CHAPTER 14

Electronic Structure and Reactivity of Transition Metal Complexes

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Transition metals are ever-present as reactive centers in biological and inorganic catalytic cycles. However, the open-shell character that gives 3$d$ transition metals unique reactive properties also makes transition metal complexes challenging to study using first-principles approaches, especially when using local or semilocal approximations to density functional theory (DFT). We describe here an approach based on Hubbard $U$ corrections—widely used in the solid-state community to describe strongly correlated systems—and show how it helps achieve predictive accuracy in DFT calculations of transition metal complexes. The success of this approach comes from counteracting the tendency of 3$d$ electrons to delocalize, driven by the imperfect cancellation of electrostatic self-interactions in common exchange correlation approximations. Since the Hubbard term $U$ is calculated through a linear response formulation—recently extended by us to allow for self-consistency—it represents a fully ab initio, nonempirical approach. We analyze the performance of the DFT$+U$ formulations on a few paradigmatic test cases, with special attention to the structure, electronic structure, and potential energy surface of Fe$_2$ dimers and the addition–elimination reaction of hydrogen or methane on FeO$^+$. Thanks to negligible computational overheads, we also show how the approach can be effortlessly applied to large-scale simulations, such as the case presented here of functionalized cobalt porphyrins on a metal support.

14.1 INTRODUCTION

Transition metals are ever-present as reactive centers in molecules active in biological and inorganic catalytic cycles. In biological systems, mid-row 3$d$ transition metals
facilitate reactions as diverse as methane-to-methanol conversion at an antiferromagnetically coupled dimetal center [1,2], unactivated alkane halogenation by a high-energy, high-spin ferryl-oxo center in the halogenase SyrB2 [3], and oxygen binding at iron porphyrins in hemoglobin [4]. In inorganic catalysts, many transition metal complexes have been designed to carry out synthetic pathways that mimic active biological catalytic cycles. However, the open-shell character that gives 3d transition metals unique reactive properties also makes transition metal complexes quite difficult to study using density functional theory (DFT) approaches, which are particularly attractive as their efficiency gives access to systems of several hundreds of atoms in size. Common implementations of DFT, however, including the local density approximation (LDA) and the generalized-gradient approximation (GGA), utilize mean-field approximations that are ill-suited to studying 3d transition metals with highly localized, open-shell orbitals [5]. Following the success of LDA+$U$ (and GGA+$U$) in accurately reproducing the ground state of transition metal oxide solids [5,6], we showed for the first time how this approach can also be applied to single- or few-site molecular systems [7]. The LDA+$U$ approach is particularly suitable for application to single- or few-site molecules because the $U$ term plays a specific role in correcting exchange self-interaction errors and tuning the hybridization in the local bonding interactions.

The LDA+$U$ or GGA+$U$ method in its original formulation is an approximation that corrects LDA or GGA in order to better describe strong electronic correlations. It is based on a Hubbard model approach for treating strongly correlated systems [8,9]. As a result, electronic structure approaches have incorporated Hubbard $U$ terms in order to better treat correlated solids for quite some time [9]. A simplified, rotationally invariant LDA+$U$ functional was introduced by Cococcioni and de Gironcoli [5]. In addition, in their approach, the $U$ term may be calculated as a property of the system from linear response theory. The general form of the LDA+$U$ functional (where LDA can really be extended to any exchange correlation functional) is as follows:

$$E_{\text{LDA}+U}[\mathbf{n}(r)] = E_{\text{LDA}}[\mathbf{n}(r)] + E_{\text{Hub}}[\mathbf{n}^{I}_{\alpha\mu\nu\sigma}] - E_{\text{dc}}[\mathbf{n}^{I\alpha}]$$  \hspace{1cm} (14.1)

In this equation $\mathbf{n}(r)$ is the electron density, while $\mathbf{n}^{I\alpha}_{\mu\nu\sigma}$ is a generalized occupation matrix for atom $I$, spin $\sigma$, which is considered the source of the strongly correlated manifold, usually given by the localized $d$ or $f$ orbitals of the free atom. The $E_{\text{LDA}}[\mathbf{n}(r)]$ term represents the contribution of the energy from the LDA or GGA functional, and, in this work, we actually employ GGA in our examples [10]. Since the GGA exchange correlation functional already includes some mean-field treatment of on-site electronic interactions, when we introduce a correction to model properly the on-site correlation (in this case $E_{\text{Hub}}[\mathbf{n}^{I\alpha}_{\mu\nu\sigma}]$), it is also necessary to subtract out the mean-field correlation in LDA using a double-counting term, $E_{\text{dc}}[\mathbf{n}^{I\alpha}]$. To recover the proper electron–electron interactions, $E_{\text{Hub}}[\mathbf{n}^{I\alpha}_{\mu\nu\sigma}]$ is broken down into a Coulomb (the parameter $U$) and exchange interaction (the parameter $J$), which have been modeled formally borrowing from atomic Hartree–Fock Slater integrals [5,9].

By neglecting the exchange term, or essentially modeling an effective interaction $U_{\text{eff}}$ that is equal to $U - J$, it is possible to greatly simplify previous expressions for the
LDA+$U$ energy functional. The double-counting term $E_{\text{dc}}[n^I]$ is approximated in terms of the $U$ and $J$ parameters as

$$E_{\text{dc}}[n^I] = \sum_I \frac{U}{2} n^I (n^I-1) - \sum_I \frac{J}{2} [n^I (n^I-1) + n^I (n^I-1)]$$  (14.2)

leading to the final form for the Hubbard + $U$ functional [5]:

$$E_U[n^I] = E_{\text{Hub}}[n^I] - E_{\text{dc}}[n^I]$$

$$= \frac{U}{2} \sum_I \sum_{m,\sigma} n^I_{nm\sigma} - \sum_{m'} n^I_{nm\sigma} n^I_{nm'm}$$

$$= \frac{U}{2} \sum_{I,\sigma} \text{Tr}[n^I(1-n^I)]$$  (14.3)

If the occupation matrix is diagonalized, this expression simplifies even further to an $E_U[n^I]$ of the form $(U/2) \sum_{I,\sigma} \sum_i \lambda_i^{I,\sigma} (1-\lambda_i^{I,\sigma})$, where $\lambda_i^{I,\sigma}$ is simply the occupation of an orbital of type $i$, spin $\sigma$, on site $I$. In general, projector operators $P^I_{nm'}$ for the localized orbital manifold on site $I$ may be used to build the occupation matrix. The projection operators may be defined by any number of bases, but we use the atomic 3$d$ orbitals, which are encoded in the pseudopotential of the atom. It is particularly key to ensure that the atomic orbitals in the pseudopotential are normalized and the best possible approximation for the appropriate charge state and electron configuration of the molecule. An alternative approach is to utilize Wannier functions as the projection manifold, but these should be kept frozen when comparing different structures [11].

In order to explain why a Hubbard approach can be useful in describing the electronic structure of molecules, it is worthwhile to recall [5] that the LDA energy of an atom in contact with a reservoir of electrons will essentially behave parabolically as a function of electron occupation, with the minimum often situated at a fractional occupation number. The true energy of this model system is instead a statistically weighted, piecewise-linear function [12]. Therefore, the $+U$ term that is added back to an LDA functional may be regarded as the correction that offsets the unphysical curvature of the original LDA energy (see Fig. 1 in Ref. 5). This curvature can be calculated from first-principles theory as the second derivative of the energy with respect to occupations. It should be noted, though, that in addition to the unphysical curvature in energy of the fully screened, interacting system, there exists some nonlinear variation in the energy of the Kohn–Sham, noninteracting system due to rehybridization after a shift in occupation number. The effective curvature that one wants to extract and cancel out should be the difference between the screened, interacting $U$ and the bare, noninteracting one.

This viewpoint allows us to forego supercell constrained-density functional calculations [5,9], and to instead apply a linear response approach in order to straightforwardly calculate $U$. This technique is implemented in the open-source
electronic structure package, QUANTUM-ESPRESSO [13]. Using Janak’s theorem, we may equate the eigenvalue of state $i$ with the derivative of the energy with respect to the occupation of the state, to recast the second-derivative problem as a first-derivative, linear response property. Thus, the partial derivative of the energy of the state with occupation $q_I$ with respect to $q_I$ is $-\alpha_I$, and an analogous expression is true for the bare Kohn–Sham system. The second derivative of the energy with respect to occupations, therefore, is simply the derivative of the potential $\alpha_I$ with respect to occupations $q_I$. Such a change of variables is key because it is difficult to constrain occupations of the localized orbitals of a system. In order to further simplify the practical details of the calculation, a Legendre transform to the energy can be used to have as independent variables a potential $\alpha_I$ of the localized orbitals. The new energy expression can then be written as a function of $\alpha_I$:

$$E[\alpha_I] = \min_{n(r)} E[n(r)] + \sum_I \alpha_I n_I$$  \hspace{1cm} (14.4)

An analogous equation may be written for the bare system. A single potential shift takes the form $\Delta V = \sum_I \alpha_I P^I$, where $P^I$ are the projector operators, and thus affects each individual localized orbital. The linear response functions of this system with respect to a local perturbation $\Delta V$ are then

$$\chi_{IJ} = \frac{\partial^2 E}{\partial \alpha_I \partial \alpha_J} = \frac{\partial n_I}{\partial \alpha_J}$$

$$\chi^0_{IJ} = \frac{\partial^2 E^0}{\partial \alpha_I^0 \partial \alpha_J^0} = \frac{\partial n_I^0}{\partial \alpha_J^0}$$  \hspace{1cm} (14.5)

where $I$ and $J$ are neighboring sites containing localized orbitals or differing manifolds of localized orbitals on the same atomic site. Response functions are obtained by measuring the change in occupations from several small potential shifts to an already converged single point density, and the associated computational cost is negligible (see Fig. 14.1). The $U$ associated with a single site $I$ is then simply $U = \chi^{-1} - \chi^{-1}$. In this approach, special care should be taken in the inversion of the response functions. As response functions approach asymptotically small numbers, their inverses will diverge. The difference of the response functions, therefore, may appear to fall within a reasonable range ($U = 0 - 10$ eV), while the value is simply an artifact of the calculation. It is key to examine the magnitude of the response functions before inversion to ensure that the linear response values are not of the same order as the numerical noise of the calculation.

Normally, we consider only 3$d$ states in transition metals to be relevant for determining $U$, but the value of $U$ is strongly dependent on the mode of bonding. If, as is true in the case of transition metal hydrides, 4$s$–3$d$ hybridization is strong or 4$s$ orbitals dominate molecular bonding, then the response of this manifold is also relevant. In this case the response functions $\chi_0$ and $\chi$ should be expressed as matrices. These matrices are then inverted and their diagonal terms are subtracted to provide
Hubbard parameters, $U_{3d}$ and $U_{4s}$, appropriate to the respective manifolds. In solids, interaction and hybridization of $3d$--$4s$ is seldom relevant, but in molecules strong mixing, particularly of $3dz^2$ and $4s$ orbitals, often occurs.

While the linear response formulation has been shown to be quite useful, some careful considerations are in order to increase the reliability and accuracy of the results derived. In the solid state, LDA+$U$ often opens a gap in Mott insulators, which are predicted by LDA to be metals [5]. Analogously for molecules, LDA may predict the wrong ground-state spin and symmetry when compared to LDA+$U$. In either case, the LDA wavefunctions will differ greatly from those obtained using LDA+$U$, and we expect that the linear response of the LDA ground state will not work well to characterize the true LDA+$U$ system. We have proposed [7] an approach that overcomes this difficulty, and in which the Hubbard $U$ may be found in a fully self-consistent (referred to as $U_{\text{scf}}$) manner. To clarify our approach, we first identify in the GGA+$U$ functional the electronic terms that have quadratic dependence on the occupations, and express these as a function of a projection matrix that has been diagonalized:

$$E_{\text{quad}} = \frac{U_{\text{scf}}}{2} \sum_I \left[ \sum_i \lambda_i^I \left( \sum_j \lambda_j^I - 1 \right) \right] + \frac{U_{\text{in}}}{2} \sum_I \sum_i \lambda_i^I (1 - \lambda_i^I)$$  \hspace{1cm} (14.6)

The first term represents the contribution already contained in the standard GGA functional, modeled here as a double-counting term, while the second term is the customary $+U$ correction. Therefore, $U_{\text{scf}}$ represents the effective on-site electron–electron interaction already present in the GGA energy functional for the GGA+$U$ ground state when $U$ is chosen to be $U_{\text{in}}$. Consistency is enforced by choosing $U_{\text{in}}$ to be equal to $U_{\text{scf}}$.
The $U$ obtained from linear response [5] (labeled here $U_{\text{out}}$) is also obtained by differentiating Equation (14.6) with respect to $\lambda^I_T$:

$$U_{\text{out}} = \frac{d^2 E_{\text{quad}}}{d(\lambda^I_T)^2} = \frac{U_{\text{scf}}}{m} - \frac{U_{\text{in}}}{m} \quad (14.7)$$

where $m = 1/\sum_i (d_i^I)^2$ can be interpreted as an effective degeneracy of the orbitals whose population is changing during the perturbation (to linear order, $\delta \lambda^I_T = \alpha^I_T \delta \lambda^I_T$ with $\sum_i \alpha^I_i = 1$ and $d^2 / d(\lambda^I_T)^2 = \sum_{ij} d_i^I d_j^I \frac{d^2}{d\alpha^I_id\lambda^I_j}$). Even if in principle $U_{\text{scf}}$ depends on $U_{\text{in}}$, we find it to be constant over a broad interval, as apparent from Figure 14.2: $U_{\text{out}}$ is linear in $U_{\text{in}}$ for the relevant range of $U_{\text{in}} \sim U_{\text{scf}}$. Thus, from few linear response calculations for different $U_{\text{in}}$ ground states, we are able to extract the $U_{\text{scf}}$ that should be used. This approach is particularly useful for transition metal dimers, as illustrated in Figure 14.2. Otherwise, the effective difference between $U_0$ and $U_{\text{scf}}$ is often small and probably minimized by the constraints we employ. In fact, for molecular systems, we constrain the total spin of the system and enforce fixed occupations without a smearing or electronic temperature in most cases. We therefore calculate the value of $U$ for each spin and symmetry independently and average over the low-lying states. Generally, $U$ is highly dependent on both spin and symmetry as well as nuclear identity and configuration and should always be calculated for the state considered. On the other hand, when comparing energetics, a single, averaged value of $U$ must be applied to all systems, as will be discussed later for the low-lying states of the iron dimer and the addition–elimination reactions of methane and molecular hydrogen on FeO$^+$. We note that the apparent tendency of the LDA+$U$ functional to disproportionately favor integer occupations competes with the LDA or GGA tendency to favor fractional occupations. Under most conditions, the bonds may become slightly elongated with the addition of a $+U$ term, but energetics are
significantly improved. The over elongation is partially due to the fact that the projection manifold we choose is that of the isolated atomic orbitals.

14.2 RESULTS

Transition metal dimers and small clusters present a formidable challenge for both experimental and theoretical techniques. These systems are of fundamental importance in our understanding as both a model for dimetal enzyme active sites [1] and as the building blocks of nanoparticle catalysts that accelerate growth of nanotubes and nanowires [14]. We’ll first consider the iron dimer as a test case for our approach. For nearly 30 years the ground state of neutral Fe$_2$ has been identified as $^7\Delta_u (3d^{14} : o_g^2 \pi_u^4 \delta_g^3 \pi_g^2 \delta_u^2 \delta_{u*}^2, 4s^2 : o_u^2)$ (where subscripts $g$ and $u$ denote gerade and ungerade, respectively) in numerous theoretical studies [15–24] and some experimental studies [25,26]. However, the configuration and the structural and vibrational properties of this electronic state are not consistent with available experimental findings. Early density functional studies lacked accuracy in exchange correlation functional approximations, which may have overstabilized certain electronic states [17,19]. A tradeoff between basis set size and active space size in early configuration interaction studies limited the accuracy of the relative energetics for the hundreds of states of various spins and symmetries considered [22,23]. Despite the need to reconsider the discrepancy between experimental and theoretical findings since the late 1970s, even recent comprehensive studies of transition metal diatomic molecules [24,27] continue to assume the $^7\Delta_u$ assignment to be the correct one for the ground state of iron dimer. There have, however, been some more recent high-level quantum chemistry calculations—multireference configuration interaction (MRCI) [28] as well as large basis set, single-reference coupled cluster [CCSD(T)] calculations [29]—which provide evidence for a more consistent alternative ground state $^9\Sigma_g^-$ for the iron dimer. All of this prompted us to examine how GGA + $U$, a method already successful at improving calculations on correlated-electron transition metal solids, would describe the low-lying states of the iron dimer. A GGA + $U$ approach is particularly appealing because it can also be extended to much larger systems because it scales favorably in comparison to much more limited post-Hartree–Fock approaches.

While experimental results are far from complete, they have provided significant clues that help to limit the scope of potential electronic states for the low-lying states of the iron dimer. Several spin multiplicities are good candidates for the dimer; these include anything from an antiferromagnetically coupled singlet to a high-spin nonet. The large variety of states is due to the close spacing of the two lowest states of the neutral iron atom. The ground state of the Fe atom, $^3\Sigma$ (valence electrons: $3d^64s^2$), is experimentally only 0.87 eV lower in energy than the excited $^5\Sigma$ state with $3d^74s^1$ configuration. Additionally, the lowest triplet Fe state, $^3\Pi$ $3d^74s^1$, lies only 1.50 eV above the ground state. While states derived by unifying some combination of these three lowest symmetries are likely the best candidates for the lowest-lying states of the iron dimer, this still leaves a large number of possible electron configurations to
consider varying from $3d^{14}4s^2$ to $3d^{12}4s^4$ and with any number of spin multiplicities. Stern–Gerlach experiments have shown the dimer to have a relatively large magnetic moment, thus ruling out an antiferromagnetic state [30], and interpretations of Mössbauer hyperfine interactions confirm the likelihood of a high-spin state [31,32]. Experimental Mössbauer results also indicated a 4$s$ occupation per atom of 1.47 in the dimer by comparing isomer shift results with those for the iron atom, which has a known ground-state configuration of $3d^64s^2$ [33], but it is worth noting that $4s^3$ configurations have been largely overlooked in nearly all theoretical studies. Both the bond length and frequency have been measured experimentally in rare-gas (both Ne and Ar) matrices and found to be 2.02 Å and 300 cm$^{-1}$, respectively [34]. This low fundamental frequency suggests a fairly weak bond order, also in contradiction with the proposed $7\Delta_u$ state, which has been suggested to have a formal bond order of 3 [35].

The piece of experimental evidence that provides the most information about the relative energies of electronic states is the photoelectron spectrum of Fe$_2^-$. This spectrum is remarkably simple, with just two peaks corresponding to transitions to Fe$_2$ [26]. This simplicity is also in direct opposition to the myriad of low-lying iron dimer electronic states that have been studied theoretically [22,23]. Experimental photoelectron spectra typically access only the bound electronic states that differ from the anion, by a single electron detachment, and, in this case, the spectrum of Fe$_2^-$ displays two prominent peaks, one at 1.0 eV and the other 0.53 eV above the first peak. Structurally, the neutral states have identical properties within the error of the experiment ($r_e = 2.02 \pm 0.02$ and $\omega_e = 300 \pm 20$ cm$^{-1}$) and are more bound than the anion, which has a bond length of 2.10 ± 0.04 Å and a vibrational frequency of 250 ± 20 cm$^{-1}$, indicating an increase in bond order from the anion to the neutral dimer. By studying both the low-lying states of the anion and the corresponding allowed neutral states of the neutral dimer, a more recent MRCI study has identified an excitation scheme in which the lowest-lying anion state is $8\Sigma_u^-$ and the two neutral peaks correspond to $9\Sigma_g^-$ and $7\Sigma_g^-$, respectively. This MRCI study also finds the previously proposed neutral iron dimer ground state, $7\Delta_u$, to be 0.7 eV above the true ground state of the dimer. While both the alternative states $9\Sigma_g^-$ and $7\Sigma_g^-$ have been considered previously, less accurate methods found these states to be significantly excited with respect to $7\Delta_u$ [23,24,33].

In order to build a GGA and GGA+$U$ description of the states present in the experimental photoelectron spectrum, we identify the lowest-lying states of the anion as $8\Delta_g(3d^{14} : \sigma_{u}^{2}\pi_{u}^{4}\delta_{g}^{3}\pi_{g}^{s}2\delta_{u}^{2}\sigma_{u}^{s}4s^{3} : \sigma_{u}^{2}\sigma_{g}^{s})$ and $8\Sigma_u(3d^{13} : \sigma_{g}^{2}\pi_{u}^{4}\delta_{g}^{2}\pi_{g}^{s}2\delta_{u}^{2}\sigma_{u}^{s}4s^{4} : g^{2}\sigma_{u}^{2}2)$. While $8\Delta_g$ is the lowest anion state as determined with GGA by 0.52 eV, a self-consistent GGA+$U$ approach favors the $8\Sigma_u^-$ state by more than 0.38 eV. The difference in state splittings between the two methods is nearly an electronvolt, and the GGA+$U$ results are in much better agreement with the previous MRCI study. For all calculations, we obtain the Hubbard $U$ from the GGA ground state ($U_0$) as well as with a self-consistent approach ($U_{scf}$) and numerically average over all states and structures of interest, giving an overall $U_0$ of 2 eV and a $U_{scf}$ of 3 eV. Strictly speaking, the iron dimer has two independent iron sites within the formalism of GGA+$U$, and thus a $U$ for each iron atom should be determined by obtaining a $2 \times 2$ matrix for the linear
response of each iron site. In practice, the $U$ we calculate here (correctly) treats the iron atoms as identical sites, and $U$ is obtained from the total response of the 3$d$ electrons of both iron sites. The net difference in the contribution to $E_U$ between the case where the iron sites are treated separately ($U_{\text{sep}}$) versus the case where they are treated identically ($U_{\text{ident}}$) is negligible; that is, the $U$ calculated differs, where $U_{\text{sep}} = 2U_{\text{ident}}$, because the $U$ is related to the inverse of the derivative in occupations and in the latter case the derivative is twice as large as the former. However, this difference cancels with the expression for $E_U$ because there is only a single site with half the occupations in $U_{\text{ident}}$, while in the $U_{\text{sep}}$ case one sums over the two sites. The only significant difference in these approaches is that the practical implementation of a separate $U$ formalism tends to enhance convergence to broken-symmetry, antiferromagnetic states. As such states are, for the most part, not highly relevant at low energies for Fe$_2$, enforcing the identical nature of the iron states is more suitable here. Naturally, in other multisite molecules, if antiferromagnetic character or multiple valence is present, a separate $U$ scheme should always be employed.

Beginning with the GGA anion ground state $^8\Delta_g$, the two lowest neutral dimer states that differ by a single electron loss are $^7\Delta_u$ and $^9\Delta_g$, respectively. The $^7\Delta_u$ state $(3d^{14}: \sigma_g^2\pi_u^4 \delta_g^3 \pi_g^* \sigma_u^2, 4s^2 : \sigma_g^2)$ is produced through ionization of the spinup 4$s$ $\sigma_u$ molecular orbital. The $^9\Delta_g$ state $(3d^{13}: \sigma_g^2\pi_u^4 \delta_g^2 \pi_g^* \sigma_u^2, 4s^2 : \sigma_g^2 \sigma_u^2)$ is produced by the loss of the spindown 3$d$ $\sigma_g$ orbital and thus is expected to possess structural properties different from those of $^7\Delta_u$, which is inconsistent with experiments. The electronic configuration of these states is illustrated in Figure 14.3, and the calculated potential energy curves (see Fig. 14.4) of these states confirm the bond order analysis.

By using a Makov–Payne estimate [36] for the true, open-boundary conditions, total energy of our charged Fe$_2$/C$^{0-}$ system, we are able to estimate the energy required to ionize the $^8\Delta_g$ anion to the neutral state $^7\Delta_u$ to be 1.5 eV with the GGA approach. The GGA

![Figure 14.3](https://example.com/fig14.3.png) Two proposed excitation schemes for the two lowest neutral states derived from known lowest-lying anion states, $^8\Delta_g$ (left, GGA) and $^8\Sigma_u^-$ (right, GGA+$U$) by a single-electron ionization (indicated by arrows and associated orbitals).
ionization energy fails to agree with experiments, as does the splitting of the two lowest neutral states (0.40 eV). The hybrid functional, B3LYP, which is also a commonly employed exchange correlation functional, performs poorly in a manner similar to that of GGA. Even though B3LYP correctly identifies the neutral ground state, $^9\Sigma_g^-$, splittings between that state and the other neutral states as well as anion state splittings are too severely underestimated to provide any qualitative agreement with experiment (see Table 14.1). For GGA, the bond length of $^7\Delta_u$ is decreased ($r_e = 1.99 \text{ Å}$) by 0.21 Å with respect to $^8\Delta_g$ ($r_e = 2.20 \text{ Å}$), while the $^9\Delta_g$ state exhibits an increased bond length ($r_e = 2.26 \text{ Å}$) with respect to the anion. Not surprisingly, the trend in fundamental frequencies for these states also fails to fit the experimental picture, with the $^7\Delta_u$ frequency of 413 cm$^{-1}$ being markedly increased from the $\omega_e$ of 360 cm$^{-1}$ for the anion, while $^9\Delta_g$ has a reduced frequency of 285 cm$^{-1}$.

The GGA+$U$ approach provides a much more consistent prediction of the excitation scheme with respect to both experiment and the highly accurate

![FIGURE 14.4](http://www.stanford.edu/~hkulik) Potential energy curves for the proposed GGA ground-state anion $^8\Delta_g$ and the two related low-lying neutral states $^9\Delta_g$ and $^7\Delta_u$.

<table>
<thead>
<tr>
<th>State</th>
<th>B3LYP</th>
<th>GGA</th>
<th>$+ U_0$ (2 eV)</th>
<th>$+ U_{\text{rel}}$ (3 eV)</th>
<th>CCSD(T)</th>
<th>MRCI$^a$</th>
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<tr>
<td>$^8\Sigma_g^-$</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$^8\Delta_u$</td>
<td>0.14</td>
<td>$-0.52$</td>
<td>0.04</td>
<td>0.38</td>
<td>0.40</td>
<td>0.45</td>
</tr>
<tr>
<td>$^9\Sigma_g^-$</td>
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<tr>
<td>$^7\Sigma_g^-$</td>
<td>0.34</td>
<td>0.65</td>
<td>0.66</td>
<td>0.60</td>
<td>0.55</td>
<td>0.62</td>
</tr>
<tr>
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<td>$-0.12$</td>
<td>0.48</td>
<td>0.72</td>
<td>0.86</td>
<td>0.69</td>
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<tr>
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<td>0.28</td>
<td>0.36</td>
<td>0.41</td>
<td>0.38</td>
<td>0.45</td>
</tr>
</tbody>
</table>

$^a$ Data from Reference 28.
CCSD(T) [37] and MRCI results. Beginning with the GGA $+ U$ ground-state anion $^8\Sigma_u^-$ $(3d^{13} : \sigma^2_8 \pi_u^4 \delta^2_8 \rho^2_8 \delta^2_8 \sigma_u^2 4s^1 : \sigma^2_8 \delta_u^2)$, the two lowest states that differ from ionization of a single electron are $^9\Sigma_g^-$ and $^7\Sigma_g^-$, in accordance with previous findings in the MRCI study [28]. The two states have nearly identical valence electron configurations (both are $3d^{13}4s^3$) but differ simply by the spin of the $4s\sigma_u^*$ orbital ionized, spin down in the case of the nonet and spin up in the case of the septet as shown in Figure 14.3. Therefore, we may expect that both bond length and frequency of the two neutral states should be nearly identical to each other. The loss of the antibonding orbital suggests a decrease in bond length and increase in frequency with respect to the anion, consistent with experiment. To obtain the most accurate relative energetics of the three states, we use an average $U_{\text{scf}}$ of 3 eV that, we note, provides improved energetics with respect to $U_0$ from GGA, which is only 2 eV. The potential energy curves of this system, shown in Figure 14.5, are consistent with experiment. The ionization energy of the $^8\Sigma_u^-$ state is approximately 1.05 eV after inclusion of the Makov–Payne correction. The splitting of the two lowest neutral states is roughly 0.6 eV, in good agreement with the experimental splitting of 0.53 eV. The trend in structural properties is also consistent with experiment. The two neutral states exhibit nearly identical structural properties (see Table 14.2). The bond length $r_e$ is observed to decrease by 0.08 Å from the anion to the neutral states (from 2.20 to 2.12 Å), while the fundamental frequency is observed to increase by roughly 35 cm$^{-1}$. While the absolute values of the bond length and frequency are not identical to those obtained by experiment, we note that these discrepancies are likely due to (1) experimental uncertainty and (2) the anharmonic effects that cannot be fully eliminated in the experimental measurement of $\omega_0$ but are excluded in our theoretical measurement of the harmonic frequency.

**FIGURE 14.5** Potential energy curves for the proposed GGA $+ U$ ground-state anion $^8\Sigma_u^-$ and the two related low-lying neutral states, $^9\Sigma_g^-$ and $^7\Sigma_g^-$. 
One additional piece of experimental evidence worth considering is the bond strength or dissociation energy of the anion and neutral iron dimers. While the bond order appears to nominally increase from the anion to the neutral states, corresponding to a shorter bond length, the experimental bond strength decreases roughly from $1.53 \pm 0.17 \text{ eV}$ for the anion to $0.78 \text{ eV} \pm 0.17 \text{ eV}$ for the lowest neutral state. On first glance at Figure 14.5, it appears that the bond strength, roughly $1.5 \text{ eV}$ for the anion, is in agreement while the neutral state demonstrates a much higher bond strength of roughly $1.9 \text{ eV}$. However, we note that the GGA+$U$ anion state dissociates into a neutral $5^D$ Fe atom and a negatively charged $4^F$ Fe ion, both in their ground-state. The proposed dissociation for the lowest neutral state, $9\Sigma_g^-$, dissociates into a ground-state neutral $5^D$ Fe and an excited-state $5^F$ Fe. Once we incorporate the strong likelihood of an avoided crossing with a nonet state that has a dissociation limit of two $5^D$ neutral Fe atoms, we recover a bond strength of roughly $0.8 \text{ eV}$, in excellent agreement with experiment. Overall, our GGA+$U$ results are in remarkable agreement with both experiment and high-level quantum chemistry in the form of both single-reference CCSD(T) and multireference MRCI (see Tables 14.1 and 14.2). These calculations on the iron dimer demonstrate the potential of GGA+$U$ to systematically improve results obtained by commonly employed exchange correlation functionals and to help systematically predict and explain experimental spin-state orderings.

The gas-phase reactions of bare diatomic 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 metal-oxo catalytic systems [38]. These paradigmatic reactions have been studied by numerous mass spectrometric techniques in detail [38–41], but initial experimental results were surprisingly discordant with classical transition-state theories [39]. The reaction of FeO$^+$ with H$_2$ has been under particularly extensive study for some time now both theoretically [42–48] and experimentally [38,39,41,49] as the most fundamental example of the two-state reactivity paradigm. Additionally, the reaction of FeO$^+$ with CH$_4$ has been studied in detail, primarily with DFT [50–56] and, to a lesser extent, experiment [38,57–59]. Methane oxidation by reaction with FeO$^+$ is relevant because of methane’s greater

<table>
<thead>
<tr>
<th>State</th>
<th>GGA</th>
<th>GGA+$U_{scf}$</th>
<th>CCSD(T)</th>
<th>MRCI$^b$</th>
<th>Experiment$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8\Sigma_u^-$</td>
<td>2.20, 305</td>
<td>2.20, 301</td>
<td>2.24, 276</td>
<td>2.23, 272</td>
<td>2.1, 250</td>
</tr>
<tr>
<td>$8\Delta_g^-$</td>
<td>2.07, 360</td>
<td>2.08, 355</td>
<td>2.12, 321</td>
<td>2.4, —</td>
<td>—</td>
</tr>
<tr>
<td>$9\Sigma_g^-$</td>
<td>2.11, 339</td>
<td>2.13, 335</td>
<td>2.17, 296</td>
<td>2.18, 299</td>
<td>2.0, 300</td>
</tr>
<tr>
<td>$7\Sigma_u^-$</td>
<td>2.10, 335</td>
<td>2.12, 331</td>
<td>2.16, 304</td>
<td>2.17, 310</td>
<td>2.0, 300</td>
</tr>
<tr>
<td>$7\Delta_u$</td>
<td>1.99, 413</td>
<td>2.00, 419</td>
<td>2.00, 404</td>
<td>2.25, 195</td>
<td>—</td>
</tr>
<tr>
<td>$9\Delta_g$</td>
<td>2.26, 285</td>
<td>2.26, 280</td>
<td>2.28, 220</td>
<td>2.35, —</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$ Fundamental frequencies $\omega_0$.

$^b$ Data from Reference 28.

$^c$ Data from Reference 26.

---

**TABLE 14.2 Bond Lengths $r_e$ (Å) and Harmonic Frequencies $\omega_e$ (cm$^{-1}$), for Fe$_2^-$ and Fe$_2$, compared to Experiment$^a$**

<table>
<thead>
<tr>
<th>State</th>
<th>GGA</th>
<th>GGA+$U_{scf}$</th>
<th>CCSD(T)</th>
<th>MRCI$^b$</th>
<th>Experiment$^c$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2.24, 276</td>
<td>2.23, 272</td>
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</tr>
<tr>
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<td>2.07, 360</td>
<td>2.08, 355</td>
<td>2.12, 321</td>
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<td>2.28, 220</td>
<td>2.35, —</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$ Fundamental frequencies $\omega_0$.

$^b$ Data from Reference 28.

$^c$ Data from Reference 26.
utility as a fuel on conversion to methanol [60,61], as well as the relevance to enzymatic systems such as methane monoxygenase [2,62].

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 [39]. This inefficiency is particularly surprising because the same-spin nature of the ground-state reactant and product species, 6\(\Sigma^+\) FeO\(^+\) and 6D Fe\(^+\), make these reactions spin-allowed [43]. There is an observed decrease in rate constant with increasing energy or temperature for both reactions, which is also in direct contradiction with the expected Arrhenius-like behavior for a spin-allowed reaction [44]. The resulting reaction inefficiency was proposed to be due to the crossing of multiple relevant spin surfaces for the reactions [44,45], a feature now expected to be relevant in larger systems that include the enzyme horseradish peroxidase [63] and model non-heme inorganic iron alkane hydroxylation catalysts [64]. It has thus been proposed that the spin crossover from the steep sextet surface to a shallow but excited quartet spin state surface\(^1\) may be the true source of inefficiency. It has also been found that radical side products can form by dissociation of the reacting complex to FeOH\(^+\) and radical H or CH\(_3\), which are weakly endothermic or exothermic by roughly 3 kcal/mol, respectively. The relative exothermicity of the dissociated radical side reaction is key in interpreting and predicting branching ratios between the two types of reactions.

While theoretical considerations pointed to crossings between the sextet and quartet potential energy surfaces as the source for this reaction inefficiency [44,45], it is nevertheless notable that subsequent studies [41,44–47], which employed density functional techniques, have failed to agree with experimental results or highly accurate quantum chemistry calculations. While most implementations of DFT predict a qualitatively correct steeper sextet surface in accordance with an experimentally observed low-efficiency, exothermic reaction, the quartet surface is not predicted to be nearly shallow enough and quantitative barrier heights are incorrect. Common exchange correlation functionals incorrectly predict a quartet Fe\(^+\) product to be stabilized with respect to the sextet [44], and by using some rough estimates to correct this erroneous splitting, researchers have suggested that a correct qualitative picture of the spin crossover between quartet and sextet surfaces could be recovered at both the entrance and exit channels.

We review 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 introduced to improve semi-local or hybrid density functional descriptions of transition metal complexes [7]. We specifically consider the generalized-gradient approximation (GGA) in density functional theory (DFT) for its efficiency and widespread use in the community [10]; nevertheless, the Hubbard correction introduced here could be applied in conjunction with other exchange correlation approximations. First and foremost, we find that the GGA+\(U\) approach systematically improves the description of the electronic

\(^1\)We refer to the two species by their spin multiplicities, defined as 2S + 1, where S is the net spin of the molecule. \(\tfrac{5}{2}\) for the sextet and \(\tfrac{3}{2}\) for the quartet.
structure of FeO$^+$ in both spin states, but it also improves the electronic structure description of intermediates that perturb the underlying diatomic molecule’s electronic structure to varying degrees throughout the reaction coordinate. In order to gauge the success of our approach on both of these reactions, we compare DFT+$U$ (GGA+$U$) results with both standard GGA results and highly accurate quantum chemistry approaches. Post-Hartree–Fock (post-HF) techniques are able to recover nearly all of the correlation energy and may be used as an accurate benchmark or reference for the DFT calculations, but these approaches suffer from poor scaling, which limits them to very small sizes such as the reactions under consideration here (i.e., no more than 10 atoms). The reaction of FeO$^+$ with molecular hydrogen is compared against CCSD(T) results [37], while the reaction with methane is compared against MRCI results [65].

The value of $U$ calculated for each intermediate and transition state for the reactions with both hydrogen and methane provides a means for identifying the broad similarities between the two cases. 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 deviations in $U_{\text{scf}}$ at any stationary point from the global average. The overall $U_{\text{scf, av}}$ that 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 transition states are as large as 1.5 eV, as is in the case of $^6$TS-2CH$_4$. For most single points in these two reactions, the individual $U_{\text{scf}}$ values are within 1 eV of the $U_{\text{scf, av}}$. In typical cases (e.g., intermediate splittings and sextet barriers), employing GGA+$U$ with a global, average value of $U_{\text{scf, av}}$ that is in a range 1 eV too small or too large for the structure considered yields energy differences in the range of 0.01–0.1 eV; this uncertainty can, in many cases, be decreased by examining splittings using a $U_{\text{scf}}$ averaged “locally” on the two intermediates and the transition state of interest.

The addition–elimination reactions of hydrogen and methane with FeO$^+$ share common intermediate and transition state structures. Namely, at the entrance channel, molecular hydrogen or methane weakly binds to the iron center (Int-1), and abstraction of a hydrogen from molecular hydrogen or methane to be shared over the iron–oxo bond (TS-1) is the first reaction step. Following the bond-breaking event, a second intermediate (Int-2) is stabilized in which one hydrogen is bound solely to the oxygen while the remainder of the reactant complex is still bound to the iron atom. The second reaction step involves the transfer of the reactants from the iron center to the oxygen over the iron–oxo bond (TS-2), which ultimately facilitates the formation of a radical–reactant complex bond with oxygen as well. On completion of the transfer of the reactants to oxygen, the newly formed water or methanol molecule is weakly bound to the cationic iron center (Int-3) and may subsequently dissociate to products. While the ground state of the intermediates is generally a sextet, shallower quartet surfaces make the quartet reaction barriers and transition states highly relevant.
The similarities of the values of $U$ for the hydrogen and methane reactions 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 eV) at the entrance channel, where the iron center is weakly three- or two-fold coordinated in the Int-1 structure. At the first reaction 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 $3d^64s^1$-like sextet’s two minority spin electrons are equally divided between the $3d$ and $4s$ manifolds, and this results in an increased prominence of the $U_{\text{scf},4s}$ for $^6$TS-2$_{\text{H}_2}$ and an overall lower $U_{\text{scf},3d}$ of $\sim$3–4 eV for both reactions. While the extension to include $4s$ 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 $3d$- and $4s$-derived molecular states are close in energy. The sextet transition state, especially in the methane case, is quite weakly bound, but the quartet transition state, which has a $3d^7$ character, is more tightly bound and the $U_{\text{scf}}$ of $^4$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. Consequently, the Fe$^+$ charge density is increasingly atom-like, 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). Since these two reactions involve unsaturated metal centers for which the number and character of metal–ligand bonds change across various spin states, they provide a far more challenging probe of the robustness of our method compared to more typical problems that involve saturated metals or fewer changes in metal–ligand bonding.

In addition to being system-dependent, the value of the self-consistent, linear response $U$ is dependent on the definition of the projection manifold. It is evident that the value of $U$ should vary if a different qualitative form of projection is used such as atomic orbitals versus maximally localized Wannier functions. However, we show here that differences in pseudopotentials can affect the value of Hubbard $U$, and, to a lesser extent, the calculated properties of a transition metal molecule. In practice, we shall show 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. As a key example relevant to results for the addition–elimination reactions, we provide here comparison of FeO$^+$ sextet and quartet-state properties calculated using pseudopotentials generated in various oxidation states. The pseudopotentials generated in the Fe$^{2+}$ ($d^{5.5}s^{0.5}$), Fe$^{0.5+}$ ($d^{6.5}s^{1.0}$), and Fe($d^{6}s^{2}$, used throughout) states had values of $U_{\text{scf}}$ of 7.0, 4.9, and 5.5 eV, respectively. As the electronic configuration of FeO$^+$ states is either $d^6s^1$ or $d^7s^0$, it is reasonable that the second pseudopotential produces the lowest value of $U$. 

**RESULTS**

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In comparing LDA + U or GGA + U calculations of different pseudopotentials, total energies are not 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 14.3). While the harmonic frequencies for $^4\Phi$ and $^6\Sigma^+$ 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 ($d^{5.5}s^{0.5}$) yields the shortest GGA value with $^4\Phi$ and $^6\Sigma^+$ at 1.52 and 1.59 Å, respectively, while the other two pseudopotentials yield bond lengths within 0.01 Å of each other. The GGA spin splittings are quite close at 0.82 and 0.84 eV for the Fe$^{0.5+}$ and Fe pseudopotentials, respectively, while the more ionic Fe$^{2+}$ is 0.76 eV. On augmentation of a Hubbard term using the $U_{scf}$ appropriate to each respective pseudopotential, the bond lengths of all three pseudopotentials are brought into agreement with each other within 0.01 Å, the harmonic frequencies agree within 6–7 cm$^{-1}$, and the spin splittings for all three pseudopotentials agree within 0.04 eV. Overall, a much smaller spread in values is observed for GGA + U than for GGA (see Table 14.3). Even a pseudopotential whose reference state is very different from the one considered seems to remedy itself so long as the proper value of $U_{scf}$, is used. These observations demonstrate, nevertheless, that while careful pseudopotential selection is not mandatory; the best pseudopotential choice is one that clearly reflects the oxidation states and charges of the physical system of interest.

Looking at the details of the addition–elimination reaction of molecular hydrogen on FeO$^+$, we see that the GGA + U reaction coordinate provides a substantial, systematic improvement over GGA when compared against experimental or highly accurate CCSD(T) reference calculations. The GGA potential energy surface (see Figs. 14.6 and 14.7) is in direct contradiction to available experimental evidence and theory because it (1) underestimates the exothermicity by over 1 eV, (2) the quartet

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**TABLE 14.3 Comparison for Several Pseudopotentials of Structural Properties Including Equilibrium Bond Length \(r_e(\text{Å})\), Harmonic Frequency \(\omega_e(\text{cm}^{-1})\), and State Splittings (in eV) of the \(^6\Sigma^+\) and \(^4\Phi\) States of FeO$^+$**

<table>
<thead>
<tr>
<th>Pseudopotential</th>
<th>(^6\Sigma^+) (r_e(\text{Å})), (\omega_e(\text{cm}^{-1}))</th>
<th>(^4\Phi) (r_e(\text{Å})), (\omega_e(\text{cm}^{-1}))</th>
<th>(\Delta E_{6\rightarrow4}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA (U = 0) eV</td>
<td>Fe$^{2+}$ ((d^{5.5}s^{0.5}))</td>
<td>Fe$^{0.5+}$ ((d^{5.5}s^1))</td>
<td>Fe ((d^6s^2))</td>
</tr>
<tr>
<td>$^6\Sigma^+$ (r_e(\text{Å})), (\omega_e(\text{cm}^{-1}))</td>
<td>1.59, 902</td>
<td>1.63, 906</td>
<td>1.62, 901</td>
</tr>
<tr>
<td>$^4\Phi$ (r_e(\text{Å})), (\omega_e(\text{cm}^{-1}))</td>
<td>1.52, 1033</td>
<td>1.57, 1040</td>
<td>1.56, 1038</td>
</tr>
<tr>
<td>(\Delta E_{6\rightarrow4}) (eV)</td>
<td>0.76</td>
<td>0.82</td>
<td>0.84</td>
</tr>
<tr>
<td>GGA + (U_{scf}) (eV)</td>
<td><strong>7.0</strong></td>
<td><strong>4.9</strong></td>
<td><strong>5.5</strong></td>
</tr>
<tr>
<td>$^6\Sigma^+$ (r_e(\text{Å})), (\omega_e(\text{cm}^{-1}))</td>
<td>1.65, 745</td>
<td>1.66, 751</td>
<td>1.66, 749</td>
</tr>
<tr>
<td>$^4\Phi$ (r_e(\text{Å})), (\omega_e(\text{cm}^{-1}))</td>
<td>1.76, 606</td>
<td>1.75, 613</td>
<td>1.75, 612</td>
</tr>
<tr>
<td>(\Delta E_{6\rightarrow4}) (eV)</td>
<td>0.50</td>
<td>0.52</td>
<td>0.54</td>
</tr>
</tbody>
</table>

*aThe GGA + \(U\) results are obtained at the respective \(U_{scf}\) of each pseudopotential.*

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2This also means that great caution should be taken in comparing band gap values for different values of \(U\), since the same arbitrary shift in energy affects eigenvalues.
surface is too steep to allow for a “shallow, barrierless” reaction \[39,45\], (3) spin splittings at intermediates show large errors, and (4) there is no spin crossover at the exit channel. The majority of these errors in the GGA reaction coordinate are localized to the second reaction barrier (see Fig. 14.7), with the exception of the errors

The potential energy surfaces calculated with different methods have been aligned at the $^6\text{Int-1}$ states. The curves associated with GGA and GGA + U reaction coordinates are interpolations of the points obtained for the minimum-energy path as determined by NEB calculations.
in the quartet Int-1 structures and barriers in the first barrier surface (see Fig. 14.6). 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 \( U \) (where \( U = 5 \) eV) reaction coordinate (see Figs. 14.6 and 14.7) correctly estimates and predicts the reaction exothermicity, the shallow but excited quartet surface, barrier heights, and spin crossover at the exit channel (see Fig. 14.7). Systematic improvements on GGA \( U_{\text{scf,av}} \) results in which \( U \) deviates locally from \( U_{\text{scf,av}} \) (e.g., at the hydrogen \( ^6\text{TS-2} \) 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. 14.6), 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. 14.7) are greatly improved upon.

In order to further measure the quantitative accuracy of the hydrogen addition–elimination reaction, we estimated equilibrium CCSD(T) geometries for each intermediate and compared against the GGA and GGA \( U \) relaxed structures.\(^4\) We also averaged the error of the GGA \( U \) and GGA splittings for each intermediate with respect to the CCSD(T) splittings for that intermediate. The average error for the five spin splittings along the reaction coordinate is 0.04 eV in GGA \( U \), to be compared with GGA, which exhibits an average error of 0.20 eV, or B3LYP that performs even more poorly with an average error of 0.30 eV in the splittings. Not only does GGA \( U \) improve errors by fivefold over GGA, but using the CCSD(T) equilibrium 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 only slightly worse than B3LYP geometries (average error of 1.3 pm). Although B3LYP shows a slight improvement in geometries, we consider the sevenfold improvement in spin splittings of GGA \( U \) to be much more key. The difference in errors between B3LYP and GGA \( U \) geometries could be attributed largely to systematic \(~1\)-pm errors in bonds between H and the other atoms, Fe and O, which are present in GGA and GGA \( U \) but not in B3LYP.

The GGA description of FeO\(^+\) on methane demonstrates even greater discordance with theoretical considerations and known experimental results. In fact, using GGA, both the reactions to create methanol and to form radical side products turn out to be endothermic by 0.2 and 0.4 eV, respectively (see Fig. 14.8). 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 consider the GGA \( U \) results and compare them to highly accurate MRCI calculations, we observe quantitative agreement between the two methods (see Fig. 14.9). The GGA \( U \) quartet surface is shallower but not barrierless, in agreement with MRCI results.

\(^4\)We note that we obtained CCSD(T) barrier height estimates by calculating single-point energies of GGA and GGA \( U \) TS structures at the CCSD(T) level.
We see in our calculations an improved estimate of exothermicity of both main and side reactions, the spin crossover at the exit channel is now preserved, and the description of the quartet Int-1 geometry is also improved. A comparison of the accuracy of GGA+$U$ geometries with MRCI is beyond the scope of this study because of 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 extracting the exothermicity for each reaction step and multiplicity, as summarized in Table 14.4. 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 quantum chemistry. The largest errors, such as the 0.30–0.32 eV

![Figure 14.8](image1)

**FIGURE 14.8** Comparison of GGA (blue) and MRCI (black) reaction coordinates for quartet (dashed) and sextet (solid) surfaces of the reaction of FeO$^+$ with CH$_4$.

![Figure 14.9](image2)

**FIGURE 14.9** Comparison of GGA+$U$ ($U=5$ eV) (blue) and MRCI (black) reaction coordinates for quartet (dashed) and sextet (solid) surfaces of the reaction of FeO$^+$ with CH$_4$. 
underestimate at the sextet TS-2H\textsubscript{2} barrier, can be systematically improved by extensions that include either a \textit{U}\textsubscript{4s} or a locally averaged \textit{U}\textsubscript{scf}.

### 14.3 CONCLUSIONS

Using the GGA approximation, we find that activation barriers, stationary-point spin splittings, and reaction energies exhibit errors as large a 1.4 eV for both the methane and the hydrogen systems discussed. By augmenting the GGA exchange correlation functional with a Hubbard correction, these errors are reduced by an order of magnitude, to 0.1 eV on average with respect to the best available quantum chemical methods [such as CCSD(T) and MRCI] as well as experimental values. We stress that the Hubbard term is not used as a fitting parameter, but it is a true first-principles linear response property of the transition metal complex that can augment any exchange correlation density functional. The practical limitations to this approach stem from the complexity of the systems studied; evolution of the coordination environment along a global reaction coordinate may result in local deviations from a globally averaged Hubbard \textit{U} or bring to the forefront the role of \textit{4s} contributions.

Overall, the DFT + \textit{U} results (here, GGA + \textit{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 \textit{U} calculation also acts as a probe for the relative importance of the DFT + \textit{U} approach for a given transition metal complex; that is, if the Hubbard \textit{U} calculated is small or nearly zero, a standard description is sufficient. We believe that this approach paves the way for large-scale simulations of systems that contain transition metal complexes with both accuracy and efficiency.

As an example, in Figure 14.10 we show the results of GGA + \textit{U} calculations on self-assembled monolayers of tetrabromophenyl porphyrins with cobalt metal centers (TBrPP-Co), which form on the (111) surface of copper [66,67]. The unit cell, which consists of the porphyrin and two layers of a Cu slab, has a total of 177 atoms (77 from the molecule, 100 from the copper slab) and 1357 electrons (257 from the molecule, 1100 from the copper). Spin-polarized calculations using either the GGA or the GGA + \textit{U} approach are of comparable cost and were carried out in about 24 h on six

<table>
<thead>
<tr>
<th>Method</th>
<th>CH\textsubscript{4} TS−1\textsuperscript{4}</th>
<th>H\textsubscript{2} TS−1\textsuperscript{4}</th>
<th>CH\textsubscript{4} TS−1\textsuperscript{6}</th>
<th>H\textsubscript{2} TS−1\textsuperscript{6}</th>
<th>CH\textsubscript{4} TS−2\textsuperscript{4}</th>
<th>H\textsubscript{2} TS−2\textsuperscript{4}</th>
<th>CH\textsubscript{4} TS−2\textsuperscript{6}</th>
<th>H\textsubscript{2} TS−2\textsuperscript{6}</th>
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</thead>
<tbody>
<tr>
<td>GGA</td>
<td>−1.14</td>
<td>−1.04</td>
<td>−0.54</td>
<td>−0.59</td>
<td>0.46</td>
<td>−0.92</td>
<td>0.61</td>
<td>−0.79</td>
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<tr>
<td>GGA + \textit{U}</td>
<td>−1.07</td>
<td>−1.42</td>
<td>−0.71</td>
<td>−1.05</td>
<td>−0.84</td>
<td>−2.02</td>
<td>−0.87</td>
<td>−2.19</td>
</tr>
<tr>
<td>Post-HF</td>
<td>−0.99</td>
<td>−1.35</td>
<td>−0.75</td>
<td>−0.96</td>
<td>−0.87</td>
<td>−1.82</td>
<td>−0.80</td>
<td>−1.87</td>
</tr>
</tbody>
</table>
Intel Core2 2.4 GHz CPUs. These GGA + U calculations show enhanced predictive accuracy over GGA and successfully identify a spin density induced throughout the molecule fully consistent with experimental results, which is not observed in GGA.

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REFERENCES