the present local and semilocal density functionals predict the wrong adsorption site for CO on Pt(111), and they do so by at least 100 meV. A point worthwhile mentioning is that—although all codes agreed on the hollow site to be more stable—the energy difference between the hollow and top site varied by almost 100 meV between the three plane wave codes, even though identical density functionals were used.

These results are a serious challenge for the prospects and future of density functional based calculations. If computational *ab initio* modeling wants to be predictive, this deficiency has to be addressed. As a first step, it is vital to understand why present density functionals fail to predict the correct adsorption site. Furthermore, one needs to know when similar failures might occur in order to be alerted of future pitfalls. In this Brief Report these two points are addressed. Additionally, possible solutions to the problem are pointed out.

The calculations presented here were performed with the Vienna *ab initio* Simulation Package (VASP),[7] using plane waves and the PAW method. The PAW method is a frozen core method which uses the exact valence-wave functions instead of pseudowave functions.[8] Generalized gradient corrections (GGC) of Perdew and Wang (PW91)[9] were utilized throughout this work. Tests with the PBE-GGC (Ref. 10) yielded within 1 meV identical energy differences between different adsorption sites. We restrict the study to 5 layer thick slabs at the theoretical lattice constant of Pt with a periodicity of $\sqrt{3}\times\sqrt{3}$ and 6×6 k points. CO was adsorbed on one side of the slab, and the two topmost layers and the CO molecule were allowed to relax. Most of the trend studies were however performed with the slab fixed at the positions determined for the clean relaxed substrate.

Figure 1 shows the orbital resolved electronic density of states (DOS) for the clean Pt(111) surface layer and for the CO covered Pt(111) surface. The commonly accepted picture for CO adsorption on a transition metal surface is the Blyholder model,[11] but it lacks some important subtleties one needs to take into account (see Refs. 12–14). For CO adsorption at the top site, the non bonding 5σ CO HOMO hybridizes with the d_{z^2} states and shifts to lower energies. The d_{z^2} states broaden significantly [thin broken line, Fig. 1(b)] and split into a 5σ-d_{z^2} bonding contribution below the Fermi level and 5σ-d_{z^2} antibonding contributions located mostly above the Fermi level. Since two almost fully occupied states interact, the interaction would be only a Pauli-like repulsion, if the Pt-CO antibonding d_{z^2}-5σ hybrid states were not pushed partly above the Fermi level.[13] The depletion of 5σ states is in accordance with the common picture that the 5σ orbital donates electrons to the substrate.[11] The 1π orbital and the $2\pi^*$ CO LUMO, on the other hand, interact with d_{yz} and d_{xz} states. The interaction is fairly complicated, and

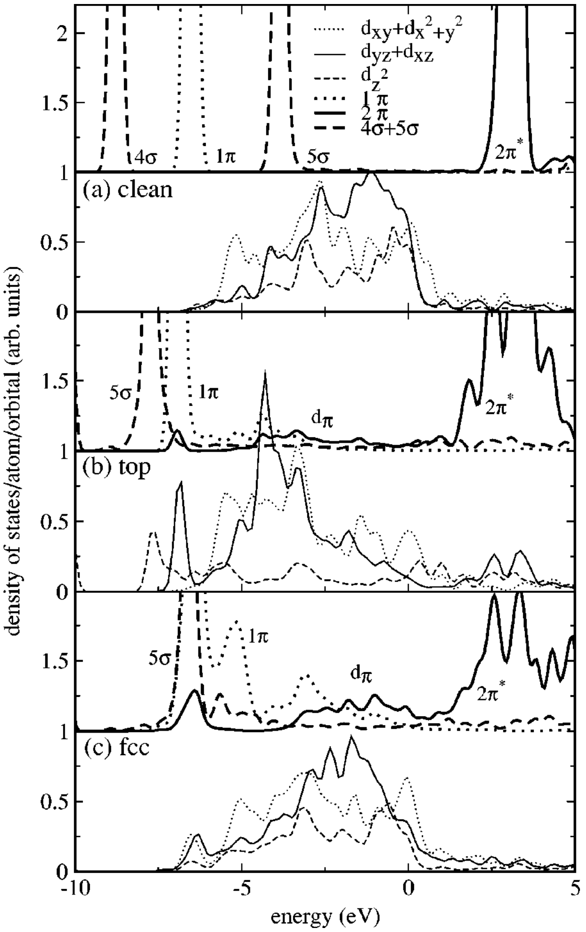

FIG. 1. Orbital resolved electronic density of states (DOS) for the top most clean Pt surface layer and for CO (a) 3 Å above the substrate and adsorbed at the (b) top and (c) hollow sites. For CO, the DOS is shown by thick lines shifted by 1.0 with respect to the abscissa. The DOS was smoothed by a Gaussian function with a width of 0.2 eV. The Fermi level is located at 0 eV.

TABLE I. Binding energy difference ΔE between adsorption of CO at the top and fcc site on Pt(111), heat of adsorption for the fcc site E_{fcc} and one-electron DFT HOMO-LUMO ($5\sigma-2\pi^*$) gap E_{gap} of the free relaxed CO for four different PAW potentials. The pseudopotential core radii of the p wave functions r_c and the relaxed CO bond length d are also specified.

	r_c (a.u.)	d(Å)	E_{gap} (eV)	ΔE (meV)	E_{fcc} (eV)
PAW hard	1.1	1.134	7.01	105	1.67
PAW standard	1.5	1.142	6.91	126	1.72
PAW	1.7	1.162	6.71	180	1.83
PAW soft	1.85	1.180	6.48	243	1.91

leads to three distinctive energy ranges.[12] At low energies, a 1π-like orbital is still visible. Through the bonding interaction with the substrate the 1π orbital is polarized towards the substrate, gaining intensity at the carbon atom ($2\pi^*$ contribution). In the medium energy range between -5 and 0 eV, a nonbonding O lone pair orbital develops (termed d_π).[12] Since this orbital is a hybrid of the unperturbed molecular 1π and $2\pi^*$ orbitals, its occupation involves a back donation of electrons from the substrate to the originally empty molecular $2\pi^*$ orbital. Finally, at higher energies (3 eV) an antibonding $2\pi^*$-d_{yz}/d_{xz} hybrid orbital is visible. The interaction with the 1π orbital, located below the metal d states, shifts the d_{yz} and d_{xz} states to higher energies, whereas interaction with the empty $2\pi^*$ orbital pushes them to lower energies. It is clearly visible in the $d_{yz}+d_{xz}$ DOS that the second effect is much stronger [downshift of the full thin line from Fig. 1(a)–(b)]. Since the 1π orbital remains additionally fully occupied, the interaction with the $2\pi^*$ orbital dominates over the interaction with the 1π state.

Turning now to the adsorption at the hollow site, it is first noted that the interaction is generally similar to CO on the top site, but since three Pt atoms interact with the CO molecule, the modifications of the DOS for a single substrate atom are smaller. To access qualitatively the interaction strength, it is useful to concentrate on the DOS on the CO. The 5σ orbital is now at higher energies, indicating a weaker interaction with d states. This also follows from simple geometrical and symmetry considerations, which indicate that the 5σ orbital interacts now mainly with d_{xy} and $d_{x^2+y^2}$ states [small peak in the thin dotted line in Fig. 1(c) at -6.5 eV]. Due to the increased Pt-C distance (2.13 Å compared to 1.88 Å), the hybridization is weaker than for the direct 5σ-d_{z^2} interaction for atop adsorption. On the other hand, the 1π and $2\pi^*$ orbitals interact remarkably effectively with the d_{yz} and d_{xz} states as corroborated by the intensive d_π peak. Furthermore it is noted, that the antibonding $2\pi^*$-d_{yz}/d_{xz} hybrid orbital has moved to much higher energies, so that one can conclude that the $2\pi^*$-d_{yz}/d_{xz} interaction is the dominant one for the CO adsorption at the hollow site (the $2\pi^*$ contributions below the Fermi level are predominantly CO-metal bonding). This leads to the first important conclusion. Both the 5σ metal d and the $2\pi^*$-metal d interactions are bonding, and donation from the 5σ orbital to the substrate tends to drive the molecule towards the top site, whereas the back-donation from the substrate to the $2\pi^*$ orbital favors the hollow sites. This conjecture is supported by the results presented below.

In a second step, four PAW potentials with different core radii were generated and the adsorption energy of the CO molecule was calculated for each potential. The substrate was kept frozen in this case. The results are summarized in Table I. The energy difference between the adsorption at the fcc and top site changes quite substantially, when the core radius changes. We relate this to the change in the calculated HOMO-LUMO gap of the free CO molecule also shown in Table I. The one-electron gap decreases when the quality of the pseudopotential is reduced. This is partly a result of the increased bond length of the CO molecule, which reduces the 1π-$2\pi^*$ splitting through a reduced lateral $p\pi$ interaction. But roughly 50% of the decrease of the HOMO-LUMO gap is related to lower pseudopotential quality: for the present PAW generation scheme, the $2\pi^*$ orbital shifts to lower energies at a fixed bond length, when the core radius increases. From the previous paragraph and from second order perturbation theory, one would expect that a shift of the $2\pi^*$ orbital to lower energies should enhance the bonding interaction between this orbital and the *d* states, since the interaction strength between two states is inverse proportional to their energy separation. This is exactly what one observes. When the pseudopotential quality decreases, the adsorption energy increases for all adsorption sites through the downshift of the $2\pi^*$ orbital. But the effect is twice as strong for the fcc site, in accordance with the observation that the $2\pi^*$ interaction is stronger for the fcc hollow site. With regard to the core radius, the present results are in contrast to one recent study,[15] which we tend to relate to a different behavior of extended normconserving potentials. For these potentials, the position of the LUMO probably shifts in a different way with increasing pseudopotential core radius.

Within the PAW approximation an upper limit for the one electron 5σ-$2\pi^*$ gap exists, which is obtained for a core radius of $r_c = 1.1$ a.u. A further improvement of the pseudopotential quality changes neither the description of the CO molecule nor the position of the eigenenergy of the $2\pi^*$ orbital. Therefore, an energy difference of 105 meV is the most precise value one can determine using a frozen substrate and the PW91 functional. If substrate relaxation is included, the energy difference reduces to 90 meV, but the site ordering remains incorrect. This value agrees well with reported calculations.[1,15] Additionally, testwise spin-orbit coupling was included, but it did not change the energy difference between adsorption sites. A slightly larger effect was observed when the RPBE (Ref. 16) instead of the PW91 density functional was used. This functional generally favors low compared to high coordination sites, but at the expense of grossly underestimating surface energies. The RPBE functional lowered the adsorption energy to 1.34 eV, but the hollow site is still 30 meV more stable than the top site.

In a final step, we have modified the DFT functional in order to shift the CO LUMO to even higher energies. To this end, a GGA+U inspired method was applied with[17]

$$E_{\mathrm{GGA}+U} = E_{\mathrm{GGA}} + \frac{U}{2} \sum_{\sigma=1}^{2} \sum_{i=1}^{2} (\rho_i^\sigma - \rho_i^\sigma \rho_i^\sigma). \qquad (1)$$

Here E_{GGA} and $E_{\mathrm{GGA}+U}$ are the conventional and modified density functionals, σ is an index for the spin, and ρ_i^σ are the occupancies of the two LUMO orbitals for the up and down spin. They are determined, by defining two projection operators, which are 1 for the two LUMO orbitals of the free CO molecule, and 0 for all other CO single particle states. It is emphasized, that this method leaves the DFT energies unmodified, if the occupancies ρ_i^σ are zero or one. Hence the bond length of the molecule and even excitation energies of the isolated CO molecule remain entirely unchanged. The important result is that despite the unmodified ground-state structure and energetics, the adsorption energies change substantially. As shown in Fig. 2, the energy difference between the top and fcc site lies on a straight line, when displayed versus the position of the LUMO (the correlation even holds for the LDA and RPBE functionals). Already for $U = 0.5$ eV a crossover from the hollow to the top site is observed, and for $U = 0.75$ eV the top site is favored by 60 meV. The adsorption energy also decreases from 1.72 to 1.39 eV for $U = 0.75$ eV, in better agreement with most experiments [1.24 (Ref. 18)–1.39 eV (Ref. 19)]. The results for different potentials and the GGA+U calculations suggest that the position of the LUMO plays a key rule in determining the site preference. An interesting point is that the energy required for transferring *one* electron from the 5σ to the $2\pi^*$ orbitals is 7.3 eV in DFT, if spin polarization is neglected (this excitation does not correspond to the triplet or the singlet transition,[21] but is similar to the process on the surface). The single particle $5\sigma \rightarrow 2\pi^*$ gap is only 6.9 eV. A correction of $U = 0.75$ eV, yields a single particle gap in close accordance with the calculated 5σ to $2\pi^*$ DFT transition energy. We will come back to this point in the discussion. It is also noted, that calculations with the B3LYP functional[24]— a functional, which adds a fraction of the exact exchange to otherwise semi local density functionals—give the correct site preference.[6] In the light of the previous arguments, this is to be expected, since the B3LYP functional also increases the HOMO-LUMO separation.[6]

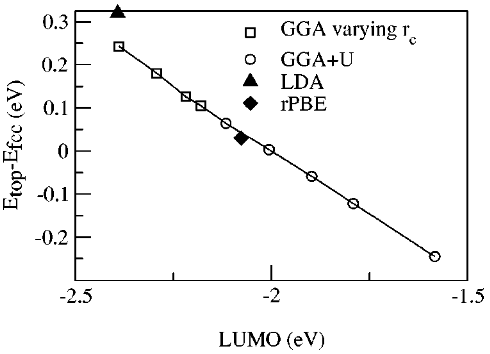

FIG. 2. Energy difference between adsorption of CO at the top and hollow site on Pt(111) verus the position of the LUMO of the free CO molecule with respect to the vacuum level. The LUMO was determined at a fixed bond length of $a = 1.142$ Å. Squares indicate results obtained with the pseudopotentials specified in Table I. Circles correspond to results with the GGA+U functional for $U = 0.25$, 0.5, 0.75, 1.0, and 1.5 (see text). LDA and RPBE results are also shown. The correlation would remain qualitatively similar (but with a larger scatter), if the LUMO were calculated at the position of the relaxed free CO molecule.

A few additional tests were performed for the present modified functional. For higher CO coverage on Pt(111), the $c(4\times2)$-2CO structure (one CO molecule ontop and the other one at a bridge site) is observed experimentally.[20] For our present setup (PAW, five layer slabs), the bridge-bridge configuration is almost degenerated with the top-bridge configuration, if no corrections are applied. Applying the U correction, the experimentally observed structure is clearly predicted among the test structures considered in Ref. 1. For CO on Rh, DFT predicts the hcp site to be more stable than the top site,[22] in disagreement with the experimentally observed atop adsorption at low coverage.[23] Again, even a modest U of 0.5 eV yields the experimentally observed top site as stable adsorption site.

In summary, we have demonstrated that the strength of the hybridization between the metal *d* states and the $2\pi^*$ CO LUMO plays a key rule in determining the binding site. By applying a GGA+U inspired method, the LUMO was shifted to higher energies, which in turn decreased the interaction between the LUMO and the metal d states. In this way, agreement with experiment for the site preference and the adsorption energy was obtained. Certainly the applied modification is an oversimplification, and less empirical approaches such as B3LYP should be applied.[6] Nevertheless, we believe that even the simple approximation captures the essential physics. It is remarked, that a recent experimental survey also came to the conclusion, that the interaction between the metal and the $2\pi^*$ orbital is overestimated in present DFT calculations.[18] Our arguments are also consistent with that of Grinberg *et al.*,[15] who argued that DFT underestimates the cost for breaking one CO bond. An upshift of the one electron $2\pi^*$ orbital makes a partial charge transfer from the 5σ to the $2\pi^*$ orbital more difficult and therefore stabilizes the third CO bond.

In view of these results, one might argue that the wrong prediction of the adsorption site is related to the deficiency of present semilocal DFT functionals to describe the one electron gap correctly. The incorrect description of this property is related to the failure of present functionals to describe the energy of molecules for noninteger electron values correctly. For the exact DFT functional, the total energy as a function of the number of electrons should be a set of straight line segments connecting the energies for integer occupancies.[25,26] But local and semilocal DFT functionals often yield a curve lying *below* these line segments. Hence states with fractional orbital occupancies and mixed states are incorrectly favored by most DFT functionals. In other words, it is too easy to partially occupy or deplete states, or to transfer the fraction of an electron from the HOMO to the LUMO orbital. Therefore, the stability of states which correspond to mixtures of single Slater determinants is overestimated. Self interaction corrected density functionals or the inclusion of a fraction of the Hartree-Fock exchange, mentioned already above, can cure this problem.

It is almost certain, that the discussed deficiency of the local and semilocal DFT functionals for the description of adsorption processes is not limited to the CO adsorption on metal surfaces. On the contrary, similar problems must be expected for all adsorption systems, where a tight competition between the donation of electrons from the molecular HOMO to the metal and backdonation of electrons from the metal to the previously empty LUMO occurs.

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