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Communication: Evaluating non-empirical double hybrid functionals for spin-state energetics in transition-metal complexes

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The computationally assisted, accelerated design of inorganic functional materials often relies on the ability of a given electronic structure method to return the correct electronic ground state of the material in question. Outlining difficulties with current density functionals and wave function-based approaches, we highlight why double hybrid density functionals represent promising candidates for this purpose. In turn, we show that PBE0-DH (and PBE-QIDH) offers a significant improvement over its hybrid parent functional PBE0 [as well as B3LYP* and coupled cluster singles and doubles with perturbative triples (CCSD(T))] when computing spin-state splitting energies, using high-level diffusion Monte Carlo calculations as a reference. We refer to the opposing influence of Hartree-Fock (HF) exchange and MP2, which permits higher levels of HF exchange and a concomitant reduction in electronic density error, as the reason for the improved performance of double-hybrid functionals relative to hybrid functionals. Additionally, using 16 transition metal (Fe and Co) complexes, we show that low-spin states are stabilised by increasing contributions from MP2 within the double hybrid formulation. Furthermore, this stabilisation effect is more prominent for high field strength ligands than low field strength ligands. *Published by AIP Publishing.* https://doi.org/10.1063/1.5019641

The prediction of spin-state ordering in transition metal complexes is essential for understanding many forms of catalysis,[1,2] including biological processes, and magnetic behaviour.[3,4] The accelerated design of functional materials within these domains through computational prediction relies on the ability of a given electronic structure method to return the correct electronic ground state of the complex in question.[5] Moreover, the ability to be able to provide an accurate estimate of the spin-state splitting energy itself would be invaluable, potentially leading to the computationally-driven identification of materials able to respond to mild external stimuli.

Its computational viability for many applications means that approximate Density Functional Theory (DFT) is used extensively to calculate such properties,[6–12] though the changeable performance of different classes of density functionals with respect to their formulation calls their reliability into question. Such property-formulation relationships have been highlighted in several recent studies.[6,7,13,14] The well-known over-delocalisation of semi-local Generalized Gradient Approximations (GGA) leads to the over-stabilisation of low-spin electronic configurations, while the incorporation of Hartree-Fock (HF) exchange within hybrid density functionals instead favours high-spin states. Both the over-stabilisation of low-spin states by GGA functionals and the extent to which this is curtailed by hybrid functionals are subject to ligand-field strength, with complexes containing strong-field ligands demonstrating greater bias towards low-spin states and larger variability in adiabatic spin-splitting energies with respect to functional formulation. By applying electron densities obtained through HF to various density functionals, this variability has been shown, in part, to be a result of the over-delocalised electron density produced by both GGA functionals and by hybrid functionals with admixtures of HF-exchange in the region of 10%–25%.[15] Simply applying hybrid density functionals with larger amounts of HF exchange does not solve the problem, since the concomitant stabilisation of configurations with greater numbers of like-spin electrons leads to unphysical high-spin ground state multiplicities for even the strongest-field ligands.[13] Together, these observations highlight a great challenge at the heart of applying DFT to transition metal complexes, namely, that increasing the HF exchange contribution in hybrid density functionals reduces error in electron density but, at the same time, increases error in the density functional itself.[15]

In this context, double hybrid density functionals,[16,17] which exhibit admixtures of both HF exchange and non-local correlation, are well-positioned to at least partially resolve this dilemma. The incorporation of non-local correlation permits higher admixtures of HF-exchange without artificial stabilisation of high-spin states and, in doing so, allows the use of more HF-like densities free from self-interaction error. Indeed, the B2PLYP[16] double-hybrid functional has previously been identified as a promising candidate for estimating the correct electronic ground state of a range of metal complexes.[18]

As an aside, it is worth mentioning that, due to the multireference character of such complexes, methods used to

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recover dynamic correlation based on complete active space self-consistent field (CASSCF) wave functions have shown promising results,[11,19] though their inherent computational cost precludes their application to both large systems and to systems which require large numbers of active orbitals.[20]

Furthermore, application of pair-density functional theory applied *a posteriori* to multiconfigurational wave functions obtained at the CASSCF level has been shown to reduce computational cost by eliminating the multiconfigurational perturbation theory step,[21] although the need for *a priori* CASSCF calculation, and the associated computational cost, remains.

Despite the identification of double-hybrid functionals as promising candidates for the calculation of spin-state ordering in transition metal complexes, no work has yet been undertaken to understand their behaviour in this context. Furthermore, the recent publication of reliable high-level calculations performed on model complexes[15] raises the possibility of explicit performance testing.

This work seeks to define the performance of double-hybrid functionals (DHs) in calculating spin-state energetics of transition metal complexes, here represented by model octahedral iron and cobalt complexes. We have used PBE0-DH[21] as a base double-hybrid model, varying contributions from HF exchange and non-local correlation to assess the sensitivity of spin-state splitting to these parameters. Relationships between these sensitivities and ligand field strengths of the coordinating ligands are identified, namely, that strong field ligands are more sensitive than weak field ligands to changes in HF exchange and non-local correlation contributions. Finally, we evaluate the accuracy of PBE0-DH and of another non-empirical DH, PBE-QIDH,[25] in evaluating adiabatic spin-splitting energies by comparing to recently reported diffusion Monte Carlo benchmark values.[15]

In addition to the HF exchange introduced within global hybrid density functionals, the double-hybrid approach introduces a fraction of second-order Møller-Plesset (MP2) correlation,[22] leading to the general expression for a given double-hybrid density functional approximation,

$$E_{XC}^{DH}\left[\rho\right] = a_x E_x^{HF} + \left(1 - a_x\right) E_x^{DFA}\left[\rho\right]$$
$$+ \left(1 - a_c\right) E_c^{DFA}\left[\rho\right] + a_c E_c^{MP2},$$

where E_x^{HF} is the Hartree-Fock exchange energy and E_x^{DFA} and E_c^{DFA} are the density functional approximations (DFAs) to the exchange and correlation energy. As is generally done in the case of hybrid density functionals, the first three terms in the expression above are determined via a self-consistent field calculation. In contrast, the final term is applied *a posteriori* as an on-top correction computed using the Kohn-Sham orbitals effectively obtained at the global hybrid level.[16] The optimal contributions of MP2 and HF to the overall functional formulation have been derived both empirically[16,23] and non-empirically.[21,24]

All calculations have been performed using Gaussian 09.[25] For each of the octahedral complexes shown in Fig. 1, geometry optimisations were carried out using the PBE0 hybrid density functional[26] in combination with the def2-TZVPP[27] basis set. Vibrational frequencies were calculated for
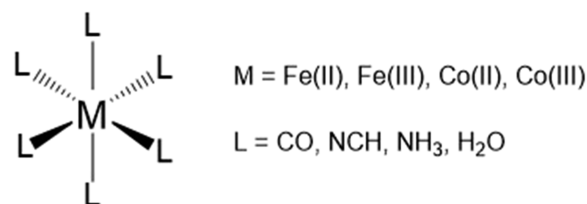

FIG. 1. Transition metal complexes studied in this work.

each of the structures obtained, ensuring the absence of any imaginary frequencies. Energies were obtained using modified forms of PBE0-DH, varying both the contribution of HF exchange (HFX%) and non-local correlation (MP2%). We focus on the PBE0-DH[21] model due to the possibility to straightforwardly tune these parameters, an option not necessarily available for other double-hybrid density functionals. In line with previous works on one-parameter DHs,[28,29] the range of HFX% and MP2% values studied was given by the relationships $a_c = a_x^2$ and $a_c = a_x^3$.

To calculate adiabatic spin-splitting energies, each complex is structurally optimized at both their high- and low-spin electronic configurations, that is, singlet and quintet states for Fe(II) and Co(III) complexes, doublet and sextet states for Fe(III) complexes, and doublet and quartet states for Co(II) complexes. No symmetry constraints are used during these optimisations. For each metal ion, four different ligands of varying ligand field strength are tested (in descending order of ligand field strength: CO, NCH, NH$_3$, and H$_2$O). In addition to PBE0-DH, energies were also calculated using the parent generalized gradient approximation functional PBE[30] and hybrid PBE0[26] functional, as well as using the PBE-QIDH[25] double hybrid model. In addition, B3LYP*,[31] where the amount of HF exchange is parametrised to 15% with the aim of producing better spin splitting energies, and M06-L,[32] a parameterised meta-GGA functional, have also been tested for comparison.

2D contour plots generated by varying HFX% and MP2% of the base PBE0-DH model computed for selected Fe(II) and Fe(III) complexes are shown in Fig. 2. As a guide to the eye, dashed lines indicate the points fulfilling the quadratic and cubic relations between a_c and a_x.[28,29] Comparing CO, NH$_3$, NCH, and H$_2$O ligands, we recover the well-established stabilisation of high-spin states with increasing HFX%, as well as differences in sensitivity to HFX% between ligands with high and low ligand field strengths. CO is most sensitive to changes in HFX%, while H$_2$O is the least sensitive, shown by the reduction in contour line density with decreasing ligand field strength. As has been previously discussed, this is a reflection of different metal-ligand bonding modes. A good π-acceptor such as CO is most affected by HFX%: as the self-interaction error is reduced in orbitals of π-symmetry, these orbitals are destabilized by increasing HFX% and the overall ligand-field strength is reduced, resulting in lower values of ΔE_{H-L}. On the other hand, good π-donors (NCH, H$_2$O) are less affected due to the increased population of more localized, antibonding d-orbitals upon ligand-to-metal donation.

From Fig. 2, it is clear that increasing MP2% leads to a stabilisation of low-spin electronic configurations, reflected
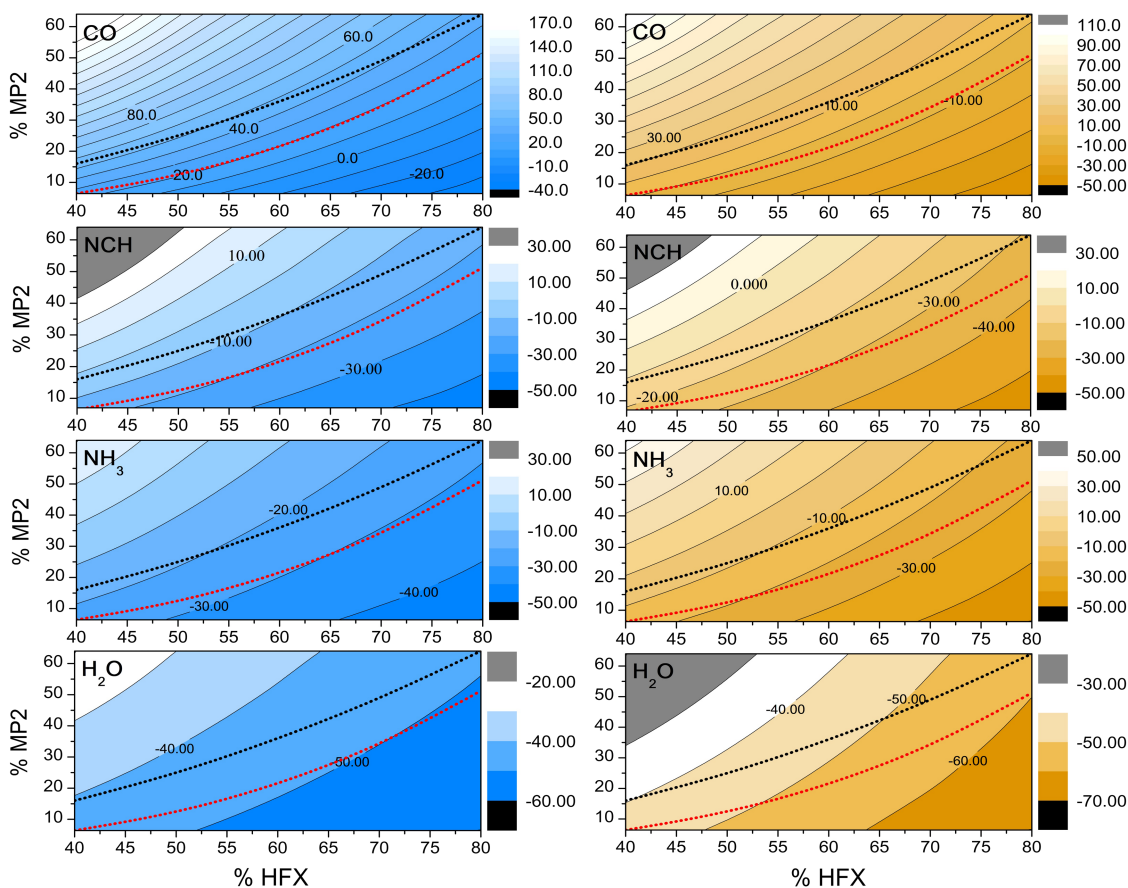
FIG. 2. Spin-state splitting, $\Delta E_{HS/LS}$, in kcal/mol as a function of both %HF exchange (%HFX, x-axis) and %MP2 contribution (%MP2, y-axis). Each ligand in the $[Fe(L)_6]^{2/3+}$ test set is shown, with results for Fe(II) and Fe(III) complexes shown by blue and orange contour plots, respectively. The spin-state splitting value is coloured according to the colour bar shown on the right of each plot. Additionally, dashed lines indicate the relationships $a_c = a_x^2$ (black) and $a_c = a_x^3$ (red).

in the increasing ΔE_{H-L} at fixed HFX%. Here we also show that different ligands respond differently to changes in MP2%. Analogously to HFX%, the sensitivity decreases with decreasing ligand field strength. Intuitively, this can be rationalised by the more compact structures produced by high-strength ligands compared to low-strength ligands giving rise

to more stable low-spin configurations. As one might expect, approaching an MP2 contribution of 100% at low values (<50%) of HFX% results in a catastrophic failure to repro-duce the expected ground state electronic configuration of complexes containing NH₃ and NCH, while ΔE_{H-L} for com-plexes containing CO is greatly overestimated. Analogous
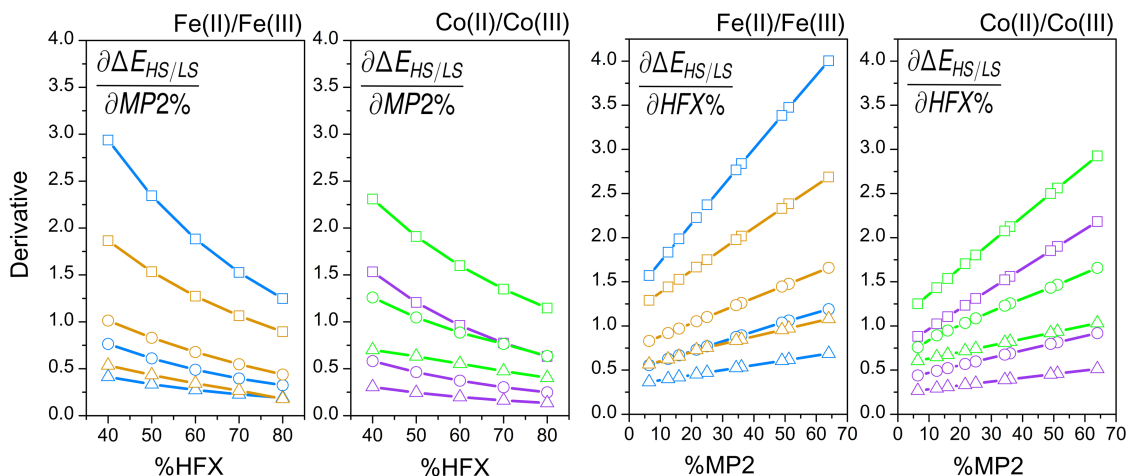

FIG. 3. Plot of the absolute derivative of the adiabatic spin-state splitting energy with respect to %MP2 as a function of %HFX (left), and with respect to %HFX as a function of %MP2 (right). Results for Fe(II) and Fe(III) complexes are shown in blue and yellow, respectively, while results for Co(II) and Co(III) complexes are shown in purple and green, respectively. Ligands CO, NH₃, and H₂O are symbolised with hollow squares, circles, and triangles, respectively.
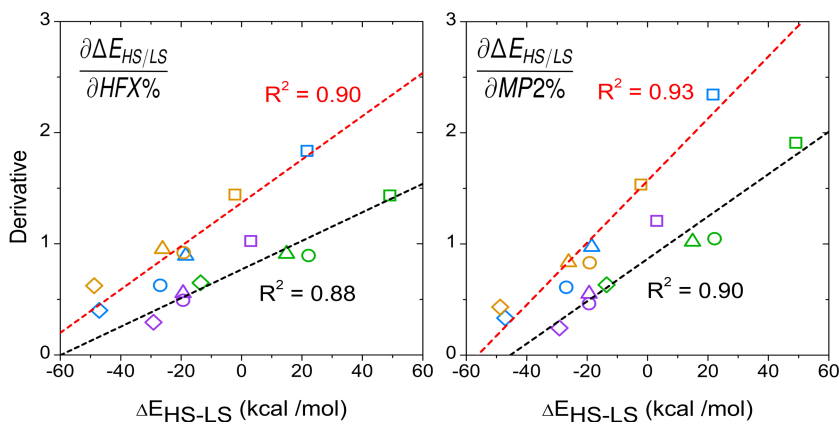
FIG. 4. Plot of the derivative of adiabatic spin-state splitting energy with respect to HFX% (left) and MP2% (right) as a function of the computed adiabatic spin-splitting energy, $\Delta E_{HS/LS}$. Dashed lines show the results of least-squares regression fits performed separately for Fe- and Co-based complexes. The adjusted R^2 values for these fits are also given. Spin spitting values and derivatives are those computed using PBE0-DH (i.e., with HFX% = 50% and MP2% = 12.5%). Squares: CO; circles: NH$_3$; triangles: NCH; diamonds: H$_2$O. Fe$_{II}$: blue; Fe$_{III}$: orange; Co$_{II}$: purple; Co$_{III}$: green.

plots are given in the supplementary material for Co(II) and Co(III) complexes.

The interplay between HFX% and MP2% parameters can be understood by plotting the derivative of ΔE_{H-L} with respect to one parameter as a function of the other, as is shown in Fig. 3. The negative derivative of ΔE_{H-L} with respect to HFX% reflects the stabilisation of high-spin states with increasing HFX%, while the positive derivative with respect to MP2% indicates the inverse with respect to increasing MP2%. The differences in the response of ligands of different ligand field strengths to MP2% and HFX% described above are also reflected. Additionally, the relative sensitivity of different ligands to changes in functional formulation is preserved at all values of HFX% and MP2%. It is noteworthy that differences in sensitivity between ligands to HFX% increases with MP2%, while differences in sensitivity between ligands to MP2% decreases with increasing HFX%. Additionally, the derivative of ΔE_{H-L} with respect to HFX% increases linearly with MP2%, while the reduction in the derivative with respect to MP2% reduces with increasing HFX%. Together, these observations indicate an unexpectedly complex interplay between HFX% and MP2% for the calculation of ΔE_{H-L}, demonstrating that altering one parameter cannot be expected to yield the same effect on ΔE_{H-L} at all other values of the other, a phenomenon that could have significant consequences for functional tuning.

Next, we look at the relationship between ΔE_{H-L} and the absolute derivatives of both HFX% and MP2% (Fig. 4). Here we show that, at least for a given transition metal,

the relationship between the sensitivity of ΔE_{H-L} to both HFX% and MP2% is near linear, with derivatives of ΔE_{H-L} with respect to HFX% and MP2% increasing linearly with ΔE_{H-L}. These observations reflect the correlation between the sensitivity to density functional composition and ligand field strength.

The linear fits performed show a distinct change in slope with respect to the transition metal, with Fe-based complexes inherently more sensitive to changes in both HFX% and MP2% than cobalt-based complexes. Furthermore, changes in the formal charge of the transition metal in question do not seem to cause significant deviation from the linear fit.

To assess the performance of DHs, we used as reference accurate spin splitting energies derived from diffusion Monte Carlo (DMC) calculations for the Fe(II) complexes recently published.[15] Table I summarizes the adiabatic spin splitting energies calculated using PBE0-DH (i.e., with HFX% = 50% and MP2% = 12.5%) and PBE-QIDH[24] (i.e., with HFX% = 70% and MP2% = 33.3%) alongside the parent global hybrid (PBE0)[26] and GGA (PBE)[30] functionals. As expected, PBE suffers from gross over-stabilisation of low spin states, yielding a MAE of 1.71 eV. While PBE0 performs significantly better, with a reduced MAE of 0.47 eV, PBE0-DH offers a significant further improvement (MAE = 0.26 eV), while PBE-QIDH performs slightly better still (MAE = 0.24 eV). Notably, we show that the double hybrid functionals tested also outperform the parametrised B3LYP* and M06-L functionals, as well as coupled cluster singles and doubles with perturbative triples (CCSD(T)). These results can be rationalised from

TABLE I. Calculated ΔE_{H-L} values (in eV) for all Fe(II) complexes studied, computed using GGA (PBE), meta-GGA (M06-L), global hybrid (PBE0, B3LYP*), and double-hybrid (PBE0-DH, PBE-QIDH) functionals. These are compared with known values obtained using high-level Diffusion Monte Carlo (DMC) as well as CCSD(T) calculations.[15] In each case, the MAE of ΔE_{H-L} computed with each functional for each complex is given, relative to the DMC benchmark values.

	PBE	PBE0	B3LYP*	M06-L	CCSD(T)[a]	PBE0-DH	PBE-QIDH	DMC[a]
Fe$_{II}$(CO)$_6$	3.45	1.36	1.79	1.77	1.33	0.94	0.88	0.59
Fe$_{II}$(NCH)$_6$	0.97	−0.40	0.14	0.08	−0.43	−0.80	−0.95	−1.17
Fe$_{II}$(NH$_3$)$_6$	0.05	−0.86	−0.38	−0.21	−0.78	−1.17	−1.31	−1.23
Fe$_{II}$(H$_2$O)$_6$	−1.19	−1.78	−1.55	−1.73	−1.75	−2.05	−2.16	−1.78
MAE vs. DMC	1.71	0.47	0.89	0.87	0.49	0.26	0.24	⋯

[a]From Ref. 15.

Figs. 2–4, in which the demonstrated sensitivity of ΔE_{H-L} to HFX% underlines the previously identified "density-driven error"[15] inherent in these types of metal complexes. It has been shown that the use of HF densities greatly reduces this error, an observation that chimes with the significantly improved performance of PBE0-DH and PBE-QIDH over PBE0, B3LYP*, and PBE. Compared with global hybrids such as PBE0, the formulation of double-hybrid functionals affords the possibility to use far greater fractions of HF exchange, thereby reducing the density driven error and yielding more accurate adiabatic spin splitting energies. This suggests that double-hybrid functionals should offer significant performance improvements over other density functional approximations in other situations where density driven error is prevalent. Finally, the effect of double hybrids on electronic density within these complexes can be visualised through density difference plots, given in the supplementary material in the case of the $[Fe(CO)_6]^{2+}$ complex. When PBE0-DH is used (relative to PBE0 and PBE), we show that density migrates towards the metal ion from the CO ligands along with the concomitant loss of density from $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals. This behaviour is indicative of reduced delocalisation of electronic density with increasing levels of HF exchange, and the latter has been speculated to be the reason for the improved quality of spin-splitting energies computed using HF-like densities over those computed with GGA and hybrid density functionals.[15]

To conclude, analysing the sensitivity of adiabatic spin-splitting energies of 16 octahedral TM complexes to parameter changes in PBE0-DH-based double-hybrid density functionals, we have shown that, in addition to the long-established stabilisation of high-spin states with increasing levels of Hartree-Fock exchange, low-spin states are stabilised by increasing contributions from MP2. Furthermore, this stabilisation effect is more prominent in high field strength ligands than low field strength ligands. Most importantly, we have shown that PBE0-DH (and PBE-QIDH) offers a significant improvement over its hybrid parent functional PBE0 when computing spin-state splitting. We point to the opposing influence of HF exchange and MP2 permitting higher levels of HF exchange and a concomitant reduction in density error as the reason for the improved performance of double-hybrid functionals relative to hybrid functionals. Due to the relatively affordable nature of double-hybrid functionals, we envisage their potential in the upper tiers of multi-level high throughput screening approaches for accelerated inorganic materials discovery, as well as an attractive, general alternative to more costly, wave function-based methods for the computation of spin-state energetics.

See supplementary material for computed spin splitting energies for all iron and cobalt complexes studied, plots of spin-state splitting, as a function of both %HF exchange and %MP2 contributions for cobalt complexes, computed spin state splitting energies at PBE, PBE0, B3LYP*, and M06-L, and density difference plots for the singlet $[Fe(CO)_6]^{2+}$ complex are provided together with Cartesian coordinates of all systems studied.

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