Re-thinking CO adsorption on transition-metal surfaces: Density-driven error?

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Adsorption of the molecule CO on metallic surfaces is an important unsolved problem in Kohn-Sham density functional theory (KS-DFT). We present a detailed study of carbon monoxide adsorption on fcc (111) surfaces of 3d, 4d and 5d metals using nonempirical semilocal density functionals for the exchange-correlation energy: the local-density approximation (LDA), two generalized gradient approximations or GGAs (PBE and PBEsol), and a meta-GGA (SCAN). The typical error pattern (as found earlier for free molecules and for free transition metal surfaces), in which results improve from LDA to PBE or PBEsol to SCAN, due to the satisfaction of more exact constraints, is not found here. Instead, for CO adsorption on transition metal surfaces, we find that, while SCAN overbinds much less than LDA, it overbinds slightly more than PBE. Moreover, the tested functionals often predict the wrong adsorption site, as first pointed out for LDA and GGA in the “CO/Pt(111) puzzle”. This abnormal pattern leads us to suspect that the errors of SCAN for this problem are density-driven self-interaction errors associated with incorrect charge transfer between molecule and metal surface. We point out that, by the variational principle, SCAN overbinding would be reduced if the SCAN functional were applied not to the SCAN selfconsistent density of the adsorbed system but to an exact or more correct density for that system.

I. INTRODUCTION

Adsorption of inorganic and organic molecules on different surfaces is an important problem in surface science,1–3 both in theory and in experiment. The adsorption of CO on metallic surfaces is a well-known example.4 For the past few decades, much effort has been devoted to studying the adsorption of CO on transition metals, which is relevant to the catalytic oxidation of CO in industry. This adsorption is considered as a “prototype” that mimics many other interesting and practically important adsorption processes.

Modern electronic structure theory, especially density functional theory (DFT)4,5,6,7,8,9,10 is widely used to describe many surface-related problems including molecular adsorption. However, in 2001 Feibelman et al.5 challenged the accuracy of GGA and LDA functionals for CO adsorption on the Pt (111) surface. Their work showed that GGA and LDA are both qualitatively and quantitatively wrong in their predictions of the adsorption site of CO on the Pt (111) surface, independent of the technical details of the calculation. This study presented a “CO/Pt (111) puzzle”, which has been investigated9,10 further by many electronic structure theory methods including different levels of approximations within Kohn-Sham-DFT (KS-DFT). By now, all five rungs of Jacob’s ladder of density functional approximations have been used to study this particular problem. The non-empirical functionals LDA4,7,8,9,10,11,12,13,14 GGAs (PBE, PBEsol13,14) and meta-GGAs (TPSS, revTPSS13,14,15) fail to agree with the picture of CO adsorption from low-energy electron diffraction (LEED) and electron energy loss spectroscopy (EELS).

Many previous studies showed that the hollow adsorption site is preferred by these semilocal approximations, while the low-coordination top site is preferred in the experiments. A recent study by Janthon et al.15 reported that the semi-empirical M06-L meta-GGA predicts both correct adsorption site and adsorption energy. Sun et al.16 showed that a revised version (revTPSS) of the TPSS meta-GGA significantly improves the surface energies and adsorption energies for transition metals. These two studies suggest that inclusion of the kinetic energy density (τ), the added ingredient that defines a meta-GGA, can be important for the surface properties of metals. A recent study16 shows that inclusion of a vdW correction20 to the nonempirical SCAN meta-GGA21 yields accurate surface energies and work functions of free transition metal surfaces. SCAN+rVV10 also correctly predicts20 chemisorption and physisorption minima in the binding of graphene to Ni(111), with the physisorption minimum in good agreement with RPA calculations22. Here we will investigate whether constraint-satisfying nonempirical meta-GGAs such as SCAN can correctly describe CO adsorption on transition-metal surfaces.

Semilocal functionals that satisfy more physical constraints are sometimes considered to be closer to exact functionals,23,24 and SCAN was constructed to satisfy all 17 exact constraints that a meta-GGA can. SCAN is considerably more accurate than PBE for molecules25,26 and for condensed matter (defects in semiconductors25,27,28,29 structural phase transitions of solids under pressure30, ferroelectrics31,32,33, liquid water34, formation energies and ground-state crystal structures of solids,35,36 cuprates,37,38, etc.). But the exact constraints embedded in SCAN can have a more directly beneficial effect upon the energy for a given density than upon the selfconsistent density, especially where there are charge transfer errors,39,40 due to self-interaction41.

The energy error of an approximate functional is the sum of a functional error (the error that it makes when
applied to the exact density) and a density-driven error (the difference between the energies of the approximate functional applied to its selfconsistent density and to the exact density). Although in most cases the functional error is larger than the density-driven error, the latter by itself can produce a non-physical result. For realistic bonding situations, a good semilocal functional like SCAN could have a small functional error but still have noticeable density-driven error. In other words, even the best semilocal functional can have a qualitatively-wrong functional derivative. We suspect that this is the case for SCAN applied to molecules chemisorbed on metal surfaces.

The most serious density-driven errors are charge-transfer errors, which are directly relevant to the strong binding of a closed-shell molecule like CO to a metal surface. The Kohn-Sham molecular orbitals of the free molecule can evolve in the adsorbed molecule into energy-broadened resonances of the bulk metallic orbitals. In Blyholder’s model, bonding of CO on metal surfaces can be described by σ bonding through electron transfer from the filled 5σ (HOMO) orbital of CO to an unfilled d-orbital of the metal, and by π bonding due to the back-donation of electrons from the filled 2τg band of the transition metal to the unfilled 2π* orbital of CO. Detailed study of the “CO/Pt(111)” puzzle in the last few decades (as referenced below) revealed that the incorrect energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the adsorbed CO relative to the transition-metal Fermi level are responsible for the incorrect prediction that the hollow site is the preferred or stable adsorption site. Self-interaction error (SIE) present in the popular local or semilocal exchange-correlation density functionals is to be blamed for this anomaly. It results in an inappropriate prediction of the HOMO level of CO and places the 2π* LUMO too low relative to the metallic Fermi level. This enhances the back-donation of electronic charge from the metal to the oxygen side of the molecule. This strong-delocalization of the electronic charge seems to be the reason for the nonphysical adsorption of CO on the fcc hollow site of (111) surfaces of Cu, Rh, and Pt. This overestimation of the back-donation of the electronic charge also accounts for the too large adsorption energies.

Many methods and techniques have been prescribed over the last few decades to correct this back-donation problem due to the SIE. Among those, the most computationally economic one is the “DFT+U” method suggested by Kresse et al. for the “CO/Pt (111)” problem, where the empirical parameter U is applied to achieve the correct top site adsorption position by adjusting the HOMO-LUMO gap of CO upward to the experimental transition energy. This method (combined with the PW91 GGA functional) was also applied successfully for Cu (111) surfaces by Gajdoš and Hafner. Mason et al. reported another empirical method to solve this back-donation problem for the CO adsorption on many metallic surfaces. In their method, CO singlet-triplet excitation energies from high-level coupled-cluster and configuration-integration method are used to obtain a linear relationship between the CO adsorption energy and the CO singlet-triplet splitting energy. These authors adjusted their C and O pseudopotential radii to reproduce the gas-phase coupled-cluster singlet-triplet splitting and HOMO-LUMO energies. For 1/4 monolayer of CO on Pt(111), the correction of Mason et al. changes the dipole moment of an adsorbed molecule from 0.026 to 0.089 eÅ (top site), and from -0.137 to -0.079 eÅ (fcc hollow site).

A fraction of exact exchange in the hybrid functionals tends to reduce the SIE in most cases, at moderate to very high computational cost compared to the LDA, GGA, and meta-GGA. The successful hybrids PBE, B3LYP, and HSE can give more accurate descriptions of the adsorption energies for some metals but not all, and correct the HOMO-LUMO gap of the adsorbed CO. Wang et al. found that PBE0 solved or nearly solved the “CO/Pt(111) puzzle”. Gil et al. had earlier found similar results from the B3LYP hybrid functional for the CO/Pt (111) problem, within a cluster model for Pt. These studies and those of Stroppa et al. show that hybrid functionals create a near degeneracy between the top and hollow sites for CO/Pt(111). However, as pointed out by Stroppa and Kresse, the hybrid functionals often worsen the properties of bulk metals.

Weak van der Waals (vdW) or dispersion interactions are largely missing in PBE, but intermediate-range vdW is included in PBEsol and SCAN, and long-range vdW in SCAN+rVV10. These interactions are not negligible for CO adsorption on metallic surfaces. For example, a study by Lazić et al. found that adding a nonlocal dispersion correction to PBE and revPBE tends to stabilize the top configuration as the preferred adsorption site.

In some recent studies, it has been reported that statistically-fitted GGA and meta-GGA functionals can reduce the error of CO adsorption energy on transition metal surfaces. These functionals show improved chemisorption energies for adsorption of CO on a metallic surface, while underestimating surface energies compared to experiments. While the performance of the mBEEF meta-GGA for CO adsorption energies is similar to that of RPBE, both fail to yield the correct adsorption site for CO/Pt (111). However, mBEEF provides its own Bayesian error estimate.

The fifth and highest rung of the ladder comprises RPA-like approximations that employ the unoccupied as well as the occupied orbitals. Schimka et al. found that the random phase approximation (applied to PBE orbitals and orbital energies) correctly described both CO adsorption energies and surface energies, while their tested semilocal functionals did not. A possible interpretation, consistent with similar results for the energy barriers to chemical reactions, is that RPA is relatively immune to density-driven error.

In this work we aim to discuss this CO adsorption prob-
lem using the new meta-GGA SCAN. In Section II we discuss the details of the computational method used in this work. Section III summarizes our results, and in Section IV we present our conclusions.

II. COMPUTATIONAL DETAILS

The results presented in this work are obtained from periodic density functional calculations performed with the Vienna Ab Initio Simulation (VASP) package. The projector-augmented-wave (PAW) method is used to describe the electron-ion interaction, with a plane-wave cut-off of 600 eV. Careful observation and previous studies revealed that a moderate to high cut-off energy can be used to study CO adsorption on transition metal surfaces. We used a PBE-PAW pseudo-potential for GGA and meta-GGA calculations, and an LDA PAW pseudo-potential for LDA calculations. The substrates in this work are modeled using 6 layers of metal with a 10 Å vacuum region on top of c(2 × 2) fcc surfaces of metals. Brillion-Zone sampling is done with a 12 × 12 × 1 Γ-centered k mesh for the metallic surface slabs. To calculate the energetics of the CO molecule, we used a 15 × 16 × 17 Å box where the CO molecule is centered in the box. The top site is modeled by placing the C atom of CO directly on top of the metal atom, whereas the fcc and hcp hollow sites are modeled so that there is no metal atom directly under the C atom of CO in the second and first layer respectively. For all metallic surfaces, we chose a 1/4 monolayer for computational efficiency and consistency. Table I of Lazić et al. shows that, for the four functionals tested there, the magnitude of the change in the adsorption energy of CO on the top site Pt(111) from 1/12 to 1/4 monolayer coverage is less than 0.025 eV and thus negligible for the purpose of our study.

We define the calculated CO adsorption energies as

$$E_{ads} = E_{CO/M(111)} - (E_{CO} + E_{M(111)})$$  \hspace{1cm} (1)

where $E_{CO/M(111)}$ is the total energy of the M (111) (M=Pd, Rh, Pt, Cu, Au, Ag) slab model with the adsorbed CO molecule, $E_{CO}$ is the energy of an isolated CO molecule, and $E_{M(111)}$ is the energy of the optimized clean M(111) surface.

III. RESULTS & DISCUSSIONS

Table I, Fig. 1, and the Supplementary Information (SI) give a complete compilation of calculated adsorption energies and related quantities for a CO molecule on several transition metal surfaces, including LDA, PBE, PBEsol, SCAN values. Table I and Fig. 1 also include the adsorption energy for the experimentally observed and thus most stable site. Figure 1 shows that all functionals capture the correct chemical trends: Stronger binding on Pd, Rh, and Pt. where the d-bands of the metal have more energy overlap with the frontier orbitals of the molecule, and weaker binding on the noble metals Cu, Au, and Ag. But there are clear discrepancies between the calculated values of adsorption energies and the experimental data. The adsorption energy magnitudes are overestimated by all the functionals tested in this work (with the exception of PBE for CO on Au and Ag). This overestimation is greatest for LDA and least for PBE. SCAN values fall between PBE and PBEsol. SCAN predicts the correct adsorption site for Pd (111) (fcc-hollow), Rh (111) (top), and Ag (111) (top). The difference in adsorption energies between the top and the fcc site for CO/Pt (111) from SCAN is 0.02 eV, better than the 0.15 eV from PBE. The functionals used in this work predict the wrong adsorption site for Cu (111), Au (111) and Pt (111). The wrong adsorption site prediction by PBE, especially for “CO/Pt(111)”, is a long-standing challenge. We do not see any changes in PBE prediction from previously published results.

The bond-length of the CO molecule and the distance between the surface metal atom and the C atom can be seen in Table S2 of SI. Our reported results from SCAN are in good agreement with LEED experimental data. The experimentally observed C-O bond length ($d_{CO}$) of 1.15 ± 0.05 Å for CO/Pt (111) is well reproduced by SCAN for all three sites. The $d_{Pd-CO}$ distance for the top site calculated from SCAN is within the experimental accuracy (1.85 ± 0.10 Å). SCAN predicts a more accurate distance than PBE. For the other two (higher-coordinated) adsorption sites (fcc and hcp), the $d_{Pd-CO}$ distances are comparable for both SCAN and PBE. SCAN is more accurate than the other functionals for the metal-to-molecule binding distances in the other systems.

We have plotted the orbital-decomposed density of states (DOS) of the adsorbed systems using PBE and SCAN in Figure S2 of the SI.
FIG. 1: Adsorption energy of CO at the top site on different d-metals calculated using different functionals. Experimental adsorption energies are for the top site, except for Pd (111). For tables of calculated adsorption energies on various sites, see the Supplementary Information. For experimental adsorption energies and calculated site dependences, see Table I.

TABLE I: Calculated difference of top and fcc-hollow adsorption energies $\Delta E_{\text{TOP-FCC}}$ (in eV) for CO on (111) surfaces of different d-metals. The letter (T= top, F= fcc, H=hcp) in the parentheses of the last row indicates the stable adsorption site from experiment. For a correct site prediction, the energy difference $\Delta E_{\text{TOP-FCC}}$ should be negative for the T cases and positive for the F case. The numbers in the last row are experimental adsorption energies.

| Methods | Pd  | Rh  | Pt  | Cu  | Au  | Ag  |
|---------|-----|-----|-----|-----|-----|-----|
| LDA     | 0.78| 0.23| 0.35| 0.33| 0.23| 0.18|
| PBE     | 0.60| -0.03| 0.15| 0.07| 0.01| -0.05|
| PBEsol  | 0.71| 0.09| 0.27| 0.04| 0.15| 0.07|
| SCAN    | 0.60| -0.12| 0.02| 0.13| 0.03| 0.00|

Expt. $-1.48 \pm 0.09$ (F) $-1.45(T)$ $-1.37(T)$ $-0.50 \pm 0.05(T)$ $-0.40(T)$ $-0.28(T)$

IV. CONCLUSION

The adsorptions we discuss are mostly overbound by the PBE GGA, and are overbound even more by the SCAN meta-GGA in self-consistent calculations. Self-consistent PBE normally overestimates covalent bond strengths (while underestimating vdW bond strengths), and SCAN is normally much more accurate than PBE for all kinds of bonds in both molecules and condensed matter (as detailed in section I). Any deviation from the self-consistent density of the bonded system for a given functional will by the variational principle reduce the computed binding, as needed for CO on a transition-metal surface. In most practical calculations the error in the DFT energy is primarily functional-driven. However, in a few special situations (e.g., when a good semilocal functional is applied to a system with a small or zero HOMO-LUMO gap and possible charge transfer) the error is primarily density driven. Here we might say that the zero energy gap of the metal allows a large den-
Sersy response to errors in the PBE or SCAN exchange-correlation potential of the adsorbed molecule. It is known that the density-driven error can be sensitive to the specific exchange-correlation potential, and can be cured by using a more accurate density then the self-consistent density of DFT. Often, the Hartree-Fock (HF) density serves this purpose for molecules and anions. Hartree-Fock theory is self-interaction-free and greatly reduces charge-transfer errors. We would have liked to apply SCAN to a Hartree-Fock or hybrid-functional density for CO on transition-metal surfaces, to check if this procedure yields the correct binding energies and adsorption sites. But the computational cost of such a calculation for large metallic supercells is high. We are looking for alternatives, e.g., the self-interaction correction or the localized orbital scaling correction.

Selfconsistent SCAN is accurate for free molecules and free transition-metal surfaces, but makes the energy of the adsorption system too low relative to these limits. This is not an unusual situation for a semilocal functional: (1) Selfconsistent SCAN is accurate for free open-shell atoms A and B (B unequal to A), but makes the energy of the stretched-bond system A...B too low relative to these limits, due to a spurious charge transfer. (2) Selfconsistent SCAN is accurate for free reactant and product molecules of a chemical reaction, but makes the energy of the transition state too low relative to these limits. Evaluating SCAN or other semilocal functionals on the self-interaction-free Hartree-Fock density can greatly reduce these density-driven errors (typically several tenths of an eV in the reaction barriers, and thus in size to the errors of the CO adsorption energies on transition metals).

Kara and collaborators have applied standard density functionals to molecular adsorption on transition and noble metals. A recent study by Garza, Bell, and Head-Gordon of chemisorption on metal surfaces found that the tested functionals (including SCAN) tend to overbind, and proposed a special-purpose meta-GGA (RTFSS) for this problem. Stroppa and Kresse concluded that “for semilocal functionals, it seems impossible to improve the description of adsorption without worsening other properties”. We suspect that this is true in selfconsistent calculations. But it is still possible that the SCAN meta-GGA, applied to an exact or more correct density when necessary, might achieve this elusive goal, finding almost the right answer for almost the right reason at almost the right price for almost all real systems of interest.

Figure 1 of Schimka et al. shows that many semilocal density functionals cannot simultaneously yield an accurate surface energy for Pt (111) or Rh(111) and an accurate CO adsorption energy on those surfaces. From our present perspective, a good general-purpose semilocal functional applied self-consistently should yield an accurate surface energy but not an accurate adsorption energy.

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