Supplementary Material: Effective yet Reliable Computation of EPR Spectra in Solution by a QM/MM Approach: Interplay Between Electrostatics and Non-electrostatic Effects

Tommaso Giovannini,[*,†] Piero Lafiosca,[†] Balasubramanian Chandramouli,[†,‡] Vincenzo Barone,[†] and Chiara Cappelli[*,†]

†*Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy.*

‡*Compunet, Istituto Italiano di Tecnologia (IIT), Via Morego 30, 16163 Genova, Italy.*

E-mail: tommaso.giovannini@sns.it; chiara.cappelli@sns.it

S1 Geometries in vacuo

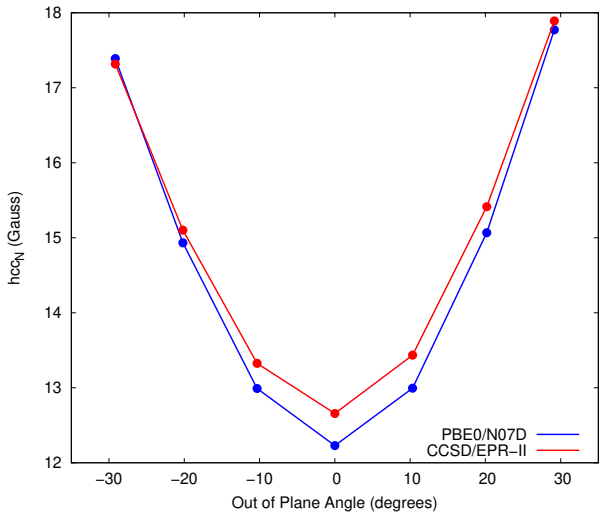

Figure S1: PBE0/N07D and CCSD/EPR-II hcc$_N$ values (Gauss) on the reduced TEMPO structure as a function of the out of plane $C_\alpha NOC_\alpha$ angle.

Table S1: Selected geometrical parameters of PROXYL and TEMPO radicals at the different levels of theory with the inclusion of Grimme empirical dispersion D3. BS1: aug-cc-pVDZ; BS2: 6-311++G(3dp,2pd).

		PBE0 + D3		B3LYP + D3	
	Parameter	BS1	BS2	BS1	BS2
PROXYL	N–O	1.262	1.257	1.274	1.267
	$\angle C_\alpha NC_\alpha$	115.2	115.1	115.2	115.1
	$C_\alpha NOC_\alpha$	±0.0	±0.0	±0.0	±0.0
TEMPO	N–O	1.271	1.265	1.283	1.277
	$\angle C_\alpha NC_\alpha$	124.9	124.0	124.0	124.1
	$C_\alpha NOC_\alpha$	±22.7	±22.1	±22.7	±22.1

S2 Energy Decomposition Analysis

Table S2: PROXYL+2w EDA obtained by expoiting PBE0/FQ with different parametrizations and SAPT0. CCSD(T) calculations include Counter-Poise corrections. All data are reported in mHartree.
[a] FQ parametrization taken from Ref.[1]
[b] FQ parametrization taken from Ref.[2]
[c] FQ parametrization proposed in this work

	jun-cc-pVDZ					N07D				
	FQ[a]	FQ[b]	FQ[c]	SAPT0	CCSD(T)	FQ[a]	FQ[b]	FQ[c]	SAPT0	CCSD(T)
Electrostatic	-21.00	-26.88	-45.22	-32.71	–	-20.25	-26.24	-45.77	-31.85	–
Induction	–	–	–	-11.33	–	–	–	–	-11.24	–
Repulsion	28.53	29.11	30.83	28.49	–	28.15	28.86	31.05	28.44	–
Dispersion	-3.28	-3.28	-3.28	-6.36	–	-3.29	-3.29	-3.29	-7.82	–
Total	4.25	-1.05	-17.67	-21.90	-17.72	4.61	-0.67	-18.01	-22.48	-18.57

S3 Electrostatic FQ parametrization

Table S3: O and H parameters for FQ calculations. η and χ are the chemical hardnesses and atomic electronegativities, respectively. All data are reported in a.u.
[a] FQ parametrization taken from Ref.[1]
[b] FQ parametrization taken from Ref.[2]
[c] FQ parametrization proposed in this work

	FQ[a]	FQ[b]	FQ[c]
η_O	0.584852	0.623700	0.523700
η_H	0.625010	0.637512	0.537512
χ_O	0.116859	0.189194	0.189194
χ_H	0.000000	0.012767	0.012767
$\Delta\chi$	0.116859	0.176427	0.176427

S4 hcc_N of PROXYL/TEMPO from MD runs

Table S4: PBE0/N07D hcc_N mean values calculated on 200 snapshots extracted from MD runs. TIP3P refers to the purely electrostatic QM/MM embedding, where the water molecules were described by means of the non-polarizable TIP3P force field. FQ refers to the purely electrostatic QM/FQ with a, b parametrization. Δ_{rep} and $\Delta_{\text{dis-rep}}$ are differences between FQ[a] and hcc_N data obtained with our method. All values are reported in Gauss.
[a] FQ parametrization taken from Ref.[1]
[b] FQ parametrization taken from Ref.[2]

	TIP3P	FQ[a]	FQ[b]	Δ_{rep}	$\Delta_{\text{dis-rep}}$
PROXYL	14.9	14.7	15.0	-0.3	-0.3
TEMPO	15.9	15.7	16.0	-0.3	-0.3

References

(1) Rick, S. W.; Stuart, S. J.; Berne, B. J. *J. Chem. Phys.* **1994**, *101*, 6141–6156.

(2) Carnimeo, I.; Cappelli, C.; Barone, V. *J. Comput. Chem.* **2015**, *36*, 2271–2290.