Supplementary Information for

# Systematic Improvement of Redox Potential Calculation of Fe(III)/Fe(II) Complexes Using a Three-Layer Microsolvation Model

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**Figure S1:** Absolute errors in redox potential calculations of Fe(III) redox potentials using different functionals. The orange bars show values for  $Fe^{+2/+3}[H_2O]_6$  structures optimized in gas phase with corrected single point calculations in implicit water continuum. Blue and green bars show results from our model with the inclusion of additional 12 waters ( $Fe^{+2/+3}[H_2O]_6.(12H_2O)$ ), and 30 water molecules ( $Fe^{+2/+3}[H_2O]_6.(12H_2O).(18H_2O)$ ), respectively.

#### **Text S1: Code and Structures Availability**

The code and structures used in this study are available at <u>https://github.com/HassanHarb92/solvation\_shells/paper\_materials</u>. Within this repository, the codes folder contains the following Python scripts:

- 1. **Hydration\_shell\_radius.py**: This script places spherical layers of water molecules around a given structure at a radius calculated as radius = max\_distance+ 1.5. It reads in optimized structure coordinates (.xyz) and generates one or more solvation shells at specified radii.
- 2. **run\_multiple\_xtb.py**: This script generates water layers around a structure and performs xTB calculations on the water molecules while freezing the coordinates of the main structure. It repeats the process twice to simulate multiple solvation layers.

Additionally, the structures folder in the main repository contains the .xyz structures of all the complexes used in this study.

The repository also includes a **web\_app** folder with stream\_app.py, a web application that visualizes the molecules in 3D within a web browser, providing an interactive view of the structures and solvation shells.

All results, energies, and structures related to this study can be found in the repository under **solvation\_shells/results**.

Parameter	Setting/Value	Details
SCF Convergence	$1 \times 10^{-8}$ hartree	SCF converged to 10 <sup>-8</sup> hartree
SCF Convergence Enhancement	QC requested if SCF fails to converge	Utilizes QC procedures when needed
Maximum SCF Cycles	500	Ensures robust SCF convergence
Optimization Maximum Steps	500	Maximum number of optimization steps
Optimization Coordinates	Cartesian	Optimization performed in Cartesian coordinates
Second Derivative Matrix	Calculated analytically	Ensures reliable determination of Hessian matrix
Fine Grid Accuracy	Energy: 1×10 <sup>-7</sup> , Gradient: 1×10 <sup>-6</sup>	Enhanced grid accuracy for DFT calculations
Force Thresholds	Maximum Force: 0.000450; RMS Force: 0.000300	Convergence criteria for forces
Displacement Thresholds	Maximum: 0.001800; RMS: 0.001200	Convergence criteria for displacements

 Table S1: Computational details including convergence criteria and optimization settings.

Text S2: Notes on computational methods:

#### A. Dispersion

When a given functional–dispersion pairing was not implemented or not well-parameterized in Gaussian, we performed single-point calculations in ORCA<sup>1</sup> to include missing dispersion corrections (e.g., D3BJ or D4). To keep the geometry consistent, we started from the B3LYP-optimized  $[Fe(H_2O)_6]^{2+/3+}$  structures in Gaussian and then varied only the electronic energy evaluation in ORCA. This strategy avoids any discrepancies that could arise from different optimization criteria between the two software packages. In total, we tested B3LYP-D3BJ, B3LYP-D4,  $\omega$ B97M-D3BJ,  $\omega$ B97M-D4,  $\omega$ B97M-V,  $\omega$ B97X-D3,  $\omega$ B97X-D3BJ,  $\omega$ B97X-D4, and  $\omega$ B97X-V across one-, two-, and three-layered Fe systems.<sup>2–7</sup> We used the 6-31+G(2df,2p) basis set in CPCM implicit solvation model with water as a dielectric.

Figure S2 shows that adding more explicit water molecules (from 6 to 18 and then 36) consistently reduces the redox potential errors across these newer functionals and dispersion corrections, mirroring the trend observed in Figure S1. Notably, the initial errors with 6 waters are in the 1.94 - 2.37 V range but drop to 0.01 - 0.25 V upon including a second solvation sphere (18 waters), and stabilize around 0.01 - 0.31 V with the third solvation sphere (36 waters). Most functionals exhibit significant improvement under enhanced solvation, although B3LYP-D3BJ and B3LYP-D4 remain higher at 0.31 V and 0.29 V errors, respectively, even with three-layer solvation. By contrast, the  $\omega$ B97(M/X) family paired with various dispersion corrections shows notably better accuracy, achieving final errors in the 0.01 - 0.13 V range with the full (36-water) micro-solvation model.

Although the original D3 correction was primarily developed for gas-phase or explicit-solvent calculations, many researchers (including us) combine it with implicit solvation models (e.g., CPCM) in practice.<sup>8–12</sup> The dispersion term still refines the electronic structure by accounting for long-range interactions between the solute and its immediate environment, even when the bulk solvent is treated implicitly. Indeed, Grimme and co-workers recommend that dispersion corrections be routinely included in all DFT calculations.<sup>13</sup>

#### B. On functionals performances and different flavors of B3LYP:

In Figure S1, we benchmark a range of functionals (e.g., B3LYP, PBE, M06, M08-HX, B3PW91) using our one-, two-, and three-layer micro-solvation protocol. We observe two key trends. First, increasing the explicit solvation from 6 to 36 waters significantly reduces redox potential errors, highlighting how more extensive solvation effectively captures hydrogen-bonding and electrostatic interactions in Fe(II)/Fe(III) complexes. Second, certain functionals—such as B3LYP and PBE—exhibit relatively modest errors ( $\sim 0.1-0.3$  V) once fully solvated, whereas others, notably M08-HX and B3PW91, still retain higher inaccuracies even when additional solvent layers

are included. These discrepancies likely result from differences in how each functional handles exchange-correlation in high-spin d-electron systems, as well as over- or under-localization that may persist despite explicit solvation.

In Figure S2, we shift focus to newer functionals—including  $\omega$ B97M and  $\omega$ B97X families—paired with advanced dispersion corrections such as D3BJ, D4, and "–V." Once again, adding more solvation (from 6 to 36 waters) leads to pronounced improvements, reducing errors from above 2.0 V (one-layer solvation) to under 0.3 V (three-layer solvation). Moreover, the  $\omega$ B97(M/X)–V series and their D3BJ/D4 analogues generally achieve very low final errors (~0.01–0.13 V) under three-layer conditions, suggesting that range-separated hybrid approaches with robust dispersion corrections are highly effective for modeling Fe redox chemistry. By contrast, B3LYP-D3BJ and B3LYP-D4 benefit from the added solvent shells but still do not match the performance of the  $\omega$ B97 family, implying that B3LYP's fraction of exact exchange and older correlation treatment can limit its accuracy in certain high-spin cases.

Overall, Figures S1 and S2 underscore two central insights: (1) incorporating multiple explicit solvation layers is essential for capturing the correct redox energetics, and (2) modern, dispersion-corrected functionals can outperform traditional GGA or hybrid methods for challenging delectron systems like Fe(II)/Fe(III). Consequently,  $\omega$ B97-type methods with D3/D4 or "–V" corrections, in conjunction with two or three layers of solvation, emerge as promising strategies for balancing computational efficiency and predictive reliability in redox potential calculations.

We note that in this study, the B3LYP functional is employed as implemented in Gaussian, which uses the VWN III parameterization for local correlation. Specifically, Gaussian's B3LYP combines Becke's 1988 exchange, Lee–Yang–Parr (LYP) non-local correlation, and the Vosko–Wilk–Nusair (VWN) functional III, which fits the random-phase approximation (RPA) solution to the uniform electron gas. In contrast, other software packages (e.g., Turbomole, ORCA) may adopt the VWN5 parameterization (functional V), which fits the Ceperley–Alder solution to the uniform electron gas. Because these parameterizations differ, the results from "B3LYP" can vary slightly depending on whether VWN III or VWN5 is used. Further details on these functionals can be found in the original VWN publication.<sup>14</sup>

C. Approach in water placements:

# 1. Spherical Radii Selection:

We define two spherical shells at **4.5** Å and **6.5** Å from the iron center, guided by known Fe–O distances in prior literature. In this range, **12 water molecules** for the inner shell and **18 water molecules** for the outer shell provide enough local solvent to capture **hydrogen bonding and electrostatic interactions** without excessively increasing the computational cost.

2. Heuristic Water Count:

Rather than using a purely surface-area-based calculation-which could lead to

substantially more water molecules and a correspondingly greater complexity—we rely on the **linear factor approach** ( $3 \times$  the integer part of the radius). This ensures a reasonable distribution of water molecules on the spherical surface, avoiding overpopulation and the challenging optimization of many additional degrees of freedom.

3. Trade-off between Accuracy and Efficiency:

While a strict  $r^2$  rule might better reflect the full theoretical surface coverage, it would **significantly amplify the number of water molecules** and require an exhaustive search among numerous possible local minima. Our simpler approach, meanwhile, **provides a representative micro-solvation environment** and yields good agreement with experimental redox potentials (Table 2). Hence, we consider it to be a balanced strategy.

### 4. Validation via Experimental Correlation:

The fact that our model **matches measured redox potentials** within acceptable error margins (e.g.,  $\sim 0.02-0.09$  V for Fe<sup>3+/</sup>Fe<sup>2+</sup> with B3LYP) supports the notion that a fully surface-area-proportional shell is not strictly necessary for capturing the critical solute–solvent interactions.

### D. Spin-entropy:

To discuss the contribution of spin-entropy, we start by defining the total degeneracy as:  $\Omega = (2S + 1) \times d$ 

where S is the total spin quantum number and d is an additional degeneracy factor.

For high-spin  $[Fe(H_2O)_6]^{2+}$  (Fe<sup>2+</sup>):

• S = 2 and d = 3, so:  $\Omega_{Fe(II)} = (2 \times 2 + 1) \times 3 = 5 \times 3 = 15$ 

For high-spin  $[Fe(H_2O)_6]^{3+}$  (Fe<sup>3+</sup>):

• S = 2.5 and d = 1, so:  $\Omega_{Fe(III)} = (2 \times 2.5 + 1) \times 1 = 6 \times 1 = 6$ 

The spin entropy is given by:  $S_{spin} = R \times ln(\Omega)$  where R is the gas constant.

Thus, the difference in spin entropy between Fe<sup>2+</sup> and Fe<sup>3+</sup> is:  $\Delta S_{spin} = R \times \ln(\Omega_{Fe(II)}) / \Omega_{Fe(III)}) = R \times \ln(15/6) = R \times \ln(2.5)$ 

At temperature T, the corresponding free energy contribution is:  $\Delta G_{spin} = -T \times \Delta S_{spin} = -T \times R \times ln(2.5)$ 

Using the Nernst equation, the change in redox potential is given by:

 $\Delta E = -\left(\Delta G_{\rm spin}\right) / (nF)$ 

For a one-electron transfer (n = 1), this becomes:  $\Delta E = (T \times R \times ln(2.5)) / F$ 

Substituting numerical values (R =  $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , T = 298 K, F = 96485 C·mol<sup>-1</sup>):  $\Delta E = (298 \times 8.314 \times 0.9163) / 96485 \approx 0.0235 \text{ V}$ 

Thus, the spin-entropy correction corresponds to a shift of approximately 23.5 mV in the redox potential.

Although the spin-entropy correction corresponds to a shift of only about 23.5 mV, this value is well below the threshold typically considered to be chemical accuracy (~1 kcal/mol, or  $\approx$ 43 mV). Thus, the correction is minor compared to the overall uncertainties in our redox potential calculations.



**Figure S2:** Structural comparison of salicylate complexes with increasing numbers of explicit water molecules (top to bottom: first, second, and third water spheres) before (left) and after (right) geometry optimization. The images illustrate the reorganization of solvent molecules, with visible hydrogen-bond rearrangements and enhanced structuring around the salicylate core following optimization.

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