A self-consistent Hubbard $U$ density-functional theory approach to the addition-elimination reactions of hydrocarbons on bare FeO$^+$

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We present a detailed analysis of the addition-elimination reaction pathways for the gas-phase conversion of molecular hydrogen and methane on FeO$^+$ to water and methanol, respectively, using first-principles calculations. These two reactions represent paradigmatic, challenging test cases for electronic structure approaches to transition-metal catalysis. We compare here density-functional approaches against state-of-the-art coupled-cluster and multireference quantum chemistry approaches. The quantum chemical approaches are found to be in close agreement between themselves as well as with the available experimental evidence. For the density-functional calculations, we employ a recently introduced $ab$ initio, self-consistent Hubbard-like correction, coupled here with a generalized-gradient approximation (GGA) for the exchange-correlation functional. We find that our formulation provides a remarkable improvement in the description of the electronic structure, hybridization, and multiplet splittings for all calculated stationary points along these reaction pathways. The Hubbard term, which is not a fitting parameter and, in principle, can augment any exchange-correlation functional, brings the density-functional theory results in close agreement with the reference calculations. In particular, thermochemical errors as large as 1.4 eV in the exit channels with the GGA functional are reduced by an order of magnitude, to less than 0.1 eV on average; additionally, close agreement with the correlated-electron reference calculations and experiments are achieved for intermediate spin splittings and structures, reaction exothermicity, and spin crossovers. The role that the Hubbard $U$ term plays in improving both quantitative and qualitative descriptions of transition-metal chemistry is examined, and its strengths as well as possible weaknesses are discussed in detail. © 2008 American Institute of Physics. [DOI: 10.1063/1.2987444]

I. INTRODUCTION

The gas-phase reactions of bare FeO$^+$ cations with hydrogen, methane, nitrogen gas, and other species have been widely studied as fundamental processes that can provide clues into the behavior of larger condensed-phase metal-oxo systems.$^{5,6}$ Paradigmatic reactions have been studied by numerous mass spectrometric techniques in detail,$^1$ but initial experimental results were surprisingly discordant with classical transition-state theories.$^2$ These results were proposed to be due to the crossing of multiple relevant spin surfaces for the reactions, a feature now expected to be relevant in larger systems, which include the enzyme horse-radish peroxidase$^7$ and model non-heme inorganic iron alkane hydroxylation catalysts.$^8$ The reaction of FeO$^+$ with H$_2$ has been under particularly extensive study for some time now both theoretically$^{6,9,13}$ and experimentally$^{1,2,4,14}$ as the most fundamental example of the two-state reactivity paradigm. Additionally, the reaction of FeO$^+$ with CH$_4$ has been studied in detail, although primarily with density-functional theory (DFT).$^{5,8,18}$ Methane oxidation on FeO$^+$ is particularly relevant because of methane’s greater utility as a fuel upon conversion to methanol, as well as the relevance to enzymatic systems such as methane monooxygenase.$^{19}$

Reactions of FeO$^+$ with CH$_4$ and H$_2$ are both known to be exothermic by about 10 and 37 kcal/mol, respectively. However, these reactions are very inefficient: only about 10% of all collisions lead to products in the case of methane and 1% of all collisions lead to products for the hydrogen case. This inefficiency is particularly surprising because the same-spin ground state reactant and product complexes, $\Sigma^+$ FeO$^+$ and $\Sigma^+$ Fe$^+$, make these reactions spin allowed.$^{10}$ It has also been found that radical side products can form by dissociation of the reacting complex to FeOH$^*$ and radical H or CH$_3$. While the former products are weakly endothermic, CH$_3$ radical formation is exothermic by roughly 3 kcal/mol. The decrease in observed rate constant with increasing energy or temperature for both reactions is also in direct contradiction with the expected Arrhenius-like behavior for a spin-allowed reaction.$^5$

Theoretical considerations pointed to crossings between the sextet and quartet potential energy surfaces as the source for this reaction inefficiency,$^{5,6}$ it is nevertheless notable that subsequent studies,$^4$–6,11,12 which employed density-functional techniques, have failed to agree with experimental...
results or highly accurate quantum chemistry calculations. We will consider in detail here the reactions of FeO\(^+\) with H\(_2\) and CH\(_4\) as a challenging test for a Hubbard \(U\) density-functional approach, which we have recently introduced to improve semilocal or hybrid density-functional descriptions of transition-metal complexes.\(^{20}\) We specifically consider the generalized-gradient approximation (GGA) in DFT for their efficiency and widespread use in the community;\(^{21}\) nevertheless, the Hubbard correction introduced here could be applied in conjunction with other exchange-correlation approximations. In order to gauge the success of our approach on both of these reactions, we will compare DFT+U (GGA+U) results with both standard GGA results and highly accurate quantum chemistry approaches.

A. The Hubbard \(U\) approach

We recently proposed augmenting semilocal exchange-correlation functionals with a Hubbard \(U\) term to improve the description and understanding of transition-metal complexes with highly localized valence states.\(^ {20}\) This approach, typically known as LDA+\(U\) or DFT+\(U\), has been very successful in improving the structural and energetic description of some strongly correlated solid-state materials.\(^ {22–24}\) We have recently shown that this method also corrects with great accuracy self-interaction errors inherent in the localized orbitals of transition-metal containing molecules. Currently, however, the most widely used approach for these molecular systems are the semiempirical density functionals known as “hybrids,” which mix in a fraction of Hartree–Fock (HF) exchange-potential with LDA or GGA exchange-correlation functionals. While these hybrids, exemplified by the highly popular Becke-exchange based B3LYP, have performed well on the first row, organic systems for which they were parametrized, their extension to transition metals has yielded mixed results.\(^ {5,25–26}\) In particular, it has been shown that some transition-metal complexes are better suited to a reduced percentage of HF exchange (e.g., the Jacobsen–Katsuki catalysts\(^ {25}\)), while others have been shown to be better described by an increased percentage of HF exchange (e.g., heats of formation of small transition-metal halide compounds.\(^ {26}\) Recent work has also explored the usefulness of a Hubbard-like correction, although in a semiempirical way.\(^ {27}\) Finally, higher order approximations, which include the Laplacian of the density, have been considered by several groups to varying degrees of success.\(^ {28–30}\) Our DFT+\(U\) approach is at variance with hybrid exchange-correlation functionals, for which the parameters are fit to experimental data or higher order quantum chemistry calculations because the Hubbard \(U\) term is a fully \textit{ab initio} property of the system that is determined directly from the calculations at little cost.

In order to further motivate the use of the DFT+\(U\) approach for single-site or few-site transition-metal complexes, we refer to an illustration suggested previously by Cococcioni and de Gironcoli.\(^ {24}\) The proper energetic description of an isolated atom in contact with a reservoir of electrons as a function of its occupation number is a piecewise linear statistical average of the integer occupation end points. On the other hand, GGA or LDA incorrectly provide parabolic behavior with a minimum often corresponding to fractional occupations.\(^ {31}\) Additionally, the GGA or LDA estimates are quite close to the exact DFT energy for integer occupations, with larger divergences at fractional numbers (hence the utility of constrained density-functional approaches).\(^ {32,33}\) The difference that remains between the exact and the GGA or LDA results is, thus, approximately piecewise parabolic and close to zero at integer occupations.

This picture is key to understanding the role of Hubbard functionals in complexes with a single transition metal, where intersite correlations are not relevant. We use here the rotationally invariant “+\(U\)” functional\(^ {34}\)

\[
E_{\text{coul}}(n_{\text{mott}}) = \frac{U}{2} \sum_{i,\sigma} \text{Tr}[n^{\sigma}(1 - n^{\bar{\sigma}})],
\]

where \(n^{\sigma}\) represents the occupation matrices of the localized manifold of states at site \(i\) with spin \(\sigma\), typically localized \(d\) or \(f\) states. In what follows, the occupation matrices are derived from projections of the molecular valence states onto the atomic states of the isolated metal center, but any number of approaches, such as maximally localized Wannier functions could be used.\(^ {34}\) As written, the Hubbard \(U\) correction is analogous to the parabolic corrections that must be made to the energy functional in order to reproduce the true piecewise linear behavior in the isolated limit we just described. In a molecular system, eliminating this curvature corresponds to improving the description of chemical hybridization by removing the tendency of \(d\) or \(f\) orbitals to overdelocalize from self-interaction errors. Moreover, the curvature of the parabola (i.e., the strength of the Hubbard \(U\) correction) is an intrinsic property of the system that can easily be determined from a linear-response calculation, as mentioned below.

Note that there is a number of approximations in Eq. (1), which we will not describe in detail (see Ref. 24). First, construction of a DFT+\(U\) (here, GGA+\(U\)) functional necessitates the inclusion of a term, which corrects for double counting of the Hubbard term by contributions already present in the approximate exchange-correlation functional (here, GGA). Second, in order to reach the simplified form of Eq. (1), the higher order interactions of electrons of different spins, traditionally identified by the term \(J\), have been incorporated into the term we use such that our \(U\) is effectively equal to the rigorously defined \(U_{11} - J_{1}\). Our definition distinguishes our results somewhat from those who employ a \(J\) explicitly, and this should be kept in mind when comparing results of other \(U\) or \(GGA+U\) codes. Additionally, we provide in the Appendix the results that show that pseudopotential oxidation state choice can have an effect on numerical values of the linear-response \(U\) while ultimately preserving a consistent description of the system.

As shown by Cococcioni and de Gironcoli, the curvature of the total energy with respect to occupation number can be recast, via Janak’s theorem, into a linear-response property
where \( \chi_0 \) represents the bare, noninteracting reorganization after a potential shift \( \alpha \) (which is in practice extracted from the first iteration of an SCF calculation), while \( \chi \) represents the self-consistent response to the same potential shift. In practice, a rigid potential shift, \( \alpha \), is applied on the localized manifold, and the resulting change in occupations is measured. This linear-response approach is both computationally affordable and easy to employ for any structure for which a well-converged single point energy calculation can be obtained.

We have recently extended this approach to take into consideration the changes in the linear-response properties of the DFT + U ground state density with respect to the standard exchange-correlation functional (here, GGA). In molecules, different electronic states may become more stable with GGA + U, or in the solid state, systems that are metallic with GGA can become insulators, leading to very different response properties. One might expect that consistency is achieved when the value of applied \( U \) yields a linear-response \( U_{\text{out}} \) that is equal to zero or alternatively, a fixed point in which \( U_{\text{out}} = U_{\text{in}} \) is reached. In fact, both assumptions neglect the fact that there is already an inherent correlation in the exchange-correlation functional that is augmented, and consistency is achieved only when the added Hubbard correlation and the one intrinsic in the exchange-correlation functional are consistent. Simple algebra and the observation that \( U_{\text{out}} \) exhibits a linear behavior over a range of \( U_{\text{in}} \) lead to the definition of a self-consistent \( U_{\text{scf}} \) as

\[
U_{\text{out}} = U_{\text{scf}} - \frac{U_{\text{in}}}{m},
\]

where \( m \) is an effective degeneracy of the perturbed manifold. In practice, we obtain \( U_{\text{scf}} \) by extrapolating over a range of points (which follow the linear relationship to \( U_{\text{in}} = 0 \)). From now on, we refer to the result of a standard-linear response calculation [obtained from Eq. (2)] as \( U_0 \) and of the self-consistent extrapolated value as \( U_{\text{scf}} \). Often, \( U_0 \) and \( U_{\text{scf}} \) are nearly identical but we have shown that \( U_{\text{scf}} \) occasionally provides a significant improvement, as in the case of the iron dimmer. Lastly, although we focus on the use of the DFT + U functional for a single localized manifold, in some cases the \( U \) terms on other manifolds can become relevant. Inclusion of the other manifolds simply requires a matrix formulation, as discussed in detail in Ref. 24, and we will discuss explicitly when these manifolds (e.g., the 4s states in select 3d\(^4\)4s\(^1\)-based intermediates) play a non-negligible role.

A significant shortcoming of the Hubbard formulation that should be highlighted is that total energies computed at different values of \( U \) cannot be directly compared. In order to construct comprehensive potential energy surfaces or reaction coordinate diagrams, we chose to use an average \( U \) across all relevant ionic structures and electronic states, a reasonable approximation because of the proximity of individual values of \( U_{\text{scf}} \) to the global \( U_{\text{scf,av}} \). In particular, systems that have differing structure (e.g., equilibrium versus stretched bonds) or coordination environments (e.g., both number and character of interaction) often fortuitously exhibit reasonably similar values of linear-response \( U \) and therefore their energetics may be easily compared at an averaged \( U_{\text{scf}} \) without bias. However, in some cases, energy splittings and barriers may be more accurately obtained by employing a locally averaged \( U \) over only a small portion of the reaction coordinate, as we will later show. While we believe that our approach has great promise for treating large-scale systems with near-chemical accuracy, thanks to its negligible computational costs, we will first demonstrate its applicability to the well-known challenging test cases of addition-elimination reactions on FeO\(^+\) that are both representative of a broader class of catalytic processes.

II. METHODS

Calculations have been carried out primarily in two forms: plane-wave, density-functional calculations, and localized basis set, post-HF calculations, which we used for a highly accurate reference to our DFT results. The plane-wave density-functional calculations were completed with the QUANTUM-ESPRESSO package\(^{35}\) using the Perdew–Burke–Ernzerhof\(^{23}\) (PBE) generalized-gradient approximation (GGA) both augmented with a linear-response, Hubbard-like \( U \) term, as previously outlined\(^{20,24}\) as well as in its standard form. The linear-response calculation of the Hubbard \( U \) term is also implemented in this package. Ultra-soft pseudopotentials were employed with a plane-wave cutoff of 40 Ry for the wave function and 480 for the charge density for most structural relaxations to ensure accurate convergence of forces as well as spin and symmetry state splittings. Structural relaxations and nudged elastic band (NEB) optimizations\(^{37}\) were carried out at integer values of the Hubbard \( U \) to further assess the \( U \) dependence of structure and energetics. In order to improve the resolution of steep reaction barriers, the climbing-image and variable spring methods were employed in conjunction with the NEB calculations. For diatomic molecules, the harmonic frequencies and anharmonic contributions were obtained with high-order polynomial fits to the potential energy surface.

Post-HF approaches were employed to provide an accurate but computationally very expensive reference to compare the density-functional calculations against. The reaction with hydrogen (\( n_\text{H}_2 = 4 \)) was studied primarily with GAUSSIAN 03\(^{30}\) and the reaction with methane (\( n_\text{CH}_4 = 7 \)) was studied with MOLPRO.\(^{40}\) The primary single-reference method employed was coupled cluster with singles, doubles, and perturbative triples [CCSD(T)]. The T1 diagnostic was used as a tool to identify structures with potentially strong multireference character or instability in the triples term, and select multireference configuration interaction (MRCI) and perturbation theory (CASPT2) calculation were employed to verify the CCSD(T) results.\(^{41}\) All multireference calculations on either reaction were carried out using MOLPRO, which was available to us on a 64 bit architecture. The same Pople-style 6-311++G(3df, 3pd) basis set was used for all post-HF calculations to ensure consistency.

In order to construct the CCSD(T) hydrogen on FeO\(^+\)
TABLE I. $U_0$ and $U_{\text{scf}}$ for intermediates (Int) and TSs along the H$_2$ and CH$_4$ reaction coordinates. Quartet surface values in upper part of the table, sextet in the lower part.

<table>
<thead>
<tr>
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<th>H$_2$</th>
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<th>CH$_4$</th>
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<td>$U_{\text{scf}}$</td>
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<td>Avg</td>
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reaction coordinate, we estimated equilibrium CCSD(T) geometries for each intermediate. The low-dimensionality of the potential energy surface permitted calculation of a fine mesh of single point energies about 0.01–0.02 Å apart and deduction of a minimum energy configuration. These geometries are also useful to determine errors in geometries in the GGA and GGA+$U$ methods. For transition states (TSs), we used GGA+$U$ or GGA geometries to calculate single point CCSD(T) energies since discretizing the PES at the TSs was too computationally expensive.\(^42\)

III. RESULTS

We consider first the value of $U$ calculated for each intermediate and transition state for the reactions with both hydrogen and methane, which helps us identify the broad similarities of the two cases (see Table I). As mentioned previously, in order to obtain a global reaction coordinate, we must use energies calculated with a single value of Hubbard $U$, which we choose as an average, $U_{\text{scf,av}}$ over all states. Since total energies at differing values of $U$ are not comparable, it is important to pay attention to large deviation in $U_{\text{scf}}$ at any stationary point from the global average. The overall $U_{\text{scf,av}}$ we obtain for the H$_2$ reaction is 4.93 eV, and the value for the CH$_4$ reaction is very similar at 5.09 eV. The $U_{\text{scf}}$ is on average larger than the value calculated from GGA ($U_0$) for most geometries. We find the smallest discrepancy between the self-consistent and non-self-consistent values of $U$ for reaction intermediates, while the differences for TSs are as large as 1.5 eV, as is in the case of $^6$TS-2H$_2$. For most single points in these two reactions, the individual $U_{\text{scf}}$ values are within 1 eV of the $U_{\text{scf,av}}$. Based upon typical cases (e.g., Int-3 splittings in Fig. 5 and sextet TS-1 barriers in Table I), employing GGA+$U$ with a value of $U_{\text{scf,av}}$, which is 1 eV too small or too large for the appropriate structure, likely yields energy differences in the range of 0.01–0.1 eV, and this uncertainty can, in many cases, be decreased by examining splittings with a locally averaged value of $U_{\text{scf}}$.

Trends in the values of $U_{\text{scf}}$ are very consistent for the two reactions’ quartets and sextets (see Table I). While the exact numbers between the two reactions are not identical, the similarities highlight the fact that coordination and electronic configuration contribute most strongly to the calculated $U$ value. Overall, we observe a larger $U_{\text{scf}}$ in the range of 5.5–6.5 at the entrance channel, where the iron center is weakly three- or twofold coordinated in the Int-1 structure (see Fig. 1). At the first reactant barrier, $U_{\text{scf}}$ decreases monotonically for all TS-1 and Int-2 structures, and this change is concomitant with a reduction in FeO$^+$ bond order and coordination.

At the second reaction barrier, the quartet and sextet surfaces exhibit different linear-response properties. This behavior of $U_{\text{scf}}$ is strongly affected by differences in the chemical coupling of the quartet and sextet Fe$^+$ centers with the organic ions in the two spin surfaces. The 3$d^4$s$^1$-like sextet’s two minority spin electrons are equally divided between the $d$ and $s$ manifolds, and this results in an increased prominence of the $U_{\text{scf,ls}}$ for $^6$TS-2H$_2$ and an overall lower $U_{\text{scf,3d}}$ around 3–4 eV for both reactions. While the extension to include 4$s$ states, and thus a $U_{4s}$, is straightforward, it plays a role exclusively in the class of weakly bound molecules where the $4s$-$3d$ hybridization dominates and 3$d$- and 4$s$-derived molecular states are close in energy. The sextet TS, especially in the methane case, is indeed quite weakly bound, and we will later discuss this in greater detail. The TS...
along the quartz surface, which has a $3d^7$ character, is more tightly bound, and the $U_{\text{scf}}$ of $4\text{TS}-2$ is close to $U_{\text{scf,av}}$. All Int-3 structures at the exit channel closely resemble a weakly bound Fe$^+$ ion with the product water or methanol (see Fig. 2). Consequently, the Fe$^+$ charge density is increasingly atomiclike, and the values of the Hubbard $U$ are significantly lower at this point in the reaction surface for the quartet at around 2 eV (the sextet displays a $U_{\text{scf}}$ considerably closer to the average).

We highlight that the $U_{\text{scf}}$ from linear response for each stationary point of a given configuration and electronic symmetry is calculated separately. We also consider the energetic evolution of each state individually and thus take into account any changes in state energetics ordering with increasing values of Hubbard $U$. Since these two reactions involve unsaturated metal centers for which the number and character of metal-ligand bonds change across various spin states, the values of the Hubbard $U$ are significantly lower at this point in the reaction surface for the quartet at around 2 eV (the sextet displays a $U_{\text{scf}}$ considerably closer to the average).

as well as the spurious tendency of the $3d$ electrons to delocalize—the latter of which is corrected and greatly reduced by the Hubbard $U$ term.

It is of particular note that the GGA+$U$ sextet-quartet splitting (0.54 eV) is in remarkable agreement with the CCSD(T) value (within three hundredths of an eV) and frequencies for the sextet and the quartet are within 25 and 21 cm$^{-1}$ of their CCSD(T) values, respectively, compared to a discrepancy as large as 400 cm$^{-1}$ for GGA. Obtaining the correct multiplet splittings for FeO$^+$ low-lying states is crucial to ensure that the entire reaction coordinate is well described.

B. The first reaction intermediate

Free hydrogen or methane complexes weakly with FeO$^+$ at the metal site to form the first intermediate (Int-1) of the reaction, which has not been isolated experimentally (see Fig. 1). Along the sextet surface (both with GGA and GGA + $U$), the electronic structure of the FeO$^+$ state is only weakly perturbed by the bound CH$_4$ or H$_2$, as is evidenced by the fact that the Fe-O bond lengthens by only 0.01 Å with respect to its bare FeO$^+$ value, and the preferred binding site for the reactant is parallel to the Fe–O bond. The H–H bond length, 0.79 Å, is lengthened by only 0.01 Å with respect to the isolated molecule. In $4\text{Int-1CH}_4$, the methane tetrahedron flattens slightly, with the three hydrogens closest to the C–Fe bond exhibiting a dihedral of 135° instead of the idealized value of 120°. While the effect is subtle, GGA+$U$ does in fact tune the relative energy of this intermediate with respect to the reactants.

In contrast to the sextet, the $4\text{Int-1}$ exhibits a more dramatic response structurally and energetically to the value of $U$, and thus demonstrates the utility of a Hubbard $U$ approach. While the binding of hydrogen or methane to the FeO cation occurs parallel to the metal-oxo bond in the sextet case, the ligand may instead preferentially bind in a manner perpendicular to the bond. Early density-functional calculations predicted that this nonplanar geometry for the $4\text{Int-1H}_2$ was the preferred structure. However, we showed that this stabilization by GGA was not preserved in the GGA+$U$ result for the reaction with hydrogen. Our GGA+$U$ results reversed the preference of GGA and stabilized the planar structure for $U$ above 3 eV and by nearly 0.5 eV at a $U$ of 5 eV, with respect to the lowest-lying planar geometry electronic state (see Fig. 1). In both planar and nonplanar orientations, the primary bonding occurs via bonding overlap between H $1s$ density and the FeO$^+$ orbitals $\sigma$ molecular orbitals ($3d_{z^2}+2p_z$). In the nonplanar geometry, additional bonding of the complex occurs via overlap of the two hydrogens’ $1s$ density with the $\delta_a$ atomiclike orbitals of the metal center.

A. The low-lying states of the FeO$^+$ reactant

We previously demonstrated that the structure and energetics of low-lying states of FeO$^+$ are described with greatly improved accuracy with GGA+$U$ over standard GGA by comparing against high level quantum chemistry methods [CCSD(T)]. For both GGA and GGA+$U$, the FeO$^+$ ground state is a $d^5s^1\ 6\Sigma^+$ with full spin up $3d$ and $4s$ manifolds, as well as fractional occupation of spin-down $\pi$ and $\sigma_{d_z^2}$ orbitals. Elongation of the FeO$^+$ bond from 1.62 Å (GGA) to 1.66 Å (GGA+$U$) is concomitant with enhancement of spin up $3d$ density in $\pi^*$ states and subsequent reduction of the partial $3d$ occupation of spin-down $\pi$ orbitals. This change in hybridization also reduced the harmonic frequency by about 150 cm$^{-1}$ in improved agreement with CCSD(T) results. Several low-lying quartet FeO$^+$ states are close in energy, including $4\Phi$, $4\Delta$, and $4\Pi$. While $4\Phi$ and $4\Delta$ are nearly degenerate in energy with GGA, GGA+$U$ stabilizes $4\Phi$ preferentially by nearly 0.75 eV over the other states, in agreement with ours and other CCSD(T) results. The equilibrium bond length of $4\Phi$ increases significantly from 1.58 (GGA) to 1.75 Å (GGA+$U$) and the harmonic frequency decreases by from 1038 to 612 cm$^{-1}$ due to an even more pronounced increase in $\pi^*$ occupation in this case than in the sextet.

For both the quartet and the sextet, two competing factors exist—a physically relevant hybridization of the Fe $3d$ electrons with O $2p$ electrons to form the bonding $\pi$ orbitals and the energetic ordering of binding sites of small organic molecules on metal surfaces. Importantly, our CCSD(T) calculations confirm the GGA+$U$ result that the planar geometry is more energetically favorable. The nonplanar geometry is not a
stable sextet intermediate because the favorable interaction occurs via the minority spin channel, which is not present in the sextet case. It follows that GGA shows a similar preference for the nonplanar geometry for methane reaction $^{4}{\text{Int-1}}$ complexes (see Fig. 1). This effect is reduced in the methane case for several reasons: the density of only one out of four hydrogens is available for overlap with the localized orbitals of Fe, it is not possible to position the hydrogens or carbon to overlap with $\delta$ states, and, moreover, C–Fe interactions are unable to contribute to formation of a bent structure. Indeed, while a nonplanar GGA structure is preferred for the $^{4}{\text{Int-1}}_{\text{CH}_4}$ by about 0.11 eV, GGA+$U$ stabilizes the planar structure for all values of $U$ greater than 1 eV and overall by about 0.5 eV at the globally averaged $U$ of 5 eV. MRCI results for the methane reaction agree with this state ordering, and our $^{4}{\text{Int-1}}$ GGA+$U$ results demonstrate the dramatic improvement in both structural and energetic description brought about by addition of a Hubbard $U$ term.

C. The first reaction barrier

The first catalytic step in the reaction of FeO$^+$ with methane or hydrogen is the abstraction of a single hydrogen from the reactants by oxygen. The TS associated with this step for all reactants and spin surfaces is four centered and all bonds to the soon to be abstracted hydrogen are highly stretched. Along the sextet surface, GGAs have been shown to properly reproduce the characteristic experimentally steep barrier$^{5,6,20}$ (see Table II). This large activation barrier for both sextet reaction surfaces stems from the short and tight bond of the $^6\Sigma^+$ FeO$^+$ molecule, which is stretched by 0.1 Å to a value of 1.72 Å in the GGA TS. The H$_2$ reactant bond is stretched to 1.05 Å, and a new, weak O–H interaction at 1.34 Å is formed. This transition-state structure changes very little from GGA to GGA+$U$, although with a slightly longer Fe–O bond and shorter H–H bond, and the barrier height estimates are similar for GGA (1.01 eV) and GGA+$U$ (0.97 eV). The methane reaction has a similarly high activation barrier along the sextet surface, which changes relatively little from GGA (1.35 eV) to GGA+$U$ (1.29 eV). Structurally, the Fe–O bond is stretched to the same extent as in the hydrogen reaction and the C–H bond is stretched by 0.3 Å from its equilibrium value of 1.10 Å, and changes in structure as a result of augmenting a $+U$ term are negligible. While the forward barriers for both reactions do not change significantly with the value of $U$, the change in the back-reaction barriers (or the step’s exothermicity) for both the hydrogen and methane case is quite large.

In contrast to the sextet surfaces, the quartet reaction barrier demonstrates considerable sensitivity to the value of the Hubbard $U$, as we would have predicted after the study of $^{4}{\text{Int-1}}$. The NEB reaction path we study uses the planar $^{4}{\text{Int-1}}$ as an end point, although it is a metastable minimum for GGA and low to intermediate $U$ values. The path also passes through a nonplanar GGA $^{4}{\text{Int-1}}$-like structure before reaching the stretched transition state, which is the global minimum for GGA but disappears as a stable intermediate for intermediate values of GGA+$U$. We previously showed$^{20}$ that a GGA barrier for the hydrogen reaction is steep, at about 0.4 eV with respect to the nonplanar Int-1, and the quartet TS-1 lies above the reactant energies, in contrast to experimental evidence$^1$ (see Fig. 3). With GGA+$U$, a shallow reaction surface is recovered with an activation energy of 0.20 eV, and the TS lies 0.16 eV below the ground state reactants. The reduction in the barrier estimate is likely derived from the weakening of the Fe–O interaction in the TS from 1.61 to 1.72 Å, thereby permitting increased bonding with the reactant complex.

As with the hydrogen case, the GGA $^{4}{\text{Int-1}}_{\text{CH}_4}$ nonplanar geometry appears in the GGA reaction coordinate as a local minimum stabilized by 0.1 eV. The TS also resembles its analogous sextet TS-1 with the methyl group sitting nearly perpendicular to the Fe–O bond and the leaving hydrogen shared equally between the carbon and oxygen.

The local minimum from the nonplanar surface disappears in the GGA+$U$ reaction coordinate, and the overall reaction barrier increases to nearly 0.65 eV for $U=5$ eV as a result of the reduced relative energy of the planar $^{4}{\text{Int-1}}$ end point (see Fig. 3). If we choose instead as a reference point either the nonplanar geometry or the crossing point of the quartet and sextet coordinates, the barrier estimate is reduced even further to 0.32 or 0.25 eV, respectively. Additionally, this GGA+$U$ transition state also lies below the reactant energy by 0.4 eV, compared to 0.3 eV for GGA. The quartet surface for both reactions demonstrates considerable sensi-

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tivity to the value of $U$ applied, which must be close to the $U_{\text{scf}}$ in order to accurately reproduce experimental and accurate theoretical estimations.

D. The second reaction intermediate

Upon abstraction of a hydrogen $H_{\text{abs}}$ from the reactants, the hydrogen in turn binds to oxygen to form the stable Int-2, and the Fe–O bond lengths further. This low symmetry structure possesses only a single low-lying electronic state and the energetic splitting of the sextet and quartet structures is close in energy ($\Delta E \approx \pm 50 \text{ meV}$) for both reactions. The sextet state is the GGA and GGA+$U$ ground state for the methane case, while GGA+$U$ preferentially stabilizes the hydrogen reaction’s $^4\text{Int-2}$ over the sextet, reversing the GGA ordering. The sextet structures have a planar configuration with the ligands at obtuse angles relative to the line of the Fe–O bond; the quartet structures instead feature a ligand-Fe–O angle of about 90° and an O–H bond directed out of the plane. For both reactions and spin surfaces, the Fe–O bond is elongated with respect to the TS-1 value. In $^6\text{Int-2}$, the Fe–O bond is about 1.74 Å for GGA and lengths further to about 1.77 Å for GGA+$U$. The total elongation for the GGA+$U$ $^1\text{Int-2}$ is 0.08 Å with respect to its 1.69 Å GGA value. The second reaction step, of which Int-2 is the starting point, is the concerted translation of the ligand (H or CH$_4$) at the iron site to a midway point atop the FeO bond concomitant with a rotation of the already abstracted hydrogen. This geometric rearrangement culminates in the formation of the water or methanol leaving group and corresponds to a dramatic change in coordination environment for the Fe center that goes from having two strong ligands to one strong and one weak ligand, finally to a single very weak ligand. These coordination changes provide a stringent test for whether GGA+$U$ can treat each of them with equal accuracy.

E. The second reaction barrier

Previous results$^{6,20}$ have shown the quartet barrier to lie below the sextet barrier, and the geometric structure plays a significant role in the relative barrier heights. In the $^4\text{Int-2}_{\text{H}_2}$ structure, a ligand-FeO angle of 90° requires less translation to position the ligand directly over the Fe–O bond. The GGA reaction barrier for the hydrogen reaction is about 0.42 eV, but it is significantly reduced by GGA+$U$ ($\approx 5$ eV) to 0.13 eV (see Fig. 4). The Fe–O bond elongates further from the length in $^3\text{Int-2}$ to 1.80 Å in the GGA+$U$ $^4\text{TS-2}_{\text{H}_2}$. The transferring hydrogen is shared nearly equally between Fe and O, with bond lengths of 1.60 and 1.44 Å, respectively. The GGA+$U$ reaction barrier for the hydrogen reaction is consistent with the shallow, barrierless quartet surface predicted by experimental evidence and our own highly accurate theoretical results.$^{2,6,20}$

For the methane reaction, the second quartet GGA barrier is very steep at nearly 1.4 eV, while with GGA+$U$ the activation energy is halved to about 0.7 eV (see Table IV). The GGA $^4\text{TS-2}_{\text{CH}_4}$ possesses rather long Fe–C and C–O bond lengths, suggestive of a weakly bound methyl radical and FeOH$^+$ complex. However, as $U$ increases above 2 eV, the Fe–C bond shortens, and there is an overall increase in the CH$_3$–FeOH$^+$ binding for the TS. The GGA+$U$ results clearly favor a bound TS, while the GGA results remain ambiguous. The relative energy to dissociated radical products is even more key in interpreting the $^6\text{TS-2}$ results, as we will later show. While the GGA+$U$ quartet surface barrier is larger than its hydrogen counterpart, $^4\text{TS-2}_{\text{CH}_4}$ remains below the reactant energies and requires less rearrangement than the sextet surface does. Generally, at the exit channel we observe a shallower quartet surface with GGA+$U$ than we did with GGA, and we also observe an increase in the back-reaction barrier consistent with increased exothermicity of the reaction.

The second barrier along the sextet surface is highly sensitive to the value of the Hubbard $U$ but in divergent ways for the hydrogen and methane reactions. Along the hydrogen reaction coordinate, the GGA sextet surface is relatively steep with an activation energy of 1.29 eV. The GGA+$U$ activation barrier is markedly decreased from GGA to 0.82 eV with the $U_{\text{scf,av}}$ of 5 eV (see Table III). We have previously shown that this value is an underestimate, and the decrease in activation energy with the value of $U$ for the hydrogen reaction is due to two factors. First, the $U_{\text{scf}}$ calculated from the 3$d$ states is low at about 3.27, and second, the 4$s$ electrons play an increasingly important role in bonding in this region of the sextet reaction coordinate. The GGA geometry of $^6\text{TS-2}$, however, is not dissimilar to the $^4\text{TS-2}$ structure with an Fe–H bond length of 1.50 Å and stretched O–H bond of 1.65 Å, which elongates further by 0.08 Å.

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FIG. 4. (Color online) Forward and back-reaction barriers as a function of increasing $U$ from 0 eV (GGA) to 5 eV (the global $U_{\text{scf,av}}$) for the second quartet barrier of both reactions with methane and hydrogen.
about 0.03 Å for GGA+U. The different reaction barrier behaviors of the two spin surfaces originates from both electronic structure differences (as evidenced by the differing values of linear-response $U$) and the differing degrees of displacement from the Int-2 geometry required to reach the TS.

Specifically, the sextet reaction coordinate is generally derived from Fe+ atomic states, which are $3d^6\,4s^1$ in configuration (unlike the quartet $3d^7$). The role of the $4s$ becomes most pronounced for weaker, long-distance binding interactions associated with the stretched bonds of the TS. By extending the linear-response calculation to a matrix formulation that takes into account the response of the $4s$ and $3d$ simultaneously, we obtain a $U_{\text{scf},4s}$ of 4 eV and an increased $U_{\text{scf},3d}$ of 4 eV as well. While a matrix formulation was already present in the original derivation,\textsuperscript{24} its application to studying both $3d$ and $4s$ electrons simultaneously has not been as crucial for solid-state applications as it is here in molecules with strong $3d-4s$ hybridization as well as close spacing of the $3d$ and $4s$ levels. By applying a Hubbard correction on both the $4s$ and $3d$ electrons (4 eV for both, as mentioned before and as obtained from linear response), we obtain an improved estimate of the barrier height of 1.16 eV, as compared to the 0.82 eV value obtained from GGA+$U_{\text{scf},4s}=5$ eV. The back-reaction barrier remains unchanged at 3.01 eV. Both forward and back-reaction barrier estimates are in improved agreement with the CCSD(T) values of 1.1 and 3.0 eV, respectively. Alternatively, a locally averaged $U_{\text{scf}}$ of the $3d$ states alone, 3.6 eV, provides an improved barrier estimate of about 0.96 eV. For cases where the role of the $3d$ states are reduced, a low $U_{\text{scf}}$ can provide a useful reminder to consider also binding interactions due to the $4s$, which are otherwise overshadowed by the $3d$ states for complexes with short bond lengths and strong metal-ligand $3d$ hybridization.

The methane $^{6}\text{TS}-2$ barrier varies strongly with Hubbard $U$ by decreasing drastically from 1.87 eV for GGA to 1.03 eV for GGA+U (see Table I). Unlike $^{6}\text{TS}-2\text{H}_2$, this TS exhibits a larger $U_{\text{scf},3d}$ of 4.35 relatively close to the $U_{\text{scf},av}$ value of 5 eV, while the linear-response $U_4$, is nearly zero, highlighting how the formalism permits detection of which manifolds are most relevant. The GGA $^{6}\text{TS}-2\text{CH}_4$ structure, like its quartet analog, resembles a methyl radical loosely bound to an FeOH\textsuperscript{+} fragment. The GGA coordination distances of 2.83 Å for Fe–C and 2.33 Å for C–O suggest that very diffuse interactions are responsible for binding. The long Fe–C bond length in the GGA structure corresponds to weak bonding via overlap of the Fe $4s$ density with the C $2p$, which is also weakly antibonding with respect to the C–O bonding. The loosely bound GGA structure points to significant competition between the elimination step and dissociation of the TS to radical side products, which are in fact both endothermic by 0.4 eV and around 0.05 eV, respectively. The similarity of the GGA $^{6}\text{TS}-2\text{CH}_4$ to a free methyl radical and FeOH\textsuperscript{+} moiety is further substantiated by comparing the TS geometries with isolated products. The C–H bond lengths and H–C–H angles are nearly identical to the isolated methyl radical (1.085 Å and 119°), and there is a very slight distortion from the plane of CH\textsubscript{3} with a dihedral of 170°. The nearly dissociated nature of the $^{6}\text{TS}-2\text{CH}_4$ GGA structure is much greater than in the quartet case as a result of the spins of the isolated radical fragments—quintet FeOH\textsuperscript{+} and doublet CH\textsubscript{3}—which couple with greater bonding interaction if the spins are opposed, as in the quartet, than if the majority spins match, as is the case in the sextet.

Bond lengths for the more tightly bound GGA+$U$ (=5 eV) TS are shortened to 2.49 Å for Fe–C and 2.26 Å for C–O. The GGA+$U$ structural differences are largely due to an increased population of three-center bonds involving the Fe $3d_{zc}$, O $2p$, and C $2p$ orbitals in lieu of weaker interactions between Fe $4s$ and C $2p$. In order to demonstrate in greater detail how the Hubbard $U$ term tunes the TS-2\textsuperscript{6} binding strength, we measure the changes in Fe–O bond length ($\Delta R_{\text{FeO}}$) as well as the difference between the TS-2\textsuperscript{6} CH\textsubscript{3} dihedral and the planar value in the isolated methyl radical ($\Delta \angle_{\text{CH}_3}$). With increasing values of $U$ up to 2 eV, we at first see a decrease in the Fe–O bond and slight decrease in the dihedral (see Table IV). However, for $U=3$ eV, the difference in the Fe–O bond length increases as charge transfer out of the Fe–O bond and into the CH\textsubscript{3} moiety increases concomitant with a dihedral change from an increased polarization of the Fe–O bond. These changes in electronic structure are evidenced by a 5% increase in the Fe–O bond length and 10% difference in the dihedral in the $U=5$ eV structure. The TS is also stabilized by over 0.6 eV when compared to the dissociated products and a now weakly exothermic side product. An accurate estimate of the relative height of this barrier both to reactants and to the radical side products is a particularly sensitive test for any \textit{ab initio} method; GGA +$U$ is in very good agreement with experimental findings and the MRCI reference calculation, while GGA fails to provide a physically reasonable description of the reaction.

### F. The third reaction intermediate

The exit channel Int-3 resembles an isolated Fe\textsuperscript{+} ion weakly ligated by the leaving oxygen of either the water or methanol (see Fig. 2). The weak metal-ligand interaction produces many closely spaced low-lying electronic states differing only by their minority spin orbital occupations, which presents the challenge to resolve ordering of states separated by a few hundreds of an eV. Based upon the $\Delta E_{0-4}=0.23$ eV splitting of isolated Fe\textsuperscript{+}, the sextet Int-3 should be most stable, but common density functionals erroneously predict the quartet instead to be most stable.\textsuperscript{5,6,20} Since the metal-ligand binding is equally weak in both reac-

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TABLE IV. $^{6}\text{TS}-2\text{CH}_4$ structural and energetic changes with $U$. The $\Delta E$ are in eV and the structures are percent difference from the bond length or dihedral for the isolated moiety at the same value of $U$ as in the transition state.
tions, the Int-3 structures of both reactions should be studied together. In the sextet case, a single 3d electron resides in the spin-down manifold, and the π and δ orbitals retain their degeneracy. For all $^4$Int-3 structures, occupation of a δ orbital, which minimizes overlap with any of the water molecules is preferred. The occupation of a π orbital yields an electronic state roughly 0.1 eV higher in energy. Population of the σ orbital is prohibitive, as it corresponds to the maximal overlap with the remainder of the electron density, and it resides roughly 0.5 eV above the lowest state. None of these relative symmetry orderings change significantly with increasing values of $U$, although the geometry does change. The two lowest GGA sextet Int-3H$_2$ states have a long Fe–O bond length of about 2.06 Å, which lengthens to 2.14 Å for GGA+U. For the methane case, the GGA equilibration Fe–O bond length is slightly shorter, about 2.03 Å, but it lengthens the same amount to about 2.11 Å with GGA+U.

For the quartet Int-3 structures, GGA Fe–O bonds are about 1.93 Å for the lowest Int-3H$_2$ states and lengthen to about 2.03 Å for GGA+U (≈5 eV). The methanol complex is similar with a GGA bond length of 1.90 Å extending to 1.99 Å for GGA+U. With quartet states, a greater number of permutations of the occupied orbitals is possible, and the degeneracy present in the sextet Int-3 π and δ orbitals is now broken. Population of the π$_{d_z^2}$ orbital yields states lower in energy than those occupying π$_{d_{z^2}}$ because π$_{d_z^2}$ forms a weakly repulsive antibonding orbital with stray 2$p_z$ density from the oxygen. The two lowest states favor instead σ orbital occupation in combination with either a δ$_{d_{x^2}-y^2}$ or π$_{d_z^2}$ orbital. The symmetries that are derived from alternative permutations of the two 3d electrons reside roughly 0.1 to 0.4 eV above these two states. For GGA, the lowest state occupies the δ orbital and is favorable by about 0.04 eV, but at a $U$ of around 3 eV, the two lowest states reverse their ordering and instead, the π occupation is preferred by about 0.09 eV (at $U$=5 eV) (Fig. 5).

While GGA erroneously predicts the Int-3 ground state to be a quartet, with increasing $U$ the two lowest sextet states become lower in energy than the lowest quartets. This is an improvement upon GGA, which found the quartet to be lower in energy by 0.1 eV and, thus, does not predict spin inversion at the exit channel. At a $U$ of 5 eV, we find the sextet-quartet ordering reversed and a state splitting of about 0.21 eV. This value may be an overestimate compared to our own and other CCSD(T) calculations, which place the sextet to quartet splitting closer to 0.12 eV. Because the splitting is very sensitive to the application of the Hubbard $U$, it is advantageous to obtain the splitting at the true $U$ of this system. Each state has an individual $U_{scf}$, which should be calculated separately and then averaged locally over all $^4$Int-3 and $^4$Int-3 states, rather than using the globally averaged $U_{scf}$, which is used to construct a global reaction coordinate. By employing an average $U_{scf}$ of 3.5 eV from the two lowest electronic states, the GGA+U splitting is found to be 0.12 eV, in improved agreement with CCSD(T) results. The lowest sextet and quartet GGA+U electronic states also exhibit consistent symmetry with those obtained from CCSD(T). Interestingly, as we show in Fig. 5, the state splittings and their dependence on Hubbard $U$ is nearly independent of ligand identity, thus showing that the GGA errors and GGA+U corrections are both systematic in nature. This analysis suggests also suggests that Int-3CH$_4$ sextet-quartet
splits for GGA+$U$ with a locally averaged $U$ is appropriate at about 0.13 eV, reduced from the value of 0.22 eV using the global $U_{\text{scf,av}}$.

IV. DISCUSSION

We have shown that for the addition-elimination of hydrogen on FeO$, GGA+$U$ reaction coordinate provides a substantial improvement over GGA when compared against experiment or highly accurate CCSD(T) reference calculations. The GGA reaction coordinate (see Figs. 6 and 7) is in direct contradiction with available experimental evidence and theory because it (1) underestimates the exothermicity by over 1 eV, (2) the quartet surface is too steep to rationalize a “shallow, barrierless” reaction,\(^2,6\) (3) spin splittings at intermediates show large errors, and (4) there is no spin crossover at the exit channel.\(^4\) The majority of these errors in the GGA reaction coordinate are localized to the second reaction barrier (see Fig. 7), with the exception of the errors in the quartet Int-1 structures and barriers in the first barrier surface (see Fig. 6). While the first GGA sextet TS barrier largely agrees with CCSD(T) results, the second GGA barrier exhibits much greater errors for the exothermicity and state ordering at Int-3. In contrast, the GGA+$U$ ($=5$ eV) reaction coordinate (see Figs. 6 and 7) correctly estimates and predicts the reaction exothermicity, the shallow but excited quartet surface, barrier heights, and spin crossover at the exit channel (see Fig. 7). Systematic improvements on GGA+$U_{\text{scf,av}}$ results on the largest discrepancies (e.g., at the hydrogen $^6$TS-2 barrier) were achieved by including explicitly the 4s manifold, highly relevant for isolated transition-metal complexes, or by locally averaging the value of $U_{\text{scf}}$. Additionally, the portions of the reaction coordinate that are properly estimated by GGA in the first TS barrier (see Fig. 6), namely, the sextet barrier steepness and structures, are preserved in GGA+$U$, while the errors of the GGA approach in the second TS barrier (see Fig. 7) are greatly improved upon.

In order to further measure the quantitative accuracy of the GGA+$U$ hydrogen on FeO$^+$ reaction coordinate, we estimated equilibrium CCSD(T) geometries for each intermediate. The low dimensionality of the potential energy surface permitted calculation of a fine mesh of single point energies about 0.01–0.02 Å apart and deduction of a minimum energy configuration. These geometries are also useful to determine errors in geometries in the GGA and GGA+$U$ methods. For TSs, we used GGA+$U$ or GGA geometries to calculate single point CCSD(T) energies since discretizing the PES at the TSs was too computationally expensive.\(^4\)

To further measure the quantitative accuracy of the GGA+$U$ reaction coordinate, we average the error of the GGA+$U$ and GGA splittings for each intermediate with respect to the CCSD(T) splittings for that intermediate. We also compare here to B3LYP results that we obtained but have not discussed in detail because they exhibited the same inaccuracies, which were previously discussed in literature.\(^5,6\) The average error for the five multiplet splittings along the reaction coordinate is greatly reduced to 0.04 eV with GGA+$U$ from GGA, which exhibits an average error of 0.20 eV. The commonly employed B3LYP functional performs poorly with an average error of 0.30 eV in splittings. Not only does GGA+$U$ improve errors by fivefold over GGA but using the CCSD(T) geometries we found from interpolating a potential energy scan, we also observe that GGA+$U$ on average produces improved geometries. Mean errors for GGA+$U$ geometries are reduced from 4.3 pm (for GGA) to 2.2 pm, and are slightly worse than B3LYP geometries with an average error of 1.3 pm. Although the B3LYP functional shows a slight improvement in geometries, the sevenfold improvement in spin splittings GGA+$U$ provides is much more key. The improvement of the B3LYP geometries over GGA and GGA+$U$ could also be attributed to differences between the bonds that hydrogen forms in all-electron, localized basis set methods and plane-wave pseudopotential methods.

The GGA description of FeO$^+$ on methane demonstrates even greater discordance with theory and known experimental results than the hydrogen reaction. In fact, using GGA we predict both the reactions to create methanol and to form radical side products to be endothermic by 0.2 and 0.4 eV, respectively (see Fig. 8). Additionally, the sextet TS-2 barrier resides slightly above the reactant energies. The remaining GGA discrepancies are comparable to those for the reaction with hydrogen and include spin splittings at intermediates,
barrier estimates, and the absence of a spin crossover at the exit channel. When we instead compare our GGA+U results to highly accurate MRCI calculations, we observe quantitative agreement between the two methods (see Fig. 9). The GGA+U quartet surface is shallower but not barrierless, in agreement with MRCI results. We should also note that experimentally a large kinetic isotope effect is observed, suggesting that quantum-mechanical tunneling through classical barriers may need also to be considered. We see an improved estimate of exothermicity of both main and side reactions and now also preserve spin crossover at the exit channel. The description of the quartet Int-1 geometry is also improved. A comparison of the accuracy of GGA+U geometries is beyond the scope of this study due to the higher dimensionality of the PES over that for the four atom reaction.

We can further examine the accuracy of GGA+U in treating the energetics of these reactions by decomposing the exothermicity for all spins and reaction steps, as summarized in Table V. While GGA produces errors as large as 1.4 eV for the methane reaction and 1.1 eV for the hydrogen reaction, GGA+U is in very good agreement with accurate quantum chemistry. The largest errors, such as the 0.32 eV underestimate at the sextet TS-2$_{H_2}$ barrier can be systematically improved by extensions that either include a $U_{4t}$ or a locally averaged $U_{act}$.

V. CONCLUSIONS

In conclusion, we have demonstrated that a novel Hubbard $U$ approach can greatly ameliorate the shortcomings of commonly employed functionals for transition-metal chemistry. Using the popular PBE-GGA approximation, we find that activation barriers, stationary point spin splittings, and reaction energies exhibit errors as large as 1.4 eV for both the methane and the hydrogen systems discussed. By augmenting our GGA exchange-correlation functional with a $+U$ term, we reduced these errors by an order of magnitude to, on average, 0.1 eV with respect to the best available quantum chemical methods [such as CCSD(T) and MRCI] as well as experimental values. Importantly, the Hubbard $U$ term is not used as a fitting parameter but it is a true linear-response property of the transition-metal complex, which may, in principle, augment any exchange-correlation density functional. The practical limitations to this approach stem from the complexity of the systems that we wish to study: Evolution of the coordination environment along a global reaction coordinate may result in local deviations from a globally averaged Hubbard $U$ or bring to the forefront the role of $4s$ contributions. Overall, the DFT+$U$ results (here, GGA+$U$) have been shown to provide for systematic improvement over GGA for all systems considered thus far by treating, for the first time within a DFT framework, the energetics of differing spin surfaces and electronic states with the same level of accuracy. The inexpensive linear-response $U$ calculation also acts as a probe for the relative utility of the DFT+$U$ approach for a given transition-metal complex, that is, if the Hubbard $U$ calculated is small or nearly zero, a standard description may be sufficient. We believe that this work paves the way for studying a myriad of large-scale systems, which contain transition metals with both accuracy and efficiency.

ACKNOWLEDGMENTS

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APPENDIX: PSEUDOPOTENTIAL DEPENDENCE

We consider here the effect that different details of the atomic projections as a consequence of pseudopotential choice can have on both the determination of the Hubbard $U$ and its effect on physical properties. It is important to note that the value of $U$ obtained for the same structure but with differing pseudopotentials may easily differ by as much as 2–3 eV, particularly if the pseudopotentials were generated in different oxidation states. Although this value might seem high, it reflects the changes that atomic orbitals undergo as a function of the total atomic charge. In addition, as the value of $U$ corresponds to how much correlation is missing from the standard LDA or GGA, it follows that the poorer the pseudopotentials, the better they are for capturing the true electronic structure.

### TABLE V. Net energy required for reaction steps (in eV) for GGA, GGA+$U$ ($+5$ eV), and post-HF methods, where the post-HF method for the $H_2$ reaction is CCSD(T) and the $CH_4$ reaction is MRCI.

<table>
<thead>
<tr>
<th>Method</th>
<th>TS-1$^4$</th>
<th>TS-1$^6$</th>
<th>TS-2$^4$</th>
<th>TS-2$^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$CH_4$</td>
<td>$H_2$</td>
<td>$CH_4$</td>
<td>$H_2$</td>
</tr>
<tr>
<td>GGA</td>
<td>-1.14</td>
<td>-1.04</td>
<td>-0.54</td>
<td>-0.59</td>
</tr>
<tr>
<td>GGA+$U$</td>
<td>-1.07</td>
<td>-1.42</td>
<td>-0.71</td>
<td>-1.05</td>
</tr>
<tr>
<td>Post-HF</td>
<td>-0.99</td>
<td>-1.35</td>
<td>-0.75</td>
<td>-0.96</td>
</tr>
</tbody>
</table>

### TABLE VI. Comparison for several pseudopotentials of structural properties including equilibrium bond length [Å], harmonic frequency [cm$^{-1}$] and state splittings (in eV) of the $^6Σ^+$ and $^4Φ$ states of FeO$^+$. The GGA+$U$ results are obtained at the respective $U_{act}$ of each pseudopotential.

<table>
<thead>
<tr>
<th>Property</th>
<th>Fe$^{2+}$($δ^5s^0$)</th>
<th>Fe$^{3+}$s($δ^6s^1$)</th>
<th>Fe($δ^6s^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6Σ^+$ $r_e$(Å)</td>
<td>1.59, 902</td>
<td>1.63, 906</td>
<td>1.62, 901</td>
</tr>
<tr>
<td>$4Φ$ $r_e$(Å)</td>
<td>1.52, 1033</td>
<td>1.57, 1040</td>
<td>1.56, 1038</td>
</tr>
<tr>
<td>$ΔE_{0→e}$(eV)</td>
<td>0.76</td>
<td>0.82</td>
<td>0.84</td>
</tr>
<tr>
<td>GGA+$U_{act}$(eV)</td>
<td>7.0</td>
<td>4.9</td>
<td>5.5</td>
</tr>
<tr>
<td>$6Σ^+$ $r_e$(Å)</td>
<td>1.65, 745</td>
<td>1.66, 751</td>
<td>1.66, 749</td>
</tr>
<tr>
<td>$4Φ$ $r_e$(Å)</td>
<td>1.76, 606</td>
<td>1.75, 613</td>
<td>1.75, 612</td>
</tr>
<tr>
<td>$ΔE_{0→e}$(eV)</td>
<td>0.50</td>
<td>0.52</td>
<td>0.54</td>
</tr>
</tbody>
</table>
match between the oxidation states of the pseudopotential and the physical system, the higher the value of the linear-response $U$ will be. For reference, we provide here comparison of FeO$^+$ sextet and quartet state properties calculated using pseudopotentials generated in various oxidation states. The Fe$^{2+}$ ($d^{5}s^{0.5}$), Fe$^{0.5+}$ ($d^{6}s^{1.0}$), and Fe ($d^{5}s^2$, used throughout the remainder of this paper) pseudopotentials had values of $U_{cf}$ of 7.0, 4.9, and 5.5 eV, respectively. As the electronic configuration of FeO$^+$ states is either $d^5s^1$ or $d^5s^0$, it is reasonable that the second pseudopotential produces the lowest value of $U$.

In comparing LDA$+U$ or GGA$+U$ calculations of differing pseudopotentials, total energies and, subsequently, highest occupied molecular-orbital-lowest unoccupied molecular orbital or band gap values for different values of $U$ are not likely to be comparable. However, the properties derived from each spin and symmetry’s ground state density, including frequencies, bond lengths, and state splittings, may be compared. The GGA results for each of the three cases show significant differences for some structural properties and energetic splittings (see Table VI). While the harmonic frequencies for $^{4}\Phi$ and $^{2}\Sigma^+$ of 1040 and 900 cm$^{-1}$ are identical for all pseudopotentials within the accuracy of the fitting procedure, more significant differences are observed in the bond lengths. The most ionic pseudopotential ($d^{5}s^{0.5}$) yields the shortest GGA value with $^{4}\Phi$ and $^{2}\Sigma^+$ at 1.52 and 1.59 Å, respectively, while the other two pseudopotentials yield bond lengths within 0.01 Å of each other. The increased harmonic frequencies agree within 6–7 cm$^{-1}$, and the spin splittings for all three pseudopotentials agree within 0.04 eV. Overall, an even smaller spread in values is observed for GGA$+U$ than for GGA (see Table VI). Even a poor pseudopotential choice will remedy itself so long as the proper value of $U$, $U_{cf}$, is used. These observations demonstrate that perfect pseudopotential selection is not mandatory, but the best pseudopotential choice is one which clearly reflects the oxidation states and charges of the physical system of interest.

References:


36. State symmetry assignments were made based upon the absolute total angular momentum, $|\alpha|$, of the density and the overall symmetry of the component densities, $\alpha$, which remain as “good” quantum numbers in our density-functional formalism. Additionally, the preserved spin quantum number of our systems is $\tilde{\alpha}$.


40. MOLPRO, a package of ab initio programs designed by H. J. Werner, P. J. Knowles, R. Lindh et al., Version 2006.1, see http://www.molpro.net, Cardiff UK, 2006.

41. See EPAPS Document No. E-ICPSA6-129-009837 for multireference and single-reference quantum chemistry details including method comparisons regarding multireference character, as well as Hubbard $U$-dependent geometries of intermediates and TSs at integer values of $U$. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.

42. We note that energetic differences at the CCSD(T) level of the different TS geometries were small and did noticeably affect barrier height estimates.


45. The reaction coordinates of different methods have been aligned at the $^3$Int–$^1$Int. The curves associated with GGA and GGA+$U$ reaction coordinates are splines of points from the minimum energy path as determined by NEB calculations.