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A comparison of density functional theory with *ab initio* approaches for systems involving first transition row metals

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Summary. Density functional theory (DFT), using the B3LYP hybrid functional, is found to give a better description of the geometries and vibrational frequencies of FeL and FeL^+ systems that second-order Møller Plesset perturbation theory (MP2). Namely, DFT correctly predicts the shift in the CO vibrational frequency between free CO and the $^5\Sigma^-$ state of FeCO and yields a good result for the Fe–C distance in the quartet states of $FeCH_4^+$. These are properties where the MP2 results are unsatisfactory. Thus DFT appears to be an excellent approach for optimizing the geometries and computing the zero-point energies of systems containing first transition row atoms. Because the DFT approach is biased in favor of the $3d^7$ occupation, whereas the more traditional approaches are biased in favor of the $3d^6$ occupation, differences are found in the relative ordering of states. It is shown that if the dissociation energy is computed relative to the most appropriate atomic asymptote and corrected to the ground state asymptote using the experimental separations, the DFT results are in good agreement with high levels of theory. The energetics at the DFT level are much superior to MP2 and in most cases they are in good agreement with high levels of theory.

Key words: Density functional theory – B3LYP – Transition metals – Binding energy

1. Introduction

The calculation of accurate binding energies can be a very computationally demanding task; this is especially true of systems containing first transition row atoms. The process can be divided into several steps: (1) the optimization of the geometry, (2) the calculation of the vibrational frequencies to determine the zero-point energy, and (3) the calculation of the total energy. In order to achieve highly accurate bond energies or heats of formation, very high levels of theory are required for the third step. In order to reduce the computational expense it is common to perform the first two steps at lower levels of theory than the third. Consider the G2(MP2) approach [1], where the geometry is optimized using second-order Møller Plesset perturbation theory [2] (MP2), the zero-point energy is determined using scaled self-consistent-field (SCF) frequencies, and the total energy is computed using the quadratic configuration interaction approach [3] including singles and doubles with a perturbational estimate of the connected triple excitations [4] [QCISD(T)]. Even this approach can be prohibitively expensive for the third step, so an MP2 calculation is used to evaluate the basis set incompleteness in the QCISD(T) calculation. For molecules containing H through Cl atoms this approach has been very successful.

In many cases the geometry determined at the SCF level is accurate and it is not necessary to use the more computationally demanding MP2 approach. This appears to be true for most molecules containing second transition row atoms [5]. For systems containing first transition row atoms, the SCF geometries and zero-point energies can be very poor, but we recently found that the MP2 geometries and frequencies (but not the binding energies) were in good agreement with higher levels of theory or experiment [6, 7]. While MP2 worked well for most cases, we have found some examples, such as $Fe(CO)_5^+$, where the MP2 geometry is in poor agreement with higher levels of theory [8]. For $Fe(CO)_n^+$, including $n = 5$, density functional theory (DFT) provided geometries in excellent agreement with higher levels of theory. The energetics computed at the DFT level were much superior to the MP2 and in good agreement with the values deduced from higher levels of theory. Since the DFT approach is significantly less computationally demanding than MP2, an obvious suggestion is to use the DFT approach to optimize the geometries and compute the vibrational frequencies. It is possible that the energetics computed at the DFT level will be sufficiently accurate to eliminate the need to perform calculations using higher levels of theory. However, even if DFT is used only to determine the geometry and zero-point energy, it will still represent a significant savings over the MP2 approach.

In this manuscript we compare the DFT results with previous results [7] obtained at the unrestricted Hartree–Fock (UHF), MP2, modified coupled pair functional [9] (MCPF), and the coupled cluster singles and doubles level of theory [10], including a perturbational estimate of the connected triples [4] [CCSD(T)]. The molecules included in the study are: $FeCO^+$, FeCO, FeH_2O^+, and $FeCH_4^+$. Iron was chosen for the metal atom because Fe and Fe^+ have low-lying excited states with a different number of $3d$ electrons than the ground state; thus Fe serves as a good test of the ability of a method to describe the mixing of atomic asymptotes in the molecules. The ligands were chosen because they represented several different bonding mechanisms, $FeCO^+$ represents a case of electrostatic bonding with some metal to ligand donation, FeCO represents a case of a large metal to ligand donation, FeH_2O^+ is a case of only electrostatic bonding, and $FeCH_4^+$ represents a case of electrostatic bonding with some ligand to metal donation. In addition to spanning a large variety of bonding situations, there are experimental binding energies for all of these systems. We should note that our best estimates for the binding energies are in excellent agreement with experiment. These best estimates were obtained using the MCPF approach in a very large basis set, including a correction for relativistic effects and for higher levels of correlation treatment. We find that DFT yields geometries as good as, or better than, the MP2 approach. In addition, in most cases the DFT binding energies are in good agreement with experiment and our best estimates from previous work.

2. Methods

We optimize the geometries and compute the harmonic frequencies and the binding energies using the Kohn–Sham version of density functional theory (DFT).

We use a hybrid functional of the form

$$(1 - A) * E_x^{\text{Slater}} + A * E_x^{\text{HF}} + B * E_x^{\text{Becke}} + C * E_c^{\text{LYP}} + (1 - C)E_c^{\text{VWN}},$$

where E_x^{Slater} is the Slater exchange, E_x^{HF} is the Hartree–Fock exchange, E_x^{Becke} is the gradient part of the exchange functional of Becke [11], E_c^{LYP} is the correlation functional of Lee et al. [12], E_c^{VWN} is the correlation functional of Vosko, Wilk, and Nusair [13], and A, B, and C are the coefficients determined by Becke [14] using his 3 parameter fit to the experimental heats of formation. This modification of the original Becke hybrid functional [14] is described in Ref. [15] and is commonly denoted B3LYP. For convenience, we discuss the ground state symmetry in terms of the orbital occupation from which the density is constructed.

In addition to the states considered previously [7], we treat the $^3\Sigma^-$ state of FeCO using the DFT approach. We therefore extend our previous UHF/MP2/MCPF/CCSD(T) study to include this state; these calculations are performed in an analogous manner to those described in Ref. [7].

The basis sets used are the same as used in our previous study [7]. Namely, the Fe set is an [8*s*4*p*3*d*] contraction of the (14*s*9*p*5*d*) primitive set developed by Wachters [16]. The *s* and *p* spaces are contracted using contraction number 3, while the *d* space is contracted (311). To this basis set two diffuse *p* functions are added; these are the functions optimized by Wachters multiplied by 1.5. A diffuse *d* function [17] and an *f* polarization function ($\alpha = 1.339$) are added. The final Fe basis set is of the form (14*s*11*p*6*d*1*f*)/[8*s*6*p*4*d*1*f*]. The hydrogen basis set is the scaled (4*s*)/[2*s*] set of Dunning and Hay [18], supplemented with a diffuse *s* (0.071) and three *p* (1.2, 0.40, and 0.13) functions. The diffuse *s* and *p* functions are added to describe the polarizability of CH_4. The C and O basis sets in CO and O basis set in H_2O are [4*s*3*p*] contractions of the (9*s*5*p*) primitive set optimized by Huzinaga [19]. A *d* polarization function is added; the exponents are: 0.75 for carbon and 0.85 for oxygen. The *s* space is contracted (5211). A smaller [3*s*2*p*] contraction [18] of the same C primitive set is used for CH_4. In addition, the C *d* function is not included in the $FeCH_4^+$ calculations. Only the pure spherical harmonic components of the basis functions are used in all calculations.

The calculations were performed using Gaussian 92/DFT [20]. The calculations were performed using the NASA Ames Central Computer Facility CRAY C90 or Computational Chemistry IBM RISC System/6000 computers.

3. Results and discussion

We first consider the $^5\text{D}(3d^64s^2) - {}^5\text{F}(3d^74s^1)$ separation in Fe and the $^6\text{D}(3d^64s^1)$–$^4\text{F}(3d^7)$ separation in Fe^+ – see Table 1. The DFT approach has the $3d^7$ occupations too low relative to the $3d^6$ occupations. This is opposite to that found at the MCPF and CCSD(T) levels where the states derived from the $3d^7$ occupation are too high in energy. The error in DFT appears to be larger than at the MCPF or CCSD(T) levels of theory. However, part of the apparent superior performance of the MCPF and CCSD(T) approaches arises from the neglect of relativistic effects, which lowers the $3d^6$ occupations with respect to the $3d^7$ occupations, because the 4*s* electrons have a larger relativistic effect than the 3*d* electrons. The relativistic lowering [21] of the $3d^6$ occupations relative to the $3d^7$ is 6.0 kcal/mol for Fe and 7.4 kcal/mol for Fe^+. If a correction for relativistic effects is added, the errors in the DFT approach are actually smaller than at the MCPF and CCSD(T) levels of theory, but of the opposite sign.

Table 1. Computed separation (kcal/mol) and error of Fe $^5\mathrm{D}(3d^64s^2)$–$^5\mathrm{F}(3d^74s^1)$ and Fe$^+$ $^6\mathrm{D}(3d^64s^1)$–$^4\mathrm{F}(3d^7)$

	UHF	MP2	MCPF	CCSD(T)	DFT	Expt[a]
Fe $^5\mathrm{D}(3d^64s^2)$–$^5\mathrm{F}(3d^74s^1)$	43.4	16.4	27.0	26.1	6.8	20.1
Error	23.3	− 3.7	6.9	6.0	− 13.3	
Error-R[b]	29.3	2.3	12.9	12.0	− 7.3	
Fe$^+$ $^6\mathrm{D}(3d^64s^1)$–$^4\mathrm{F}(3d^7)$	38.0	4.2	10.4	8.3	− 3.8	5.8
Error	32.2	− 1.6	4.6	2.5	− 9.6	
Error-R[b]	39.6	5.8	12.0	9.9	− 2.2	

[a] C.E. Moore, Atomic energy levels, Natl. Bur. Stand. (US) circ. 467 (1949)

[b] This includes a correction for relativistic effects that are not included in any of the theoretical approaches

Table 2. Summary of the FeCO$^+$ $^4\Sigma^-$ results. The results for free CO are given for comparison. The bond lengths are in Å. The harmonic frequencies are in cm^{-1}. The dissociation energy (in kcal/mol) is given with respect to Fe$^+$ $^6\mathrm{D}(3d^64s^1)$

	UHF	MP2	MCPF	CCSD(T)	DFT
FeCO$^+$					
r(Fe–C)	2.139	1.880	1.922	1.910	1.887
r(C–O)	1.098	1.145	1.136	1.140	1.129
D_e	− 29.0[a]	26.6	20.0	23.1	42.3
D_e(corr)	3.9	25.0	24.6	25.6	32.7
ω(bend)	264	321			319
ω(Fe–CO)	243	405			423
ω(C–O)	2522	2153			2225
CO					
r(C–O)[b]	1.108	1.146	1.139	1.143	1.130
ω_e[c]	2432	2110		2138	2213

[a] The negative sign indicates that it is unbound with respect to ^{6}D, but it is bound with respect to ^{4}F, the asymptote to which it dissociates

[b] The experimental value [22] is 1.128 Å

[c] The experimental value [22] is 2170 cm^{-1}

The FeCO$^+$ results are summarized in Table 2. The DFT geometry is in good agreement with those from the MP2, MCPF, and CCSD(T) levels of theory. The DFT and MP2 harmonic frequencies are in good agreement. The biggest difference between DFT and other levels of theory is for r(C–O) and ω(C–O); this difference also shows up in free CO. For Free CO, the DFT r_e value is in the best agreement with experiment [22], while for ω_e the CCSD(T) result is the best. The error in ω_e at the DFT level is smaller than in the MP2 approach. The D_e value computed to CO $^1\Sigma^+$ + Fe$^+$ $^6\mathrm{D}(3d4s^1)$ is much larger for the DFT method than that obtained using any of the other approaches. It is also much larger than the experimental D_0 value [23] of 31.3 ± 1.8 kcal/mol. Much of this overbinding arises from the fact that Fe$^+$ in FeCO$^+$ is $3d^7$, which is described much better than the $3d^64s^1$ occupation by the

Table 3. Summary of the FeCO results. The bond lengths are in Å. The harmonic frequencies are in cm^{-1}. The dissociation energy (in kcal/mol) is given with respect to Fe $^5D(3d^64s^2)$

FeCO			$^5\Sigma^-$		
	UHF	MP2	MCPF	CCSD(T)	DFT
r(Fe–C)	1.981	1.954	1.898	1.899	1.912
r(C–O)	1.119	1.150	1.158	1.159	1.149
D_e	− 50.8	2.3	− 7.0	− 7.0	10.8
D_e(corr)	− 27.5	− 1.4	− 0.1	− 1.0	− 2.4
ω(bend)	266	178			61
ω(Fe–CO)	296	425		414	410
ω(C–O)	2218	2352		2020	2075
			$^3\Sigma^-$		
	UHF	MP2	MCPF	CCSD(T)	DFT
r(Fe–C)	2.000	1.874	1.694	1.807	1.770
r(C–O)	1.114	1.149	1.175	1.160	1.154
D_e	− 59.2	− 5.5	− 8.3	− 9.3	13.3
D_e(corr)	− 35.9	− 9.2	− 1.4	− 3.3	0.1
ω(bend)	245	220			316
ω(Fe–CO)	266	436		489	455
ω(C–O)	2290	2370		1929	2031
CO					
r(C–O)	1.108	1.146	1.139	1.143	1.130
ω_e	2432	2110		2138	2213

DFT approach. It is possible to avoid this problem, by dissociating to Fe^+ $^4F(3d^7)$ and correcting this binding energy to the ground state asymptote using the experimental ^6D–^4F separation. This value is denoted D_e(corr) in the table. This improves the agreement between the DFT and other approaches, but the DFT value is still significantly larger. Using the DFT harmonic frequencies leads to a D_0 value of 31.0 kcal/mol at the DFT level. We note that this is in excellent agreement with our previous [7] best estimate of 30.7 kcal/mol and with experiment [23]. It is clear that DFT gives results superior to the MP2 approach.

The results for FeCO are summarized in Table 3. From experiment [24] it is known that the ground state is $^3\Sigma^-$ with the $^5\Sigma^-$ state lying 3.2 ± 0.7 kcal/mol higher in energy. The Fe–C distance in the $^3\Sigma^-$ state is 0.15 ± 0.04 Å shorter and the C–O distance 0.05 ± 0.02 Å longer than in the $^5\Sigma^-$ state. The vibrational frequencies are also known for the $^3\Sigma^-(^5\Sigma^-)$ state: $\nu(\text{C–O}) = 1950 \pm 10(1990 \pm 15)$, $\nu(\text{Fe–C}) = 530 \pm 10(460 \pm 15)$, and $\nu(\text{bend}) = 330 \pm 50(180 \pm 60)$ cm^{-1}. In our previous work we considered the $^5\Sigma^-$ state because it is better described by a single configuration reference. We then corrected the computed D_0 value for the $^5\Sigma^-$ state to that for the ground state using the experimental $^5\Sigma^-$–$^3\Sigma^-$ separation. In this work we extend our previous UHF, MP2, MCPF, and CCSD(T) treatments to include the $^3\Sigma^-$ state – see Table 3. UHF, MP2, MCPF, and CCSD(T) all incorrectly place $^3\Sigma^-$ above $^5\Sigma^-$, which is consistent with the fact that the $^3\Sigma^-$ state is harder to describe, and also supports our previous decision to use the $^5\Sigma^-$ state in conjunction with experiment to study FeCO. The UHF obtains an Fe–C distance that is longer and a C–O distance that is shorter than in the $^5\Sigma^-$ state; this is inconsistent with experiment. The MP2, MCPF, and CCSD(T) all yield an Fe–C distance that is shorter than in the $^5\Sigma^-$ state, however, the MP2 and CCSD(T) contractions are smaller than the experimental value [24], while that at the MCPF level is larger. The MP2 $^3\Sigma^-$ C–O frequency suffers from the same problem as that for the $^5\Sigma^-$ state, namely it is shifted to higher frequency relative to free CO instead of lower frequency. In fact the error in the MP2 is even larger for the $^3\Sigma^-$ than the $^5\Sigma^-$ state.

For DFT we consider the orbital occupations that correspond to both the $^3\Sigma^-$ and $^5\Sigma^-$ states. For the $^5\Sigma^-$ state, we find the geometry and Fe–C frequency to be in good agreement with the other approaches. Unlike the MP2, where the ω(C–O) shift relative to free CO has the wrong sign, the DFT shows a shift of -138 cm^{-1}, which is in good agreement with the CCSD(T) result of -118 cm^{-1} and the -153 ± 15 cm^{-1} found in experiment [24] (note that the computed values are harmonic frequencies, while experiment corresponds to fundamentals). The DFT bending frequency is only about 1/3 that at the MP2 level and is smaller than the somewhat uncertain measured fundamental. As for the $^5\Sigma^-$ state, the $^3\Sigma^-$ CO shift relative to free CO is in good agreement with experiment, which is a marked improvement over the MP2. Overall, the harmonic frequencies computed using the DFT approach are in reasonable agreement with the experimental fundamentals. The $^3\Sigma^-$ state is 2.5 kcal/mol below the $^5\Sigma^-$ state. The Fe–C bond length shows the expected shortening and the C–O the expected lengthening, however, the C–O increase is smaller than that found in experiment. Thus even though it is not rigorous to consider the DFT results for the two occupations as two states, the agreement with experiment is very good. While the geometry and frequencies at the DFT level seem quite acceptable, the binding energies are too small. On the basis of the $FeCO^+$ results we would have expected D_e to be too large and D_e(corr) to be much better. While the DFT D_e(corr) value agrees well with the CCSD(T) result in the same basis set, higher levels of theory increase the binding energy leading to our previous best estimate of 7.6 kcal/mol for D_0, which was in good agreement with the experimental values of 9.9 ± 3.7 [24] and 7.5 ± 3.5 kcal/mol [25] (note the experimental values have been converted to 0 K). Thus DFT behaves differently for $FeCO^+$ and FeCO, in the first case the binding energy agrees well with the best estimate, while in the second case it agrees better with the MCPF and CCSD(T) results in the same basis set.

The bonding in FeH_2O^+ is very simple, involving little to no donation between the metal and H_2O. The Fe^+ can either be in the $3d^64s^1$ occupation leading to the $^6A_1$ state of FeH_2O^+, where the 4*s* mixes in 4*p* character to reduce metal-ligand repulsion by polarizing away from the H_2O. The Fe^+ could also promote to the more compact $3d^7$ occupation which has a smaller overlap and hence smaller repulsion with the water. Previous MCPF calculations [26] found the $^4A_1$ state to be more strongly bound relative to the $^4F(3d^7)$ asymptote than the $^6A_1$ state is bound relative to the $^6D(3d^64s^1)$, but the $^4A_1$ state was higher in energy than the $^6A_1$ state. That is the reduced repulsion in the $^4A_1$ state does not cover the cost of the promotion energy to reach the $3d^7$ occupation. We consider the occupations associated with both states at the DFT level – see Table 4.

The DFT approach places the $^4A_1$ state 8.8 kcal/mol below the $^6A_1$ state. However, as noted above DFT is biased in favor of the $3d^7$ occupation. The D_e for

Table 4. Summary of the FeH_2O^+ results. The results for free H_2O are given for comparison. The bond lengths are in Å and the angles are in degrees. The harmonic frequencies are in cm^{-1}. The dissociation energy (in kcal/mol) is given with respect to Fe^+ $^6D(3d^64s^1)$

	$^6A_1$					$^4A_1$
	UHF	MP2	MCPF	CCSD(T)	DFT	DFT
FeH_2O^+						
r(Fe–O)	2.150	2.126	2.121	2.119	2.071	1.998
r(O–H)	0.951	0.972	0.970	0.972	0.974	0.970
∠(H–O–H)	107.4	106.4	106.6	106.5	107.6	108.0
D_e	29.7	31.7	32.1	32.2	34.6	43.4
D_e(corr)						33.8
ω(Fe–O stretch)	325	333			403	457
ω(Fe out-of-plane rock)	409	323			322	230
ω(Fe in-plane rock)	549	517			520	550
ω(HOH bend)	1784	1675			1638	1635
ω(O–H s-stretch)	4024	3750			3681	3741
ω(O–H a-stretch)	4110	3851			3772	3834
H_2O						
r(O–H)	0.944	0.965	0.964	0.966	0.964	0.964
∠(H–O–H)	106.1	103.5	103.8	103.6	104.8	104.8
ω(HOH bend)	1747	1654			1628	1628
ω(O–H s-stretch)	4129	3837			3806	3806
ω(O–H a-stretch)	4233	3956			3908	3908

the $^4A_1$ state is significantly larger than experiment [27–29], which suggests that it is not appropriate to directly compute the dissociation energy of this state to the Fe^+ ^6D asymptote. The D_e(corr) value for the $^4A_1$ state actually places it 0.8 kcal/mol above the $^6A_1$ state. This is the same as found at the MCPF level if the $^4A_1$ is computed using the D_e(corr) approach [26]. Thus the DFT results must be corrected for errors in atomic separation in the same manner as the MCPF results. The D_0 computed at the DFT level is 33.2 kcal/mol, which is in good agreement with our previous best estimate of 32.5 kcal/mol and with experiment: 30.6 ± 1.2 [27], 32.8 ± 4 [28], and 28.8 ± 3 kcal/mol [29].

The final example we consider is $FeCH_4^+$, which is summarized in Table 5. For the sextet states, derived from the $3d^64s^1$ occupation, the DFT yields slightly shorter Fe–C bond lengths than found at the MP2 or MCPF levels of theory. The DFT binding energies are slightly larger; this is consistent with the MCPF results that showed the binding energy increased by 2.7 kcal/mol with basis set improvement. The shorter bond length at the DFT level is consistent with the slightly larger binding energy at the DFT level, the difference between the DFT and CCSD(T) is probably larger than in other cases because of the flat Fe–C potential. The DFT approach yields the η^3 to be more stable than the η^2 structure, as in the other methods, but the DFT energy difference is a bit larger than in the other methods.

For the quartet states, which are derived from the Fe $3d^7$ occupation, the DFT approach yields bond lengths that are slightly shorter than the MCPF or CCSD(T) approaches. However, the DFT results are much superior to the MP2 that yields Fe–C bond lengths which are much too long. The DFT yields the η^3 structure to be more stable than the η^2; as with the sextet states, the energy difference is larger than

Table 5. Summary of the $FeCH_4^+$ results. The Fe–C bond length is in Å. The dissociation energy (in kcal/mol) is given with respect to Fe^+ $^6D(3d^64s^1)$. The values in square brackets are taken from the MP2 and not optimized

	UHF	MP2	MCPF	CCSD(T)	DFT
Fe^+ $3d^64s^1$ η^2					
r(Fe–C)	2.880	2.690	2.694	[2.690]	2.622
D_e	3.5	7.3	7.6	8.1	10.2
Fe^+ $3d^64s^1$ η^3					
r(Fe–C)	2.753	2.573	2.572	[2.573]	2.490
D_e	4.13	7.8	8.0	8.4	11.4
Fe^+ $3d^7$ η^2					
r(Fe–C)		2.516	2.386	2.292	2.222
D_e		−8.7	5.7	3.5	24.0
Fe^+ $3d^7$ η^3					
r(Fe–C)	2.607	2.386	2.162	2.124	2.107
D_e	−13.8	8.4	6.5	4.4	25.5
D_e(corr)	18.5	−10.0	11.1	6.9	16.0

found at the MCPF or CCSD(T) levels. As for the quartet state of FeH_2O^+, the directly computed binding energy is much too large. If the binding energy is computed with respect to ^4F and corrected to the ground state asymptotes using the experimental separation, the binding energy is much smaller. As was found using the MP2 frequencies, there is essentially no (0.02 kcal/mol) zero-point contribution to the binding energy. The DFT D_0 value of 16.0 kcal/mol is in good agreement with our previous best estimate of 14.0 kcal/mol (note this value supersedes our previous value, which was slightly in error) and with experiment [30] (13.7 ± 0.8 kcal/mol). The agreement between the DFT D_0 value and that obtained at higher levels of theory is good, and much better than that obtained at the MP2 level of theory.

4. Conclusions

DFT (using the B3LYP functional) gives a much better zeroth-order description of the systems considered in this work than the MP2 approach. DFT correctly predicts the direction of the shift in the CO frequency between free CO and in the $^5\Sigma^-$ state of FeCO. DFT also yields good Fe–C distances for the quartet states of $FeCH_4^+$. Both of these properties were determined poorly at the MP2 level. It is important to consider which atomic occupation the bonding is being derived from and to compute the dissociation energy in a manner that minimizes the difference in the metal atom between equilibrium and infinite separation. This approach has been used extensively in traditional approaches and must be used in DFT. The energetics at the DFT level are in very good agreement with experiment and the best estimates obtained from high levels of theory for $FeCO^+$, FeH_2O^+, and $FeCH_4^+$. However, for FeCO DFT yields a binding energy that is too small. Overall DFT appears to be a much better method than MP2 to determine the geometry and zero-point energies for systems containing first transition row atoms.

This is especially pleasing considering that the DFT approach uses significantly less computer resources that MP2. The DFT is clearly much better than the MP2 for energetics, and the DFT approach in a modest sized basis set appears to yield quite reasonable results. However, the DFT method is not yet a replacement for highly accurate calculations.

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