Density Functional Theory in Transition-Metal Chemistry: A Self-Consistent Hubbard U Approach

Heather J. Kulik, Matteo Cococcioni, Damian A. Scherlis,* and Nicola Marzari
Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
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Transition-metal centers are the active sites for a broad variety of biological and inorganic chemical reactions. Notwithstanding this central importance, density-functional theory calculations based on generalized-gradient approximations often fail to describe energetics, multiplet structures, reaction barriers, and geometries around the active sites. We suggest here an alternative approach, derived from the Hubbard U correction to solid-state problems, that provides an excellent agreement with correlated-electron quantum chemistry calculations in test cases that range from the ground state of Fe₂⁺ and Fe₂⁻ to the addition elimination of molecular hydrogen on FeO⁺. The Hubbard U is determined with a novel self-consistent procedure based on a linear-response approach.

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Transition metals are central to our understanding of many fundamental reactions, as active sites in naturally existing or synthetic molecules that range from metalloporphyrins and oxidoreductases [1] to alkene metathesis catalysts [2] to light-harvesting photosynthetic complexes [3]. Despite this relevance, most electronic-structure approaches fail to describe consistently or accurately transition-metal centers. Examples include neutral and charged iron dimers [4], FeO⁺ [5], Mn(salen) epoxidation catalysts [6], or hemeproteins [7].

In this Letter, we argue that generalized-gradient approximations (GGA) [8] augmented by a Hubbard U term [9], already very successful in the solid state [10,11], also greatly improve single-site or few-site energies, thanks to a more accurate description of self- and intra-atomic interactions. Nevertheless, U is not a fitting parameter, but an intrinsic response property: as shown by Cococcioni and de Gironcoli [12], U measures the spurious curvature of the GGA energy functional as a function of occupations, and GGA + U largely recovers the piecewise-linear behavior of the exact ground-state energy. U is determined by the difference between the screened and bare second derivative of the energy with respect to on-site occupations \( \lambda_i^f = \sum_j \lambda_i^f (i \text{ is the spin orbital, and } I \text{ the atomic site}) [12] \). While in the original derivation U was calculated from the GGA ground state, we argue here that U should be consistently obtained from the GGA + U ground state itself. This becomes especially relevant when GGA and GGA + U differ qualitatively (metal versus insulator in the solid state, different symmetry in a molecule). To clarify our approach, we first identify in the GGA + U functional the electronic terms that have quadratic dependence on the occupations:

\[
E_{\text{quad}} = \frac{U_{\text{scf}}}{2} \sum_I \left[ \sum_i \lambda_i^f \left( \sum_j \lambda_j^f - 1 \right) \right] + \frac{U_{\text{in}}}{2} \sum_I \sum_j \lambda_j^f (1 - \lambda_j^f) \tag{1}
\]

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 second derivative with respect to \( \lambda_i^f \) of our model for e-e interactions in Eq. (1) also corresponds to the \( U_{\text{out}} \) obtained from linear-response [12]:

\[
U_{\text{out}} = \frac{d^2 E_{\text{quad}}}{d(\lambda_i^f)^2} = U_{\text{scf}} - \frac{U_{\text{in}}}{m}, \tag{2}
\]

where \( m = 1/\sum_i (a_i^f)^2 \) can be interpreted as an effective degeneracy of the orbitals whose population is changing during the perturbation (to linear order, \( \delta \lambda_i^f = a_i^f \delta \lambda^f \) with \( \sum_i a_i^f = 1 \) and \( \frac{d^2 E}{d(\lambda_i^f)^2} = \sum_i a_i^f \left( \frac{d^2 E}{d\lambda_i^f} \right) \)). 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 Fig. 1: \( U_{\text{out}} \) is linear in \( U_{\text{in}} \) for the relevant range of \( U_{\text{in}} \). Thus, from few linear-

\[ U_{\text{in}} = 2.4 \]

\[ U_{\text{scf}} = 3.1 \]

\[ U_0 = 2.4 \]

FIG. 1 (color online). Linear response \( U_{\text{out}} \) calculated from the GGA + \( U_{\text{in}} \) ground state of \( ^7\Delta_g \) Fe₂, together with the extrapolated \( U_{\text{scf}} \). \( U_0 \) is \( U_{\text{out}} \) calculated for \( U_{\text{in}} = 0 \).
response calculations for different $U_{\text{in}}$ ground states we are able to extract the $U_{\text{scf}}$ that should be used.

We employ this formulation in the study of the Fe$_2^-$ and Fe$_2^+$ dimers and the addition-elimination reaction of molecular hydrogen on FeO$^+$; these are paradigmatic cases of the challenges for first principles methods to accurately reproduce the many low-lying multiplet potential energy surfaces associated with transition metals. It has been argued that spin density-functional theory can describe the lowest-lying state of a given spatial and spin symmetry [13,14], but difficulties remain in obtaining accurate multiplet splittings [15]. Our GGA or GGA + $U$ calculations have been performed with QUANTUM-ESPRESSO [16]; coupled cluster [CCSD(T)] and B3LYP calculations have been performed with Gaussian03 [17].

The iron dimer has been investigated both theoretically [4,18–20] and experimentally [21–23]. The experimental photoelectron spectrum of Fe$_2^-$ below 2 eV is remarkably simple—there are only two prominent peaks, one at 1.0 eV and a second peak 0.53 eV above it, corresponding to two allowed transitions to different neutral Fe$_2$ states [22]. A recent multiplicity configuration-interaction (MRCI) study [19] has assigned the three experimental electronic states to $^8\Sigma_g^-$ for Fe$_2^-$ and $^9\Sigma_g^-$ and $^7\Sigma_g^+$ for Fe$_2^+$; more recently, CCSD(T) has been shown to be in overall agreement [20]. Importantly, these electronic states are consistent with the experimental measurements for the anion (fundamental frequency $\omega_0 = 250 \pm 20$ cm$^{-1}$ and bond length $R_e = 2.10 \pm 0.04$ Å), and the two neutral Fe$_2$ states, which display similar properties ($\omega_0 = 300 \pm 15$ cm$^{-1}$ and $R_e = 2.02 \pm 0.02$ Å) [22].

We first apply our approach to Fe$_2^-$ and Fe$_2^+$. We obtain a $U_0$ of 2 eV (i.e., when calculated from the GGA ground state) and a $U_{\text{scf}}$ of 3 eV (since energies at different $U$ are not directly comparable, we average $U_0$ and $U_{\text{scf}}$ over all states). GGA + $U_{\text{scf}}$ shows a striking and consistent agreement with MRCI [19] and our CCSD(T) results, correctly identifying both the lowest anion state $^8\Sigma_g^-$ (3$d^{13}$: $\sigma_g^2\pi_u^2\delta_g^2\delta_u^*\pi_u^*$) and the first excited state, $^8\Delta_g$, 0.38 eV above. The lowest, singly ionized neutral state, which differ from Fe$_2^-$ only by the loss of the spin-down or spin-up $\sigma_u^*(4s)$ orbital, are $^9\Sigma_g^- + ^7\Sigma_g^+$. The $^9\Sigma_g^- + ^7\Sigma_g^+$ GGA + $U_{\text{scf}}$ splitting of 0.6 eV compares very well with theoretical [MRCI and CCSD(T)] and experimental (0.53 eV) results in Table I. The structure of these two states (see Table II) is also consistent with experimentally observed close similarity of $R_e$ and $\omega_0$ for the two neutral states and the modest decrease in $R_e$ (0.08 Å) and increase in $\omega_0$ (~50 cm$^{-1}$) with respect to Fe$_2^+$ [24].

In stark contrast with MRCI, CCSD(T) and GGA + $U_{\text{scf}}$, GGA favors the $^8\Delta_g$ Fe$_2^-$ state (3$d^{14}$: $\pi_u^2\delta_u^2\pi_g^*\sigma_u^*\sigma_u^*$, $4s^3$: $\pi_u^2\sigma_u^*$) by as much as 0.9 eV relative to other methods. Neutral states arising from single ionization of the $^8\Delta_g$ state are $^7\Delta_u$ (3$d^{14}4s^3$) and $^9\Delta_g$ (3$d^{13}4s^3$) which result from the loss of $\sigma_u^*(4s)$ and $\sigma_g^*(3d)$ electrons, respectively. In addition, these two states have differing bond lengths ($R_e$ of 1.99 and 2.26 Å) and frequencies ($\omega_e$ of 413 cm$^{-1}$ and 285 cm$^{-1}$), and thus are not compatible with experiment [4,22].

Our second test case explores the potential energy surfaces of the highly exothermic ($\Delta H < -1.6$ eV) addition-elimination reaction of molecular hydrogen on bare FeO$^+$. This spin-allowed reaction occurs with exceedingly low efficiency (1 in every 100–1000 gas-phase collisions results in products), yet when it does proceed it is observed to be barrierless [25–27]. This apparent contradiction has been explained by a two-state-reactivity model [5,28,29], wherein the steep reaction barriers along the spin surface of the reactants and products (sextets in both cases) preclude an efficient, exothermic reaction. Instead, the reaction must occur along a shallow but excited spin surface (here, the quartet), and the reaction bottleneck is the coupling of the two surfaces which permits the necessary spin-inversion at the entrance and exit channels. For several exchange-correlation functionals (including B3LYP) [5,29], the reaction coordinates have failed to agree qualitatively with experiments [25–27], higher level correlated-electron calculations [28,30], or with the established paradigm of a two-state model [29].

For the bare FeO$^+$ reactant, GGA predicts a $^6\Sigma^+$ ground state and two nearly degenerate low-lying quartet states, $^4\Delta$ and $^4\Phi$, 0.84 eV above. GGA + $U_{\text{scf}}$ (5.5 eV) preferentially stabilizes $^4\Phi$ FeO$^+$ and yields a $^6\Sigma^+ \rightarrow ^4\Phi$ split-

### Table I. Multiplet splittings (in eV) for Fe$_2^-$ (first two lines) and Fe$_2^+$ at several levels of theory.

<table>
<thead>
<tr>
<th>State</th>
<th>B3LYP</th>
<th>GGA</th>
<th>$+U_0$ (2 eV)</th>
<th>$+U_{\text{scf}}$ (3 eV)</th>
<th>CCSD(T)</th>
<th>MRCI$^a$</th>
</tr>
</thead>
<tbody>
<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>$^8\Delta_g^-$</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>
<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>$^7\Sigma_g^+$</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>
<td>$^7\Delta_u^-$</td>
<td>0.18</td>
<td>-0.12</td>
<td>0.48</td>
<td>0.72</td>
<td>0.86</td>
<td>0.69</td>
</tr>
<tr>
<td>$^9\Sigma_g^+$</td>
<td>0.36</td>
<td>0.28</td>
<td>0.36</td>
<td>0.41</td>
<td>0.38</td>
<td>0.45</td>
</tr>
</tbody>
</table>

$^a$Reference [19].

### Table II. Bond lengths (Å) and harmonic frequencies, $\omega_e$ (cm$^{-1}$), for Fe$_2^-$ (first two lines) and Fe$_2^+$, compared to experiment (here, fundamental frequencies, $\omega_0$).

<table>
<thead>
<tr>
<th>State</th>
<th>GGA</th>
<th>$+U_{\text{scf}}$</th>
<th>CCSD(T)</th>
<th>MRCI$^a$</th>
<th>Experiment$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^8\Sigma_g^-$</td>
<td>2.20</td>
<td>2.20, 305</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</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</td>
<td>2.13, 335</td>
<td>2.17, 296</td>
<td>2.18, 299</td>
<td>2.0, 300</td>
</tr>
<tr>
<td>$^7\Sigma_g^+$</td>
<td>2.10</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</td>
<td>2.00, 419</td>
<td>2.00, 404</td>
<td>2.25, 195</td>
<td>-</td>
</tr>
<tr>
<td>$^9\Sigma_g^+$</td>
<td>2.26</td>
<td>2.28, 280</td>
<td>2.28, 220</td>
<td>2.35</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$Reference [19].

$^b$Reference [22].
states possess a U while dashed indicates quartet. Solid indicates sextet U 5 eV, very close to the average of the CCSD(T) states also possess consistent orbital occupations and symmetry. We thus proceed to study the full sextet and quartet potential energy surfaces (PES) for this reaction. We stress that, as is commonly found for open-shell transition-metal molecules, several low-lying PES exist for each multiplicity and we present results for the lowest-lying symmetry of each multiplicity. The U applied in this global PES is 5 eV, very close to the average of the U (4.93 eV) calculated for the quartet (5.02 eV) and sextet (4.84 eV) at each stationary point; the values of U are similar (quartet = 4.71 eV; sextet = 4.76 eV). Although most states possess a U close to the global average, the few deviations will be highlighted later.

Our GGA results for the intermediates (Int) and transition states (TS) along the reaction coordinate confirm the previously noted failures. Aside from the overestimate of FeO splitting, the most notable deviations are unusually steep barriers (0.54 eV) along the quartet surface, lack of spin-crossing near the products, and a dramatic underestimate in the exothermicity, as depicted in Fig. 2 [31].

With GGA + U (5 eV), we obtain consistency with CCSD(T), as shown in Fig. 3. The reactant FeO splitting is reduced, the splitting at Int-1 increases, corresponding to a shallow quartet reaction coordinate, and the exothermicity and spin crossover near the products are in good agreement with experiment and theoretical paradigm [5]. The quantitative accuracy of GGA + U becomes fully evident in the intermediate splittings (Table IV), forward and backreaction barriers (Table V), and overall mean absolute errors (MAE) in multiplet splittings that are reduced [with respect to CCSD(T) reference] from 0.20 eV for GGA to 0.04 eV for GGA + U. Geometries are also improved: the MAE for bond lengths are reduced from 4.3 pm (GGA) to 2.2 pm (GGA + U) [32]. The GGA + U and CCSD(T) states also possess consistent orbital occupations and symmetry.

The few examples of U deviating from 5 eV are primarily at the exit channel, where large changes in hybridization occur. The quartet Int-3 is the only case for which we obtain a low U (2 eV) which originates from the reduced hybridization of Fe 3d states. We chose to recalculate the splitting with a U that was a local average on the Int-3 states. With this U of 3.5 eV, we obtain a splitting of 0.12 eV, in even closer agreement with CCSD(T). While this reduced hybridization of the 3d states is unusual, we stress that it is consistently predicted in our linear-response approach. Along the sextet surface, the iron valence occupations correspond to 3dx, and we find that the interplay of 3d and 4s states to be critical for describing the second barrier along the sextet reaction.

<table>
<thead>
<tr>
<th>Method</th>
<th>6FeO⁺</th>
<th>⁴FeO⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA</td>
<td>1.62</td>
<td>901</td>
</tr>
<tr>
<td>GGA + U</td>
<td>1.66</td>
<td>749</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>1.66</td>
<td>724</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Relative Energy (eV)</th>
<th>Int-3; av</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA</td>
<td>5.02</td>
</tr>
<tr>
<td>GGA + U</td>
<td>4.84</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ΔE₆→₄</th>
<th>GGA</th>
<th>GGA + U</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO⁺</td>
<td>0.84</td>
<td>0.54</td>
<td>0.57</td>
</tr>
<tr>
<td>Int-1</td>
<td>0.20</td>
<td>0.38</td>
<td>0.43</td>
</tr>
<tr>
<td>Int-2</td>
<td>-0.05</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>Int-3</td>
<td>-0.09</td>
<td>0.19(0.12)</td>
<td>0.09</td>
</tr>
<tr>
<td>Fe⁺</td>
<td>0.25</td>
<td>0.22</td>
<td>0.18</td>
</tr>
</tbody>
</table>
surface. A matrix extension of our formalism [12] considers also the response of the 4s orbitals, and we obtain \( U_{4s,scf} = 4.0 \) eV and \( U_{3d,scf} = 4.0 \) eV around the barrier (\( U_{4s} \) is instead found to be nearly zero elsewhere). Inclusion of the 4s response for both sextets Int-2 and Int-3 increases the forward reaction barrier to 1.16 eV while the backward reaction remains unchanged—in accordance with CCSD(T).

In conclusion, we have shown how a self-consistent GGA + \( U \) approach can provide a dramatic improvement to the description of multiplet potential energy surfaces for transition-metal complexes that are otherwise poorly described by common exchange-correlation functionals, while preserving the very favorable computational costs and scaling of local density-based functionals. These improvements include spin energetics, state symmetries, and quantitative description of complex reaction coordinates. \( U \) has been treated as an intrinsic, nonempirical property of the system considered, and never as a fitting parameter, and it has been obtained through a self-consistent extension to the linear-response formulation of Cococcioni and de Gironcoli [12]. Such development will allow large-scale and accurate calculations [33] on transition-metal complexes, with applications in the field of catalysis, biochemistry, and environmental science.

We thank F. de Angelis for pointing out the \( \mathrm{H}_2 \) on FeO\(^+\) reaction and S. de Gironcoli for helpful discussions on \( U_{\text{scf}} \). This work was supported by the NSF and ARO-MURI DAAD-19-03-1-0169. Computational facilities were provided through NSF Grant No. DMR-0414849 and PNNL Grant No. EMSL-UP-9597.

*Current Address: Departamento de Química Inorgánica, Analítica y Química Física, Universidad de Buenos Aires, Buenos Aires, Argentina.

[15] Multiplets are defined by their spin component along the z axis and are thus not eigenstates of the square of the spin operator. Consequences and alternatives are discussed more fully in M. Filatov and S. Shaik, J. Chem. Phys. 110, 116 (1999) and references therein.
[16] S. Baroni et al., http://www.quantum-espresso.org. Calculations are completed in the Perdew Burke Ernzerhof (GGA) approximation [8] using ultrasoft pseudopotentials with a plane wave cutoff of 40 Ry and density cutoff of 480 Ry; transition states are obtained with the nudged elastic band method [34].
[17] M. J. Frisch et al., Gaussian 03, Revision B.05 (Gaussian, Inc., Wallingford, CT, 2004). Hybrid functional B3LYP (Becke’s 3-parameter exchange and Lee, Yang, and Parr’s correlation) and CCSD(T) calculations use the 6-311 + + G(3df, 3pd) basis set.
[24] The \( \omega_0 \) are obtained with a power law fit following Hollas, High Resolution Spectroscopy (Wiley, New York, 1998). Anharmonicity prevents direct comparison to the experimental \( \omega_0 \).
[31] The PES of Figs. 2 and 3 have been aligned at \( ^1\text{Int}-1 \).
[32] CCSD(T) geometries are from an 0.01 Å interpolation in each degree of freedom (up to five) in total as much as 800 for a structure. The states considered are reactants and intermediates for each quartet and sextet PES.