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Density Functional Theory in Transition-Metal Chemistry: Relative Energies of Low-Lying States of Iron Compounds and the Effect of Spatial Symmetry Breaking

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Abstract: The ground and lower excited states of Fe_2, Fe_2^-, and FeO^+ were studied using a number of density functional theory (DFT) methods. Specific attention was paid to the relative state energies, the internuclear distances (r_e), and the harmonic vibrational frequencies (ω_e). A number of factors influencing the calculated values of these properties were examined. These include basis sets, the nature of the density functional chosen, the percentage of Hartree–Fock exchange in the density functional, and constraints on orbital symmetry. A number of different types of generalized gradient approximation (GGA) density functionals (straight GGA, hybrid GGA, meta-GGA, and hybrid meta-GGA) were examined, and it was found that the best results were obtained with hybrid GGA or hybrid meta-GGA functionals that contain nonzero fractions of HF exchange; specifically, the best overall results were obtained with B3LYP, M05, and M06, closely followed by B1LYP. One significant observation was the effect of enforcing symmetry on the orbitals. When a degenerate orbital (π or δ) is partially occupied in the $^4\Phi$ excited state of FeO^+, reducing the enforced symmetry (from C_{6v} to C_{4v} to C_{2v}) results in a lower energy since these degenerate orbitals are split in the lower symmetries. The results obtained were compared to higher level ab initio results from the literature and to recent PBE+U plane wave results by Kulik et al. (*Phys. Rev. Lett.* **2006,** *97,* 103001). It was found that some of the improvements that were afforded by the semiempirical +U correction can also be accomplished by improving the form of the DFT functional and, in one case, by not enforcing high symmetry on the orbitals.

1. Introduction

Transition-metal centers have great versatility in their bonding. Consequently, accurate theoretical treatment of transition-metal chemistry demands a flexible theoretical framework that treats all energetically accessible spin states, spin couplings, and valence states in an even-handed fashion, which in wave function theory requires a multiconfigurational treatment. This poses a difficult problem for the Kohn–Sham density functional theory (DFT) because all information on the multiconfigurational character of the wave function is contained in the exchange-correlation energy E_{XC}, which is computed from an electron density that is in turn obtained from a single Hartree product of orbitals.[1,2] Even when a single antisymmetrized product (Slater determinant) of orbitals does not describe the true electronic wave function well, the Kohn–Sham ground-state energy is correct if one solves the Kohn–Sham equations for the orbitals that give the lowest-energy solution,[1] even though the Kohn–Sham orbitals and eigenvalues, except for the highest orbital eigenvalue,[3] do not have any strict physical significance,[4–6] and the Kohn–Sham Slater determinant that generates the accurate electron density may have different spin properties than the true wave function.[7–9] Nevertheless, great progress has been made in understanding transition-metal chemistry in terms of the Kohn–Sham theory.[10–13]

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One especially difficult issue for the Kohn−Sham theory (as well as multiconfigurational wave function theory) is the calculation of relative spin-state energetics.[9,11,12,14−17] Hartree−Fock exchange[18] and Hubbard-like corrections[19] have been found[9,14,15,17] to have large effects on the ordering of the various spin-coupled states predicted by the Kohn−Sham theory.

In an effort to obtain practical and accurate predictions of relative spin-state energies of polynuclear transition-metal complexes or to determine which spin state is the ground state, it has become common to use an analysis based on the approximate (and not uniquely defined) Heisenberg−Dirac spin Hamiltonian.[12,20−22] In this analysis, a broken-spatial-symmetry spin-unrestricted Kohn−Sham determinant is treated as a weighted average of spin multiplets. The method is often considered an improvement over treating the variationally fully optimized broken-symmetry-solution to the Kohn−Sham equations as the best approximation to the ground state.[12] A key feature of the broken-spatial symmetry solution used in this method is that electrons with opposite spins may localize on different metal centers so that the Slater determinant corresponds to an antiferromagnetically coupled state.[23] A large literature has developed on this and related broken-symmetry approaches.[24−33] Broken-symmetry solutions have also been studied in other contexts, and it has often been found that it is important to allow the orbitals to break symmetry in order to get a qualitatively correct description of the system.[33−42] The energies of the broken-symmetry states are often used without correcting for their spin character.[34−42] In fact, it has been argued on theoretical grounds that the fully self-consistent broken-symmetry single Slater determinant of lowest total energy is the correct solution to the problem.[7] Other aspects of broken-symmetry solutions have also been discussed recently, usually in the context that broken symmetry is considered to be an artifact best avoided.[43−47] Thus, there is not a unified consensus on the use and interpretation of broken-symmetry solutions.

There have been several recent studies of the accuracy of various density functionals for transition-metal−ligand bond energies, relative spin-state energetics, and geometries,[48−70] and the interpretation of these studies depends in part on how one considers symmetry. The present paper uses the Kohn−Sham theory to calculate spin-state energies and geometries for Fe_2, Fe_2^-, and FeO^+ (which were chosen to allow comparison to the results of ref 15), and in each case we studied the stability of the solution to breaking symmetry. When symmetry is broken, we compare results for broken-symmetry and restricted solutions.

2. Methods

All calculations in this paper were carried out using the *NWChem* version 5.0 quantum chemistry package,[71,72] to which the M06 patch[73] was applied.

We carried out calculations with several density functionals,[18,61,70,74−78] which are explained in Table 1. In this Table, X denotes the percentage of Hartree−Fock exchange. We will also include Hartree−Fock (HF) calculations[79] for comparison. The typing of density functionals in Table 1

Table 1. Density Functionals Used for the Present Calculations

type	functional	X	ref
GGA	BLYP	0	74,75
	PBE	0	77
meta-GGA[a]	M06-L	0	67
hybrid GGA	B3LYP	20	74−76
	B1LYP	25	74,75,78
	BHandHLYP	50	18[b]
	HFLYP	100	75,79[c]
hybrid meta-GGA[a]	M06	27	70
	M05	28	61

[a] Meta-GGA and hybrid meta-GGA functionals depend on spin kinetic energy density, but the other functionals do not. [b] As modified in the *Gaussian* computer package. [c] HF exchange with LYP correlation.

Table 2. Sizes of Basis Sets Employed for Fe

basis	primitive	contracted
TZQ	15s11p6d1f	10s7p4d1f
TZQ(3df)	15s11p6d3f1g	10s7p4d3f1g
QZVP	25s19p11d3f1g	12s7p6d3f1g

follows the usual notation. Thus, generalized gradient approximation (GGA) functionals depend only on the local spin densities for up-spin and down-spin electrons and the magnitudes of the gradients of these spin densities. Meta-GGAs also depend on spin kinetic energy densities, and hybrid GGAs and hybrid meta-GGAs also include Hartree−Fock exchange.

The BLYP, B3LYP, B1LYP, BHandHLYP, and HFLYP functionals[18,74−76,78] form a sequence differing mainly in the value of X (in addition, B3LYP incorporates empirical scaling in the correlation energy). PBE is similar in spirit to BLYP but with theoretically more justifiable exchange and correlation functionals.[77] M05 and M06, in contrast, are more complicated functionals in which kinetic energy density and improved functional forms are employed in the exchange functional to make it more compatible with a wide range of X, and this in turn allows the correlation functional, which also depends on kinetic energy density and which is optimized simultaneously with exchange, to become more physical by not being required to be consistent with less physical exchange.[61,70] In contrast, the GGA correlation is more compatible with GGA exchange than with exact exchange.[80]

Three different basis sets were used for Fe: the basis called TZQ by Schultz et al.[36,59] which is taken from Wachters, Hay, Raghavachari, and Trucks[82] and is denoted 6-311+G* in *Gaussian*;[82] a basis we call TZQ(3fg), which is called 6-311+G(3df) in *Gaussian*; and the QZVP basis of Weigend et al.[83] The sizes of these basis sets are compared in Table 2. For O, the 6-311+G(3df) basis set[84] was used in all calculations.

All calculations are spin unrestricted; thus HF could be called UHF, B3LYP could be called UB3LYP, etc. We assign spin in the usual way,[5] where S is taken as M_S rather than attempting to assign spin states by interpreting the Kohn−Sham determinant as if it were a wave function.

Table 3. Electronic Configurations of the Various Spin States of Fe$_2$, Fe$_2^-$, and FeO$^+$

molecule	symmetry	electronic configuration
Fe$_2$	$^9\Sigma_g^-$	3d^{13}: $\sigma_g^2\pi_u^4\delta_g^2\pi_g^2\delta_u^2\sigma_u$; 4s^3: $\sigma_g^2\sigma_u$
	$^7\Sigma_g^-$	3d^{13}: $\sigma_g^2\pi_u^4\delta_g^2\pi_g^2\delta_u^2\sigma_u$; 4s^3: $\sigma_g^2\sigma_u$
	$^7\Delta_u$	3d^{14}: $\sigma_g^2\pi_u^4\delta_g^3\pi_g^2\delta_u^2\sigma_u$; 4s^2: σ_g^2
	$^9\Delta_g$	3d^{13}: $\sigma_g^2\pi_u^4\delta_g^2\pi_g^2\delta_u^2\sigma_u$; 4s^3: $\sigma_g^2\sigma_u$
Fe$^-$	$^8\Sigma_u^-$	3d^{13}: $\sigma_g^2\pi_u^4\delta_g^2\pi_g^2\delta_u^2\sigma_u$; 4s^4: $\sigma_g^2\sigma_u$
	$^8\Delta_g$	3d^{14}: $\sigma_g^2\pi_u^4\delta_g^3\pi_g^2\delta_u^2$; 4s^3: $\sigma_g^2\sigma_u$
FeO$^+$	$^6\Sigma^+$	1$\sigma^2$2$\sigma^2$1$\pi^4$1$\delta^3$3$\sigma^1$2π^2
	$^4\Phi$	1$\sigma^2$2$\sigma^2$1$\pi^4$1$\delta^3$3$\sigma^1$2π^1

(Setting $S = M_S$ would be correct for spin-restricted orbital products with the highest possible M_S of a given configuration.[85])

The calculations were carried out for the spin states of Fe$_2$, Fe$_2^-$, and FeO$^+$ listed in Table 3. The diatomic molecules studied in this paper have $D_{\infty h}$ (Fe$_2$, Fe$_2^-$) and $C_{\infty v}$ (FeO$^+$) symmetries, but most electronic structure codes do not allow the use of these high symmetries. For Fe$_2$, we performed checks on some of the states (namely $^9\Sigma_g^-$, $^9\Delta_g$, and $^7\Delta_u$), and for Fe$_2^-$ we performed checks for the $^8\Delta_g$ state; we found that one gets the same results in C_{2v} and D_{4h} symmetries, so only the D_{4h} results are presented for Fe$_2$ and Fe$_2^-$. For FeO$^+$ we present results for three different symmetries: C_{2v}, C_{4v}, and C_{6v}.

All calculations are nonrelativistic. One would expect that relativistic effects would be small but not completely negligible.[69,86] Relativistic effects should be included for quantitative comparison with experiment, but one of our main goals here was to compare to previous theoretical calculations,[15,87−92] which all neglected relativistic effects.[15,87−92]

It should also be noted that in *NWChem*, while analytical gradients are available for open-shell DFT, analytical Hessians are not. Therefore, the DFT harmonic vibrational frequencies ω_e were calculated by numerical central differences.

We checked that the results are independent of the starting guesses for the orbitals.

3. Results and Discussion

Our results for relative state energies ΔE, equilibrium internuclear distance r_e, and harmonic vibrational frequencies ω_e are given in Tables 4−9, where they are also compared to previous theoretical[15,87−92] and experimental[93−95] results. A point of special interest is the comparison to DFT+U[19,96] calculations,[15,92] in particular PBE+U, where +U denotes a Hubbard-like[96] correction, carried out with a plane wave (PW) basis. The DFT+U model has become very popular in solid-state physics where it is intended to correct for excessively delocalized states sometimes predicted by Kohn−Sham calculations with the local spin density approximation or with GGA functionals.[19,96,98−108]

All energies in tables are electronic energy plus nuclear repulsion and do not include vibrational energy.

In the tables, "/3fg" denotes use of the TZQ(3df) basis for Fe and "/f" denotes use of the TZQ basis for Fe; both are combined with 6-311+G(3df) for O in FeO$^+$.

3.1. Fe$_2$. Experimental spectra[94] show that the ground state of Fe$_2$ is the 4s^{3}3d^{13} $^9\Sigma_g^-$ state, there are only two states below 1 eV (namely the ground state and a state with an excitation energy of 0.53 eV),[94] the ground-state harmonic vibrational frequency ω_e is 300 cm^{-1},[93] and r_e and ω_e are almost the same for the two lowest electronic states.[94] These results were reasonably well confirmed by Hübner and Sauer[89] employing wave function theory (WFT) calculations, in particular multireference configuration interaction with single and double excitations[109] and a Pople cluster correction[110] (MRCISD+Q^P) with an atomic natural orbital[111] (ANO) basis set. Shortly afterward though, Bauschlicher and Ricca[90] presented an internally contracted multireference configuration interaction[112] with Davidson correction[113] (IC-MRCI+Q) calculations with a different ANO basis set.[114] They also presented some corrections for additional correlation effects and for basis set extension; we will call these corrected MRCI or "cor. MRCI". These calculations[90] agree with previous work[89,94] that the $^9\Sigma_g^-$ state is the ground state, but the authors cautioned that the calculations are not definitive and raised the possibility of a $^7\Delta_u$ ground state. Based on the experimental[94] and high-level theoretical[89,90] results, we will consider, for the purposes of evaluating our DFT result, the $^9\Sigma_g^-$ state to be the ground state.

The PBE calculations with the TZQ/3fg and TZQ/f Gaussian-basis-set choices in Table 4 agree well with each other and reasonably well with the PBE plane wave calculations of Rollman et al.[92] but less well with the plane wave calculations of Kulik et al.[15] (The requirements for agreement between such calculations on molecules have been studied recently.[115])

The relative state energies are particularly interesting because they include three states with three electrons in 4s orbitals and 13 electrons in 3d orbitals ($^9\Sigma_g^-$, $^7\Sigma_g^-$, and $^9\Delta_g$, see Table 3) and one state with two electrons in 4s orbitals and 14 in 3d orbitals states ($^7\Delta_u$). The $^7\Sigma_g^-$ state has the same dominant configuration as the $^9\Sigma_g^-$ state but differs in the spin coupling between the 3d and 4s subshells.[89] Table 4 shows that certain DFT methods predict negative values for $\Delta E(^7\Sigma_g^-)$, $\Delta E(^7\Delta_u)$, or $\Delta E(^9\Delta_g)$ and thus predict the wrong ground state. The PBE functional predicts the wrong ground state, whereas PBE+U corrects this. Furthermore, the BLYP and M06-L density functionals, which are the other two functionals studied (besides PBE) that have neither Hartree−Fock exchange nor a Hubbard correction, also predict the incorrect ground state. In contrast, the hybrid GGA (B3LYP and BHandHLYP) and the hybrid meta-GGA (M06 and M05) functionals, like PBE+U, predict the correct ground state. Of the methods that predict the correct ground state, M05 and PBU+U predict the most accurate bond distances, but only PBE+U gets the correct order of all four states studied.

It is well-known that, all other factors being equal, Hartree−Fock exchange favors high-spin states relative to low-spin ones. One reason for this is that Hartree−Fock exchange introduces the Fermi hole[116] (by which same-spin electrons avoid one another), and high-spin states have more same-spin interactions. For the sequence BLYP, B1LYP, BHandHLYP, and HFLYP, all factors other than X are

Table 4. Relative State Energies (Relative to the $^9\Sigma_g^-$ Ground State) and Bond Distances of Fe_2

method	ref	ΔE (eV)[a]			r_e (Å)			
		$^7\Sigma_g^-$	$^7\Delta_u$	$^9\Delta_g$	$^9\Sigma_g^-$	$^7\Sigma_g^-$	$^7\Delta_u$	$^9\Delta_u$
HF/3fg	present	−1.09	3.43	1.08	2.187	2.426	2.109	2.286
/f	present	−1.10	3.40	1.13	2.186	2.422	2.114	2.299
BLYP/3fg	present		−0.61	0.05	2.166		2.019	2.277
/f	present	0.31	−0.62	0.04	2.168	2.163	2.023	2.282
PBE/3fg	present		−0.48	0.06	2.147		2.004	2.250
/f	present		−0.50	0.05	2.148	2.145	2.010	2.256
/PW	Rollmann et al.[92]		−0.32		2.144		2.005	
/PW	Kulik et al.[15]	0.65	−0.12	0.28	2.11	2.10	1.99	2.26
M06-L/3fg	present		0.09	−0.11	2.150		2.006	2.273
/f	present	0.55	0.07	−0.12	2.151	2.143	2.009	2.280
B3LYP/3fg	present	0.36	0.20	0.36	2.111	2.118	1.979	2.232
/f	present	0.35	0.18	0.36	2.113	2.119	1.984	2.237
/6-311++G(3df)	Kulik et al.[15]	0.34	0.18	0.36				
B1LYP/3fg	Present	0.37	0.43	0.42	2.106	2.114	1.977	2.227
/f	present	0.36	0.41	0.42	2.108	2.116	1.983	2.233
BHandHLYP/3fg	present	0.43	1.32	0.70	2.073	2.087	1.959	2.182
/f	present	0.42	1.30	0.71	2.074	2.089	1.965	2.188
HFLYP/3fg	present	−1.45	2.73	1.13	2.076	2.323	1.999	2.164
/f	present	−1.42	2.72	1.17	2.076	2.319	2.006	2.171
M06/3fg	present	0.09	0.47	0.59	2.119	2.122	1.980	2.232
/f	present	0.10	0.47	0.58	2.118	2.121	1.982	2.234
M05/3fg	present	0.10	0.32	0.74	2.135	2.145	2.005	2.238
/f	present	0.11	0.33	0.73	2.137	2.144	2.008	2.244
PBE+U/PW	Rollmann et al.[92]				2.143		2.005	
/PW	Kulik et al.[15]	0.60	0.72	0.41	2.13	2.12	2.00	2.26
CCSD(T)/GTO[b]	Kulik et al.[15]	0.55	0.86	0.38	2.17	2.16	2.00	2.18
MRCISD+Q^P/ANO	Hübner and Sauer[89]	0.48[c]	0.70[d]	~0.4	2.187	2.180	2.140	>2.3
IC-MRCI+Q/ANO	Bauschlicher and Ricca[90]	0.53	0.58	<1.05	2.178	2.093	2.081	>2.3
cor. MRCI	Bauschlicher and Ricca[90]		0.30					
experiment	Leopold et al.[94]	0.53						

[a] Relative to the $^9\Sigma_g^-$ ground state. [b] GTO denotes the 6-311++G(3df,3pd) Gaussian-type-orbital basis set. [c] 0.34 eV if corrected for the MRCISD+Q^P error in the separated atoms. [d] 0.56 eV if corrected for MRCSID+Q^P error in the separated atoms.

invariant, and for B3LYP there is only a relatively small change in the correlation functional. However, Table 4 shows that the septet−nonet energy differences do not vary monotonically with X. Thus other features in the orbital interactions and in the density functional cannot be ignored in analyzing the predicted spin states.

The frequencies in Table 5 show no great surprise for the $^9\Sigma_g^-$ and $^7\Delta_u$ states, at least based on experience with main-group molecules, because for main-group molecules density functionals with no Hartree−Fock exchange have smaller systematic errors for frequencies,[117] and they do better here as well. It is not clear why the MRCISD+Q^P and IC-MRCI+Q calculations give a much lower frequency for the $^7\Delta_u$ state than all other methods; this low-frequency results from a very flat potential curve for this state in the MRCISD+Q^P calculations—perhaps the static correlation is unbalanced in these calculations. In fact, Bauschlicher and Ricca,[90] because of their concern about this aspect, reported averaged coupled pair functional[118] (ACPF) calculations that yield 2.038 Å and 335 cm^{-1} for the $^7\Delta_u$ state and complete active space second-order perturbation theory[119] (CASPT2) calculations that yield 1.979 Å and 429 cm^{-1}, both in much better agreement with the Kohn−Sham calculations.

An interesting conclusion that emerges from Table 4 is

Table 5. Harmonic Vibrational Frequencies for Fe_2

method	ref	$^9\Sigma_g^-$	$^7\Sigma_g^-$	$^7\Delta_u$	$^9\Delta_g$
HF/f	present	369	289	394	308
BLYP/f	present	320	332	393	268
PBE/f	present	331	340	417	279
/PW	Rollman et al.[92]	329		414	
/PW	Kulik et al.[15]	339	335	413	285
M06-L/f	present	337	341	402	281
B3LYP/f	present	361	359	427	301
B1LYP/f	present	367	364	432	304
BHandHLYP/f	present	402	393	459	338
HFLYP/f	present	433	331	451	370
M06/f	present	357	364	429	306
M05/f	present	352	355	417	309
PBE+U/PW	Rollmann et al.[92]	346		414	
PBE+U/PW	Kulik et al.[15]	335	331	419	280
CCSD(T)/GTO	Kulik et al.[15]	296	304	404	220
MRCISD+Q^P/ANO	Hübner and Sauer[89]	303	310	224	
IC-MRCI+Q/ANO	Bauschlicher and Ricca[90]	327	296	291	
experiment	Moskovits and DiLello[93]	300			

that functionals with a large percentage of Hartree−Fock exchange are the most sensitive to changes in the basis set.

Table 6. Excitation Energy (Relative to the $^8\Sigma_u^-$ Ground State), Equilibrium Intermolecular Distances, and Harmonic Vibrational Frequencies for Fe₂⁻

method[a]	ΔE^b (eV) $^8\Delta_g$	r_e (Å) $^8\Sigma_u^-$	r_e (Å) $^8\Delta_g$	ω_e (cm⁻¹) $^8\Sigma_u^-$	ω_e (cm⁻¹) $^8\Delta_g$
HF/f	4.79	2.640	2.330	206	297
BLYP/3fg			2.076		
/f	−0.02	2.231	2.081	281	349
PBE/3fg			2.063		
/f	−0.68	2.209	2.068	295	357
/PW[15]	−0.52	2.20	2.07	305	360
M06-L/3fg			2.097		
/f	−0.12	2.212	2.099	299	337
B3LYP/3fg	0.15	2.176	2.041		
/f	0.14	2.178	2.046	316	375
/6-311++G(3df)[15]	0.14				
B1LYP/3fg	0.36	2.172	2.044		
/f	0.35	2.174	2.048	316	375
BHandHLYP/3fg	1.08	2.171	2.052		
/f	1.07	2.176	2.056	321	374
HFLYP/3fg	1.43	2.227	2.141		
/f	4.50	2.508	2.146	247	388
M06/3fg	0.60	2.188	2.045		
/f	0.72	2.188	2.048	315	375
M05/3fg	0.74	2.196	2.059		
/f	0.73	2.198	2.064	316	371
PBE+U/PW[15]	0.38	2.20	2.08	301	355
CCSD(T)/GTO[15]	0.40	2.24	2.12	276	321
MRCI+QP/ANO[89]	0.8	2.266		255	
IC-MRCI+Q/ANO[90]	0.70	2.350	2.233	261	165
experiment[94]				250	

[a] References are the same as in Tables 3 and 4. [b] Relative to the $^8\Sigma_u^-$ ground state.

Table 7. Excitation Energy ($E(^4\Phi) - E(^6\Sigma^+)$, in eV) of FeO⁺ Calculated in C_{6v}, C_{4v}, and C_{2v} Symmetries

method	symmetry C_{6v}	symmetry C_{4v}	symmetry C_{2v}	not stated
HF/3fg	11.21	1.80	−1.80	
/f	11.12	1.82	−1.76	
BLYP/3fg	0.85	0.53	0.44	
/f	0.86	0.54	0.45	
PBE/QZVP	0.94			
/3fg	0.94	0.63	0.56	
/f	0.94	0.52	0.55	
/PW[a]				0.84
M06-L/3fg	1.48	0.96	0.59	
/f	1.49	0.97	0.60	
B3LYP/3fg	2.57	1.24	0.32	
/f	2.58	1.27	0.33	
/TZ2P[b]				0.34[c]
B1LYP/3fg	2.91	1.33	0.19	
/f	2.92	1.35	0.21	
BHandHLYP/3fg	4.44	1.63	−0.43	
/f	4.45	1.65	−0.41	
HFLYP/3fg	7.16	1.98	−1.70	
/f	7.17	2.01	−1.67	
M06/3fg	2.85	1.67	0.55	
/f	2.86	1.69	0.56	
M05/3fg	2.82	1.78	0.64	
/f	2.83	1.79	0.63	
PBE+U/PW[a]				0.54
CCSD(T)/GTO[a]				0.57
CCSD(T)/3df+//B3LYP[d,e]				0.54
QMC//B3LYP[f]				0.36

[a] Kulik et al.[15] [b] Filatov and Shaik.[87] [c] C_s symmetry. [d] Irigoras et al.[88] [e] CCSD(T)/3df+//B3LYP denotes CCSD(T)/TZVP+G(3df,2p) single-point energy calculations at B3LYP/TZVP+G(3df,2p) geometries. [f] Matxain et al.[91]

3.2. Fe₂⁻. The anion presents a slightly different kind of test because the two states studied have the same multiplicity. The ground state is the $^8\Sigma_u^-$ state with a dominant 3d¹³: $\sigma_g^2\pi_u^4\delta_g^2\pi_g^2\delta_u^2\sigma_u$; 4s⁴: $\sigma_g^2\sigma_u^2$ configuration, whereas the $^8\Delta_g$ state is 3d¹⁴4s³.[89,94] The high-level calculations (CCSD(T) and MRCI+QP) in Table 6 indicate an energy spacing of 0.4−0.8 eV. The PBE plane wave and TZQ calculations in Table 6 agree reasonably well (better than in Table 4), but again the GGA and meta-GGA functionals predict the wrong ground state, while the hybrid GGAs, hybrid meta-GGAs, and PBE+U methods predict the correct ground state. B1LYP, M06, M05, and PBE+U appear to be the most accurate methods for the relative energies. Despite the poor performance for relative energies, M06-L is the most accurate functional for internuclear distances and vibrational frequencies (as already mentioned, functionals with no Hartree− Fock exchange often have small systematic errors for frequencies[117]). Of the three functionals with the best performance for relative state energies, PBE+U is best for bond distances and frequencies closely followed by M05.

The case of Fe₂⁻ is very illuminating. The prediction of relative state energies in transition-metal chemistry is often discussed entirely in terms of the competition between high spin and low spin, but here both states are octets and the key role of the relative energies of the 3d and 4s orbitals is clearly exposed. Hartree−Fock theory and functionals with

a high percentage of Hartree−Fock exchange yield a higher energy for the 4s(σ_u) orbital relative to the energies of orbitals with 3d parentage.

3.3. FeO⁺. The FeO⁺ molecule has been carefully studied in the past, primarily to explain the low efficiency of its gas-phase reaction with H₂ to make Fe⁺ + H₂O[91,120] and the related reverse reaction.[88] CCSD(T) calculations with an augmented TZQ(3df) basis on Fe and a 6-311++G(2df) basis on O (this basis will be abbreviated "3df+") were carried out by Irigoras et al.[88] and yielded a state splitting $E(^4\Phi) - E(^6\Sigma^+)$ of 0.54 eV. Quantum Monte Carlo (QMC) calculations with a fixed-mode approximation by Matxain et al.[91] lowered the calculated splitting to 0.36 eV. These results are compared to our HF and Kohn−Sham calculations and to calculations by Kulik et al.[15] in Table 7. The immediately obvious conclusion is that the lower-symmetry Kohn−Sham solutions ("broken-symmetry" solutions) are in much better agreement with the high-level results than the results where spatial symmetry of the orbitals is enforced.

A complicating issue in Table 7 is the spatial symmetry in the plane wave calculations. For example, the PBE+U/ PW calculations have a state splitting 0.30 eV lower than PBE/PW and are in good agreement with the CCSD(T) results, but the PBE/PW calculations do not agree well with the fully optimized (C_{2v}) PBE calculations with Gaussian-

Table 8. Internuclear Distance for the $^6\Sigma^+$ Ground State of FeO$^+$

method	r (Å)
HF/3fg	1.822
BLYP/3fg	1.648
PBE/3fg	1.631
/PW[b]	1.620
M06-L/3fg	1.634
B3LYP/3fg	1.635
/TZ2P[c]	1.643
/DZVP[d]	1.655
/3fg+[d]	1.637
B1LYP/3fg	1.640
BHandHLYP/3fg	1.655
HFLYP/3fg	1.705
M06/3fg	1.617
M05/3fg	1.623
PBE+U/PW[b]	1.660
CCSD(T)/GTO[b]	1.660
experiment[e]	1.643

[a] Results for the /f basis (not shown) are all very similar to those for the /3fg basis. [b] Kulik et al.[15] [c] Filatov and Shaik.[87] [d] Irigoras et al.[88] [e] Aguirre et al.[95]

Table 9. Equilibrium Internuclear Distances for the $^4\Phi$ Excited State of FeO$^+$ Calculated in C_{6v}, C_{4v}, and C_{2v} Symmetries[a]

	C_{6v}	C_{4v}	C_{2v}	not stated
HF/3fg	2.273	1.803	1.814	
BLYP/3fg	1.596	1.601	1.614	
PBE/3fg	1.582	1.588	1.600	
/PW[b]				1.560
M06-L/3fg	1.624	1.625	1.676	
B3LYP/3fg	1.663	1.671	1.694	
/TZ2P[c]				1.703[c]
/DZVP[d]				1.698
/3fg+[d]				1.696
B1LYP/3fg	1.687	1.690	1.713	
BHandHLYP/3fg	1.742	1.744	1.746	
HFLYP/3fg	1.798	1.788	1.773	
M06/3fg	1.675	1.668	1.699	
M05/3fg	1.689	1.678	1.708	
PBE+U/PW[b]				1.750
CCSD(T)/PW[b]				1.700

[a] Results for the /f basis (not shown) are all very similar to those for the /3fg basis. [b] Kulik et al.[15] [c] Filatov and Shaik, C_s.[87] [d] Irigoras et al.[88]

Table 10. Absolute Energies (in Hartrees) of the $^4\Phi$ Excited State of FeO$^+$ as Calculated in C_{6v}, C_{4v}, and C_{2v} Symmetries

method	C_{6v}	C_{4v}	C_{2v}
BLYP/3fg	−1338.6092	−1338.6212	−1338.6245
/f	−1338.6063	−1338.6181	−1338.6214
B3LYP/3fg	−1338.4902	−1338.5390	−1338.5729
/f	−1338.4874	−1338.5356	−1338.5698
M06/3fg	−1338.3478	−1338.3910	−1338.4324
/f	−1338.3456	−1338.3886	−1338.4301

type orbital (GTO) basis sets. If the +U correction were to reduce the PBE/GTO state splitting by 0.30 eV, the resulting splitting would be 0.14 eV, which would be too low. Thus, unless careful attention is paid to symmetry breaking, one can draw spurious conclusions about the validity of various functionals.

Table 8 compares the calculated r_e values of the $^6\Sigma^+$ ground state of FeO$^+$ to the experimental r_0 value[95] of 1.643 Å. In general, there is reasonable agreement between the calculated and experimental bond distances. One striking exception is the class of methods that involve large fractions of HF exchange (i.e., HF, HFLYP and BHandHLYP). The high fraction of HF exchange results in bond lengths that are significantly lengthened. A second exception is the hybrid meta-GGA functionals (M05 and M06) that give significant bond contraction. However, the more traditional hybrid GGA functions (B1LYP and B3LYP), and to a lesser extent the sole meta-GGA functional (M06-L), yield bond lengths consistent with experiment. It should also be noted that CCSD(T) predicts a bond length that is somewhat larger than experiment, and it is to this number that Kulik et al. favorably compare their PBE+U/PW value.[15]

Table 9 shows equilibrium internuclear distances for the $^4\Phi$ state. When the symmetry is lowered, the equilibrium internuclear distance increases for the GGAs, the meta-GGA, and the hybrid meta-GGAs with 20−50% Hartree−Fock exchange but decreases for HF and HFLYP. It is nonmonotonic for M06 and M05. Nevertheless, except for B1LYP, amazingly it is always closer to CCSD(T) for the C_{2v} solution than for C_{6v}. An experimental value for the bond length in the excited $^4\Phi$ state could not be found in the literature.

If we assume that the correct state splitting for FeO$^+$ is in the range 0.36−0.56 eV, we would single out any method predicting state splittings in the range 0.26−0.66 eV as performing acceptably. Seven of the ten methods meet this criterion.

For all functionals, the energy of the $^4\Phi$ state decreases strongly when we lower the symmetry from C_{6v} to C_{4v} to C_{2v}. Examples are given in Table 10. Notice that the effect of symmetry is larger than the effect of the basis set. The nature of the symmetry breaking in FeO$^+$ is very unusual and very interesting. The energies of the $^4\Phi$ state strongly depend on the symmetry, while those of the $^6\Sigma^+$ ground state, like those for Fe$_2$ and Fe$_2^-$, do not. A Φ state corresponds to B$_1$, E, and B$_2$, in C_{6v}, C_{4v}, and C_{2v}, respectively.[121] The energy decreases because orbitals that are degenerate in $C_{\infty v}$ and C_{6v} symmetries can be split in lower symmetries. The electronic configuration of the $^4\Phi$ state is $1\sigma^2 2\sigma^2 1\pi^4 1\delta^3 3\sigma^1 2\pi^1$. The π and δ orbitals are degenerate in $C_{\infty v}$ and C_{6v}. In C_{6v} the π and δ orbitals have e$_1$ and e$_2$ symmetry, respectively, whereas in C_{4v}, the δ orbitals are split into b$_1$ and b$_2$, while π remains degenerate in e symmetry. In C_{2v} symmetry, the δ orbitals transform as a$_1$ and a$_2$, and the π orbitals are also split, transforming as b$_1$ and b$_2$.[121] An example of the splitting in orbital energies is shown in Table 11. In general, GGA exchange includes static correlation,[122] and functionals with small X (that is, with a high percentage of GGA exchange) show less dependence on symmetry. The greater tendency to symmetry breaking in the calculations with a higher percentage of Hartree−Fock exchange may be attributable to the tendency of higher Hartree−Fock

Table 11. Energies of the Outer Orbitals (in Hartrees) for the $^4\Phi$ State of FeO$^+$ Calculated in C_{6v}, C_{4v}, and C_{2v} Symmetries Using B3LYP/3fg

spin	orbital	C_{6v}	C_{4v}	C_{2v}
α	1 σ	−1.169	−1.169	−1.159
	2 σ	−0.719	−0.717	−0.708
	1 π	−0.702	−0.698	−0.700
	1 π	−0.702	−0.698	−0.685
	1δ	−0.657	−0.670	−0.640
	1 δ	0.657	−0.634	−0.628
	3 σ	−0.567	−0.565	−0.561
	2 π	−0.497	−0.496	−0.558
β	1 σ	−1.210	−1.210	−1.204
	2 σ	−0.646	−0.645	−0.639
	1 π	−0.634	−0.634	−0.660
	1 π	−0.634	−0.634	−0.595
	1 δ	−0.468	−0.562	−0.554

exchange to relatively favor greater electronic localization on the atomic sites.

3.4. Overall Assessment. Considering Tables 4−9 as a whole, the PBE+U calculations perform quite well. A particular difficulty with the DFT+U, though, is the necessity to choose a value for the parameter U, which is system dependent and often highly uncertain, as emphasized, for example, in a recent study of Fe$_3$O$_4$.[123] (Progress in making U less arbitrary has been reported recently, but it is still system dependent.[103]) The density functionals without +U contain parameters, but these parameters do not depend on the system. Among the functionals without system-dependent parameters, B3LYP, M06, and M05 do best, followed closely by B1LYP. In fact, given the uncertainty in the accurate data, one could argue that M05 does as well as PBE+U. For example, it agrees very well with the cor. MRCI value of ΔE for the $^7\Delta_u$ state in Table 4 and with the IC-MRCI+Q/ANO value of ΔE for the $^8\Delta_g$ state in Table 6.

4. Conclusions

We carried out DFT calculations on various states of Fe$_2$, Fe$_2^-$, and FeO$^+$, using GGA, hybrid GGA, meta-GGA, and hybrid meta-GGA DFT functionals. No single functional was found to yield a satisfactory description of all characteristics for all states of these species. The DFT+U calculations performed previously by Kulik et al.[15] are more accurate than DFT in comparison with CCSD(T) and MRCI calculations, although DFT calculations with the M05 functionals are also reasonably accurate; a definitive comparison of these functionals is precluded by uncertainties in the most accurate available data. Functionals with larger percentages of Hartree−Fock exchange are found to be more sensitive to the choice of the basis set.

The FeO$^+$ calculations were carried out in three different symmetries (C_{6v}, C_{4v}, and C_{2v}). The quartet spin state $^4\Phi$ shows spatial-symmetry-breaking, which is especially prominent in functionals with large percentages of Hartree−Fock exchange. Of particular interest is that accurate results can be obtained for the $^4\Phi$ state of FeO$^+$ only when symmetry-breaking solutions are allowed, a situation that has also been observed in some other problems.[7,33−37,40]

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