Supporting Information for Excited-State Solvation Structure of Transition Metal Complexes from Molecular Dynamics Simulations and Assessment of Partial Atomic Charge Methods

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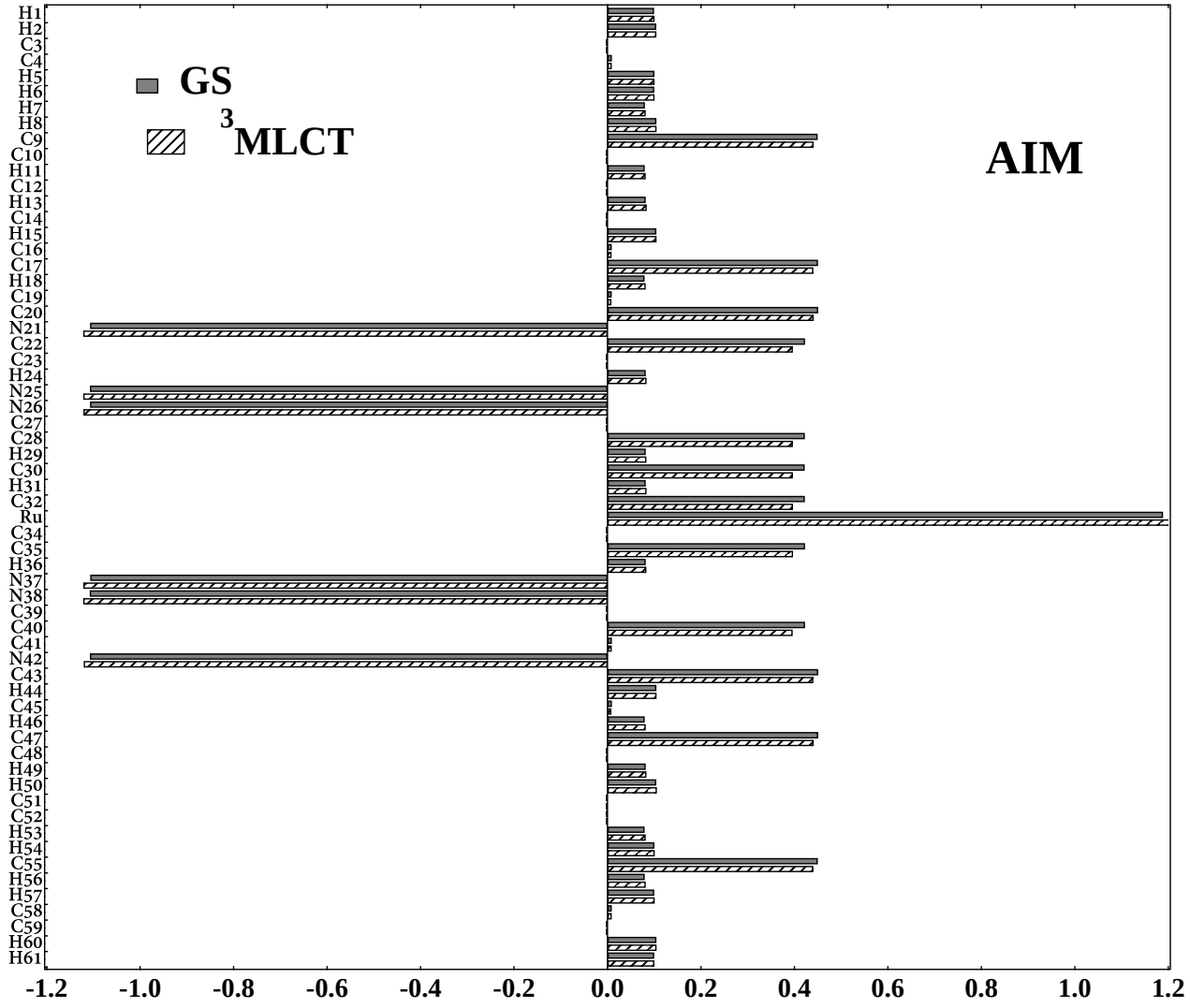

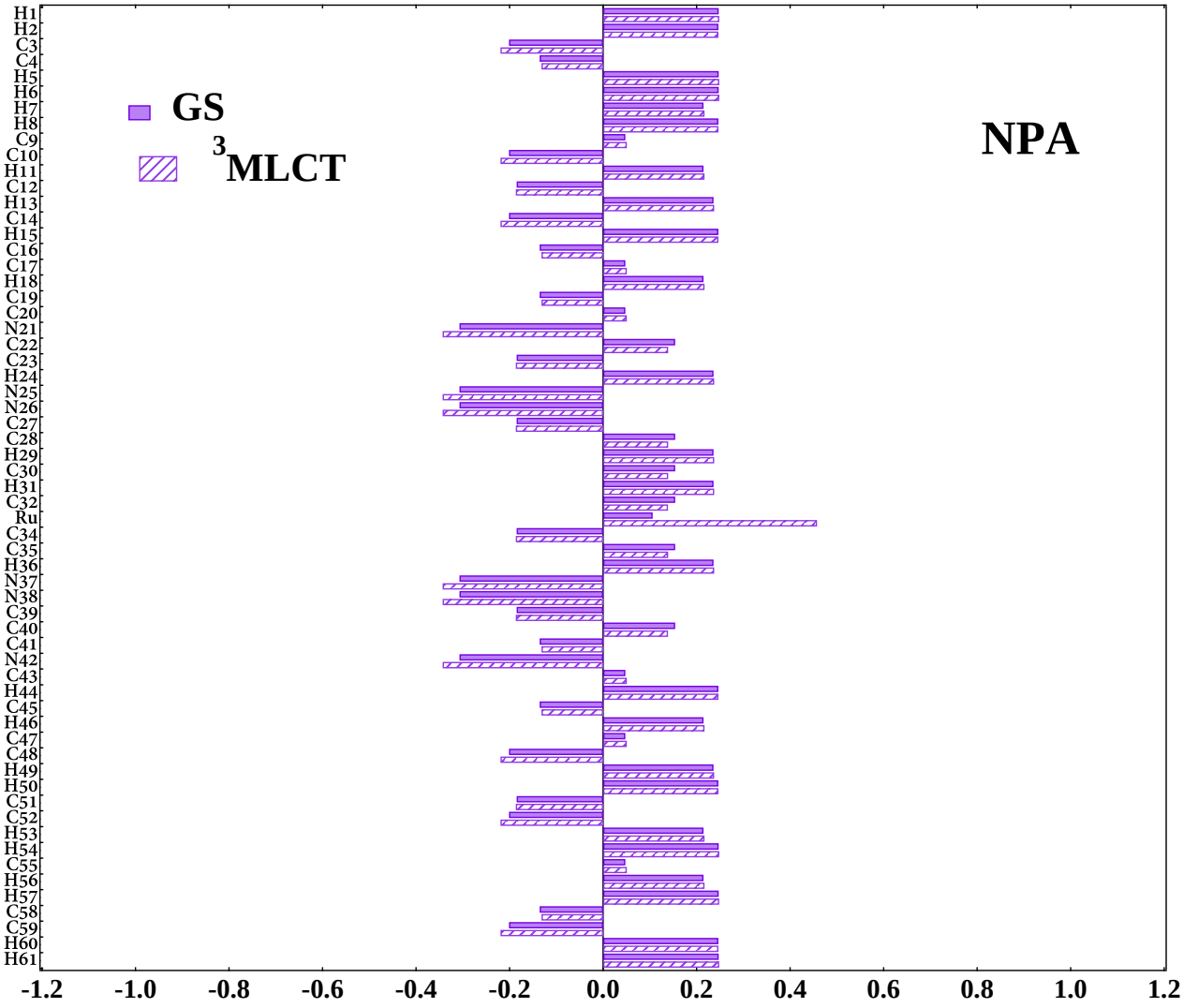
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H2
C3
C4
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H24
N25
N26
C27
C28
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C30
H31
C32
Ru
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C35
H36
N37
N38
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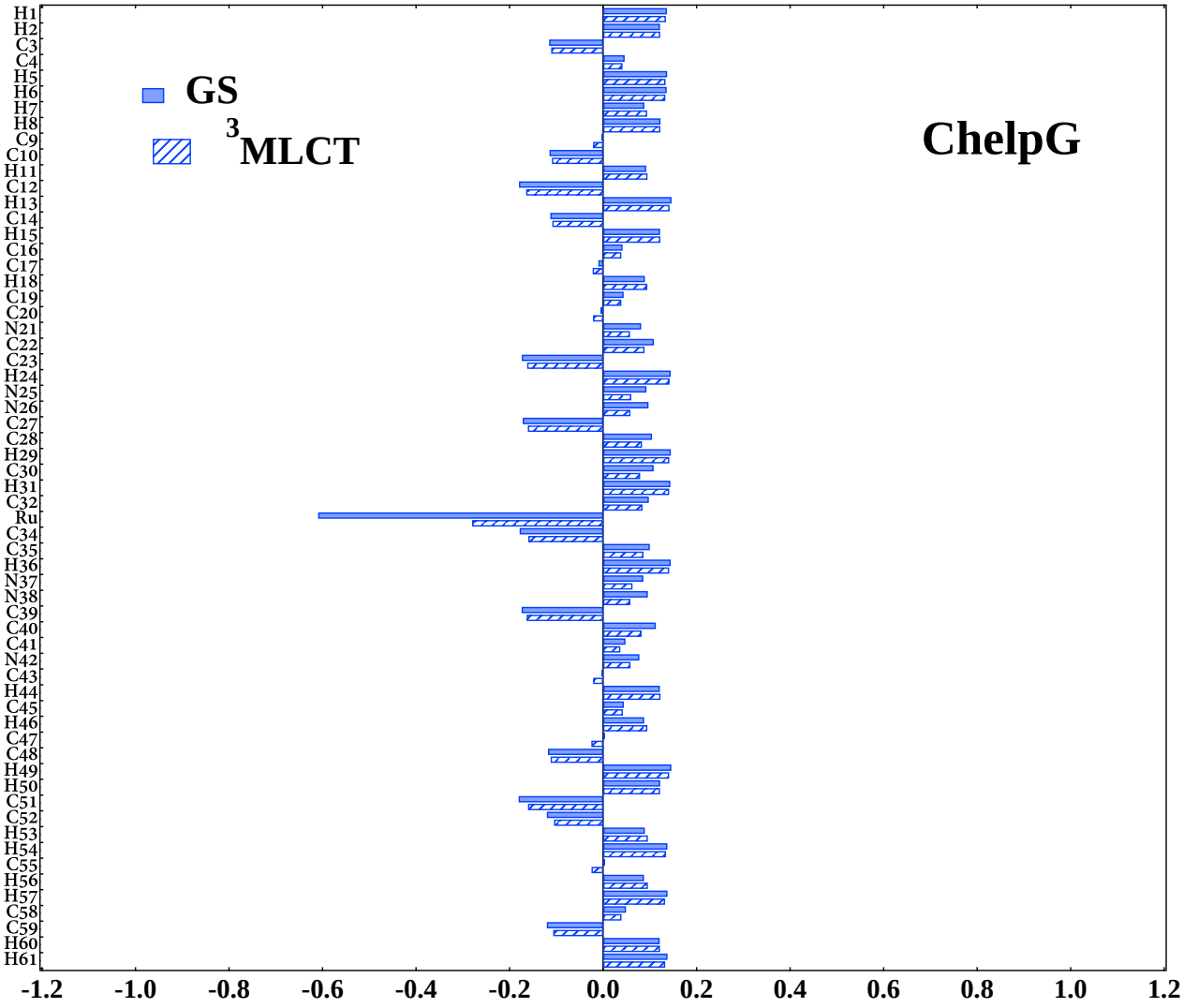
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H60
H61
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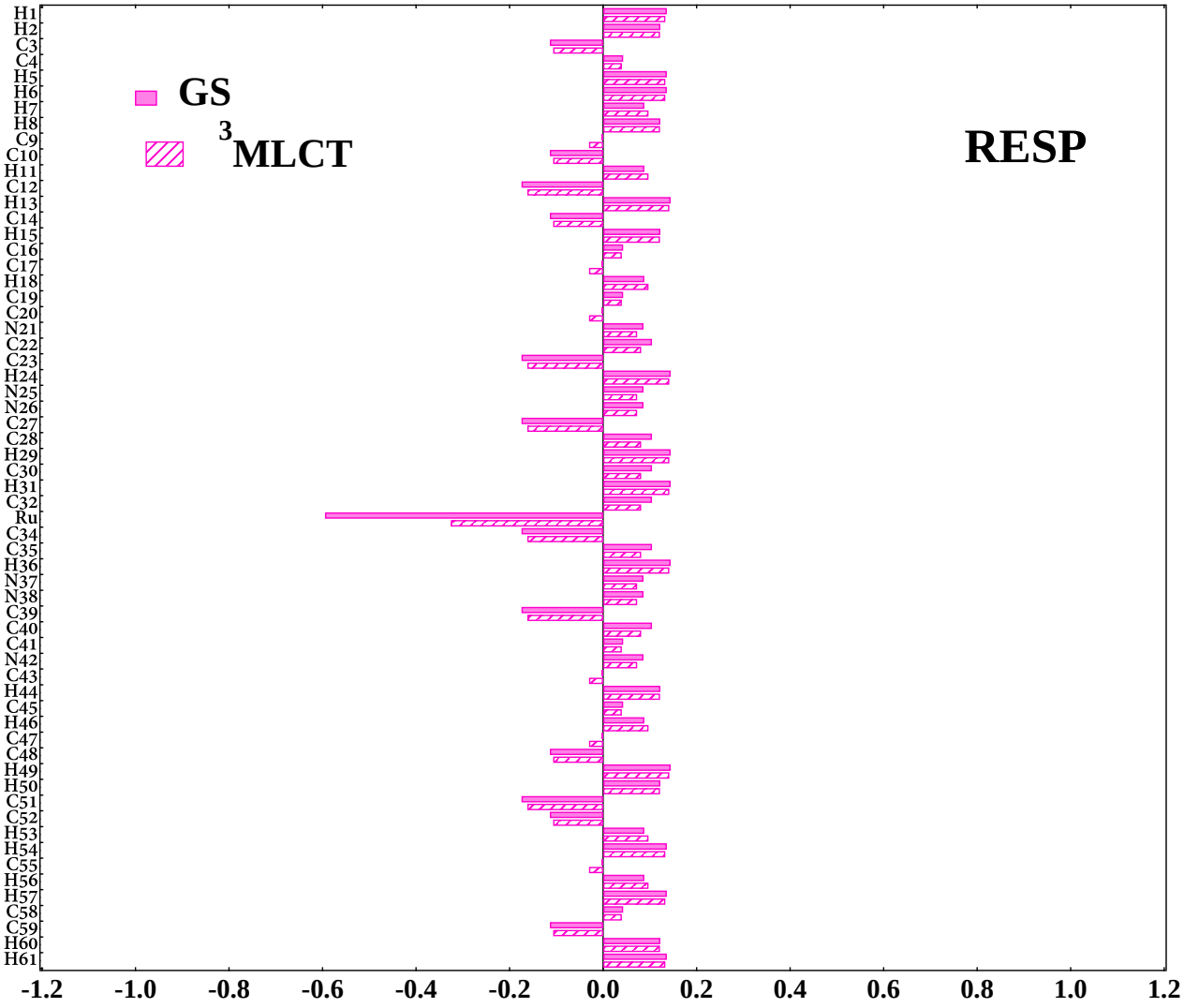
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RESP
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H61
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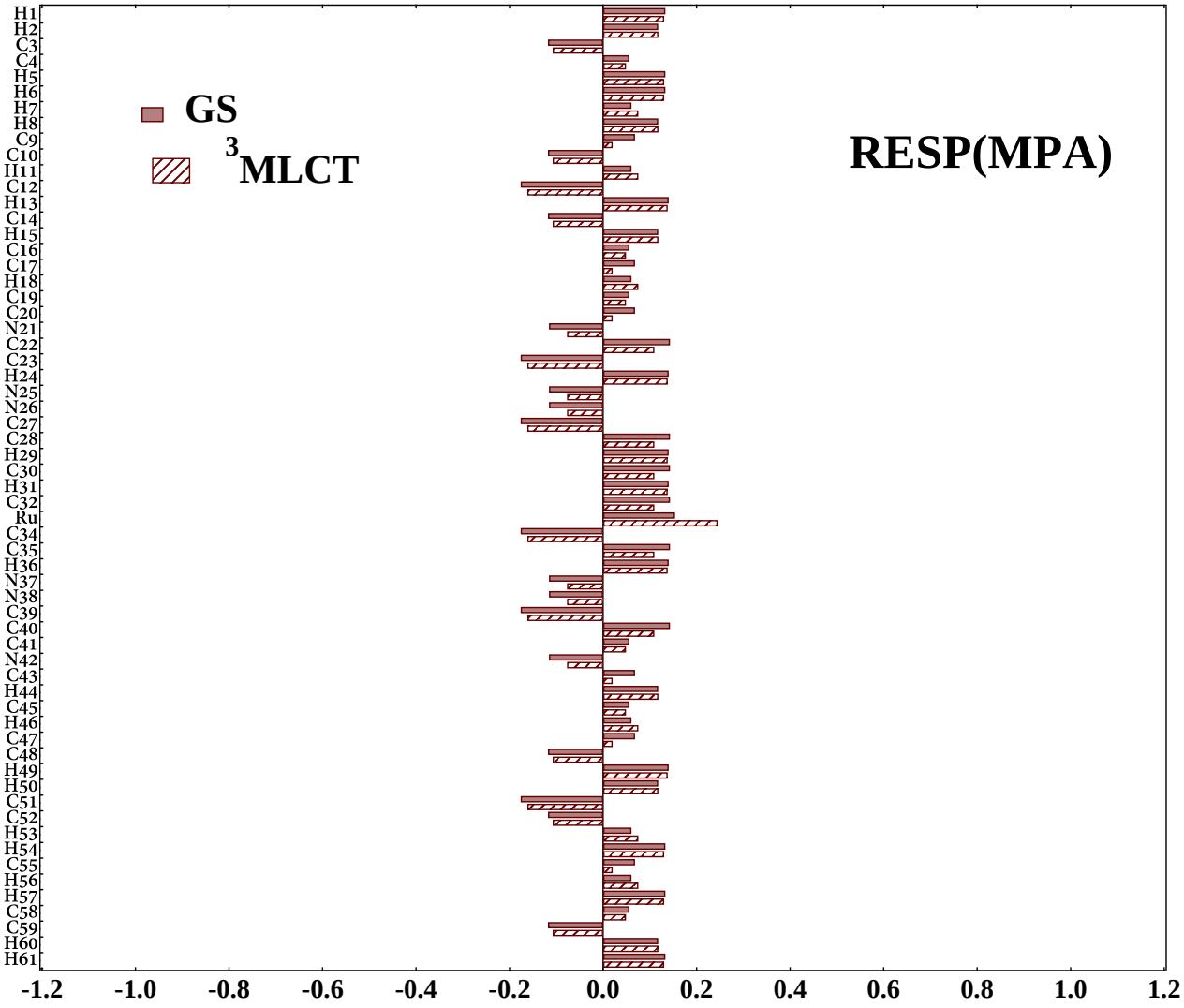
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3MLCT
RESP(MPA)
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H2
C3
C4
H5
H6
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N21
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N26
C27
C28
H29
C30
H31
C32
Ru
C34
C35
H36
N37
N38
C39
C40
C41
N42
C43
H44
C45
H46
C47
C48
H49
H50
C51
C52
H53
H54
C55
H56
H57
C58
C59
H60
H61
-1.2
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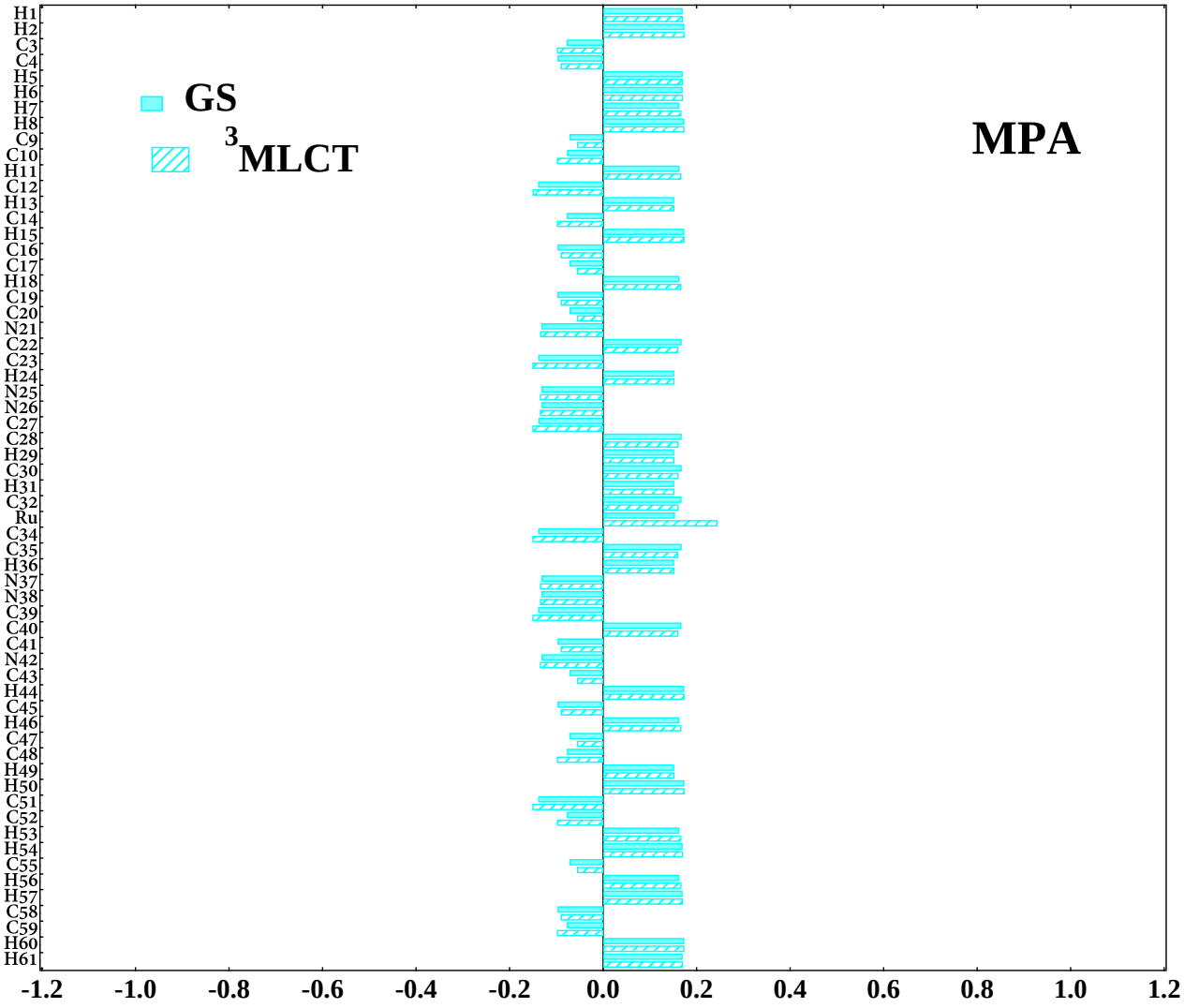
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H1
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H31
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Ru
C34
C35
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H61
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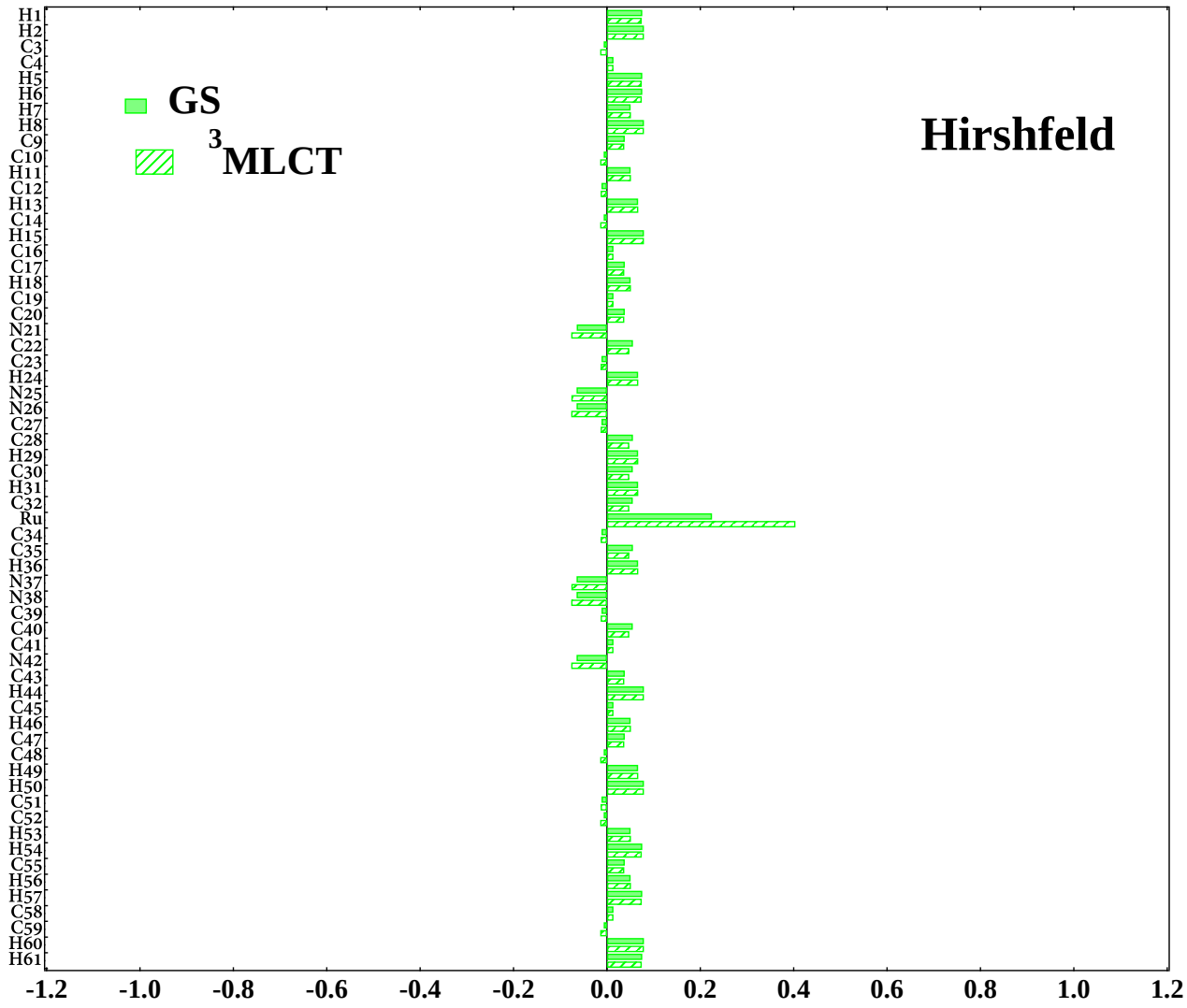
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Hirshfeld
H1
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C4
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H6
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H24
N25
N26
C27
C28
H29
C30
H31
C32
Ru
C34
C35
H36
N37
N38
C39
C40
C41
N42
C43
H44
C45
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C47
C48
H49
H50
C51
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H61
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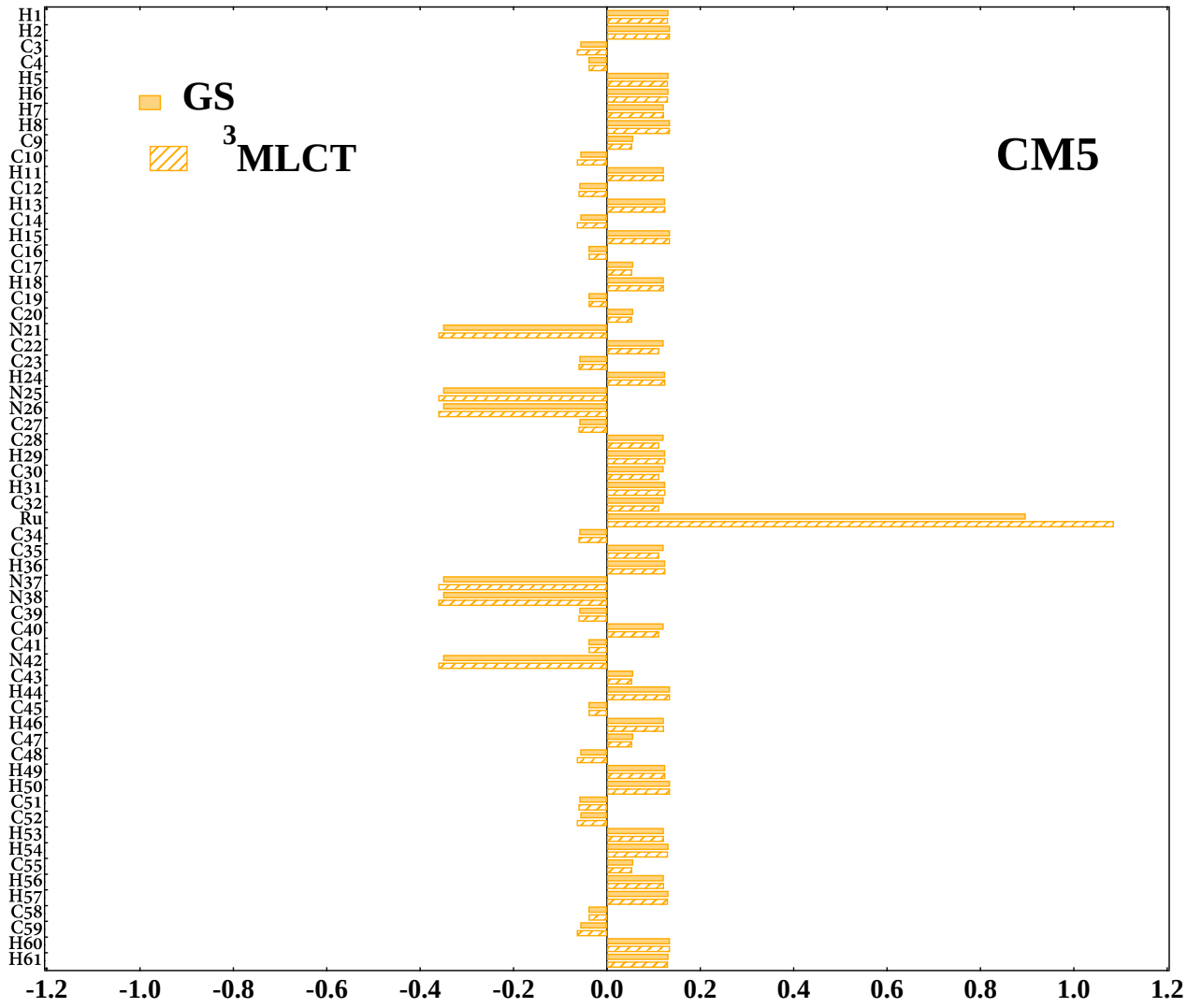
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3MLCT
CM5
H1
H2
C3
C4
H5
H6
H7
H8
C9
C10
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C14
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H56
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C58
C59
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H61
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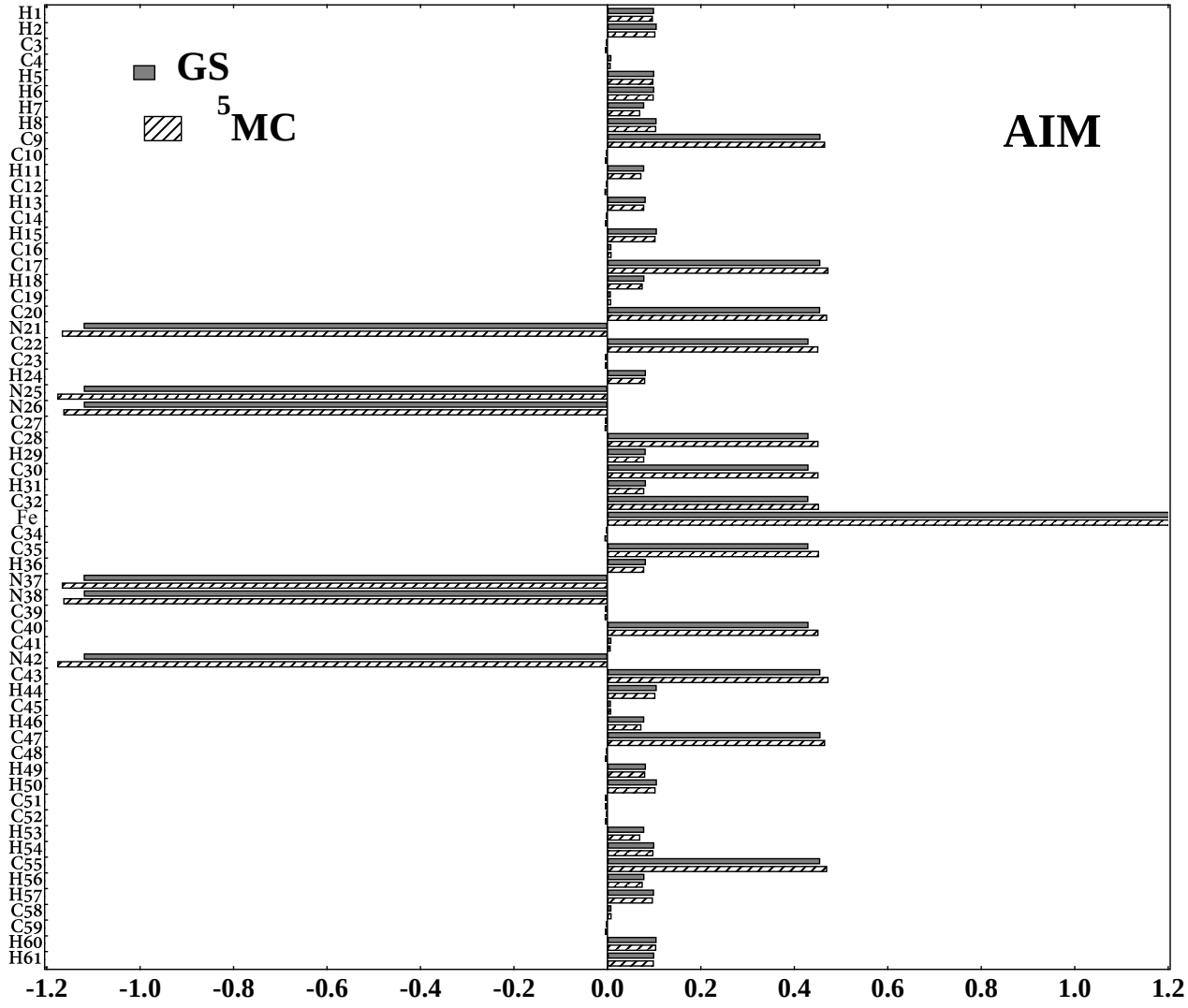
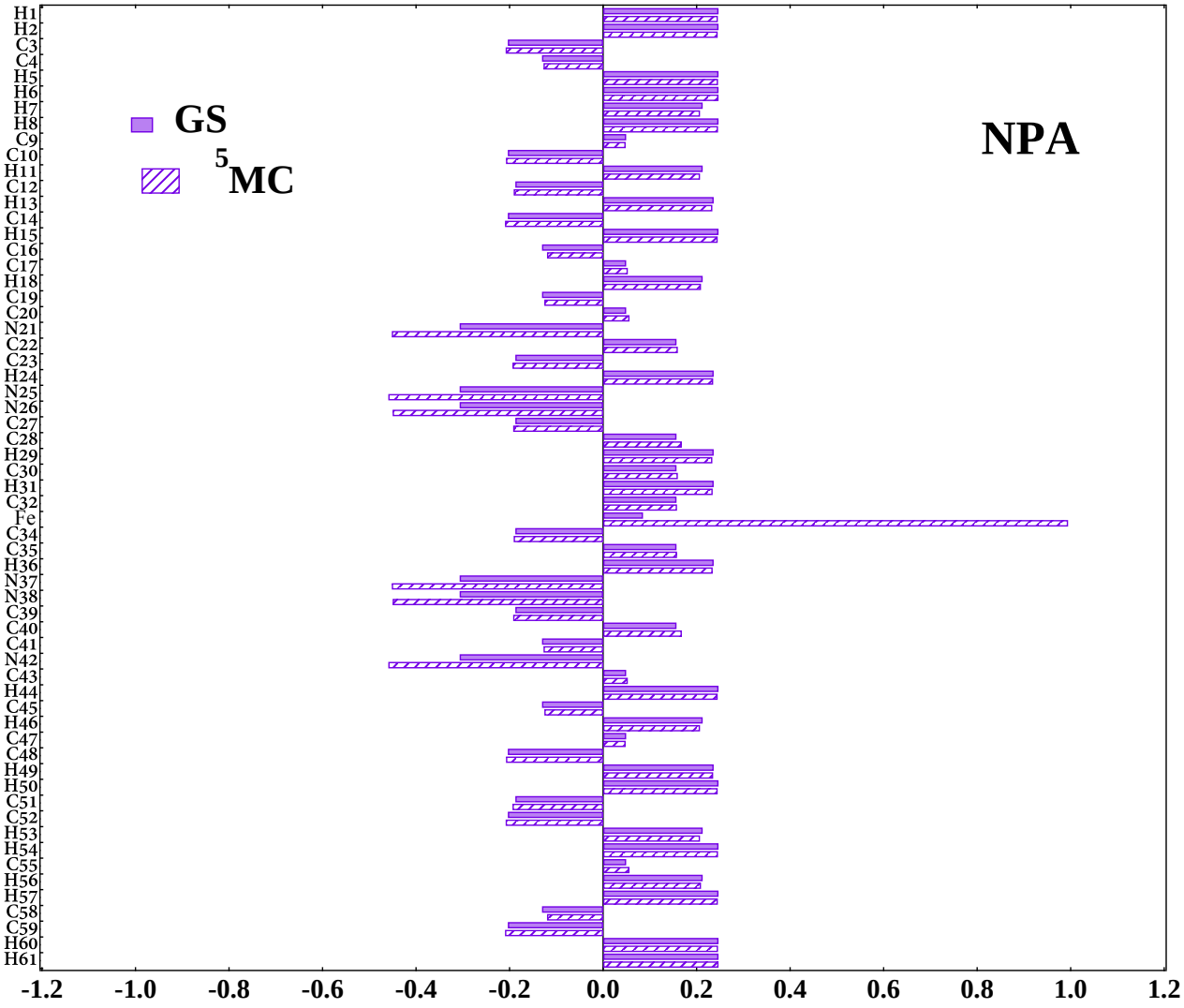
1.2

Fig. S2: Representation of PACs of $[Fe(bpy)_3]^{2+}$ in elementary charge unit (e) obtained from different methods.

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NPA
H1
H2
C3
C4
H5
H6
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H8
C9
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C12
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C14
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H61
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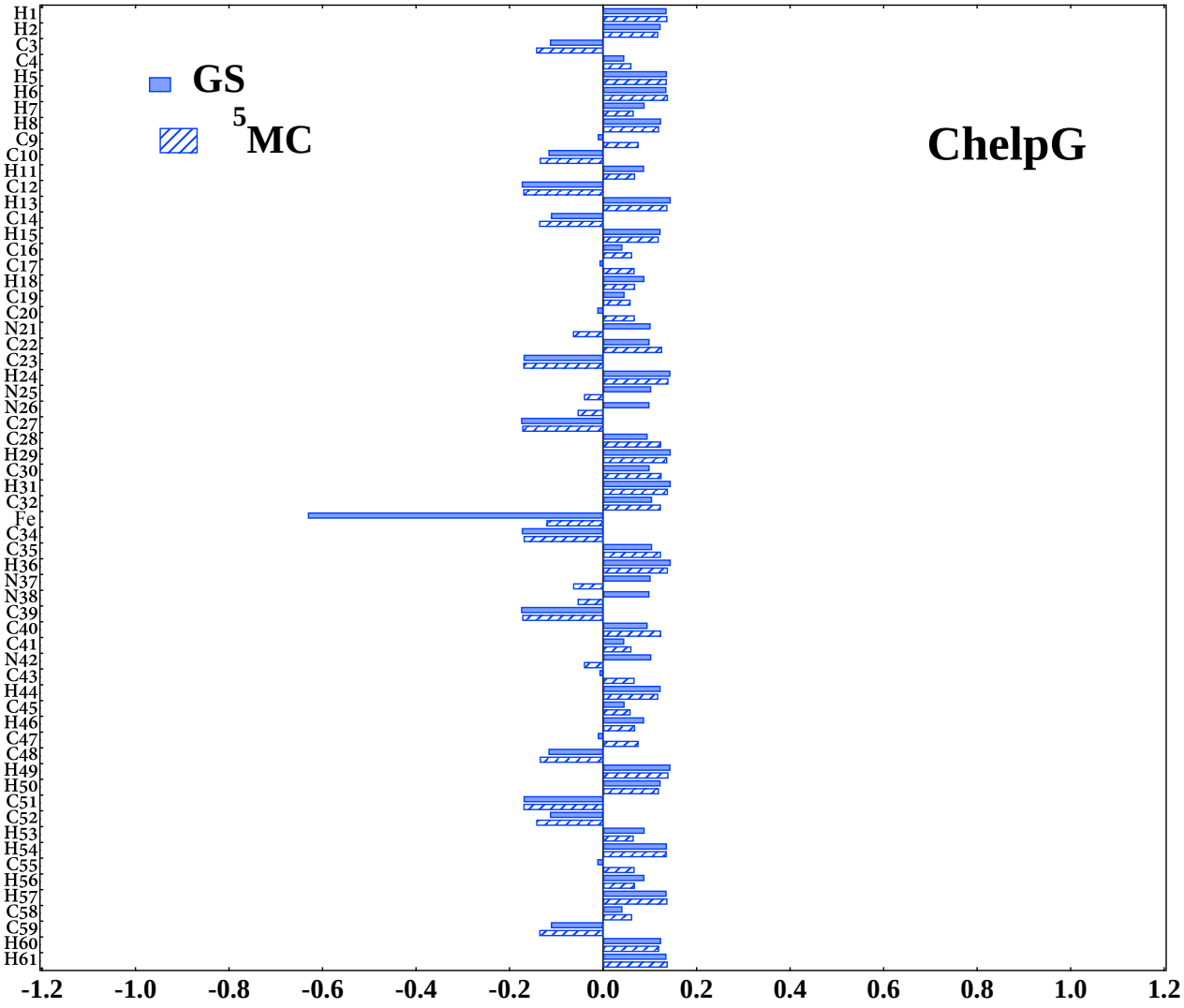
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ChelpG
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H50
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C59
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H61
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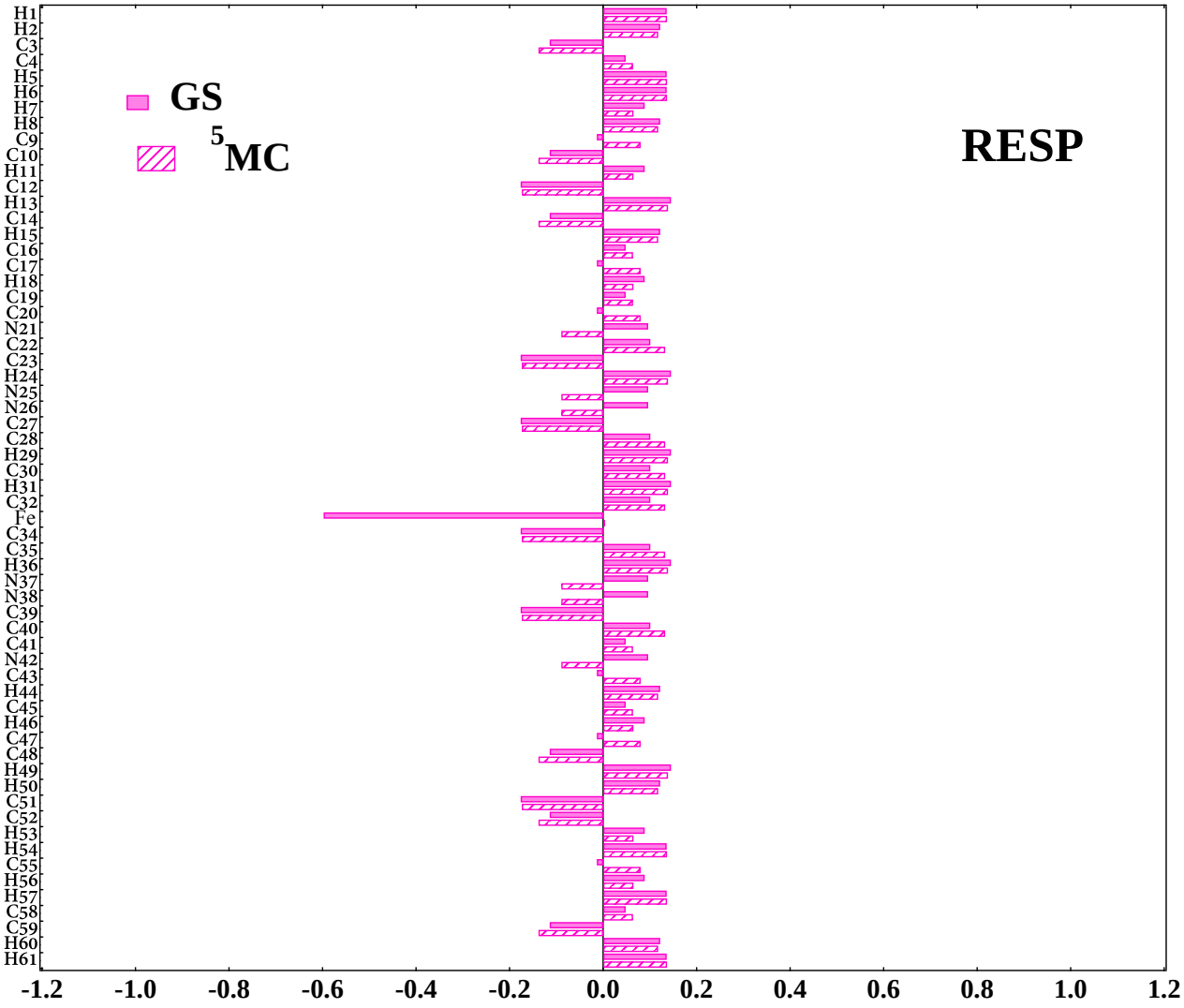
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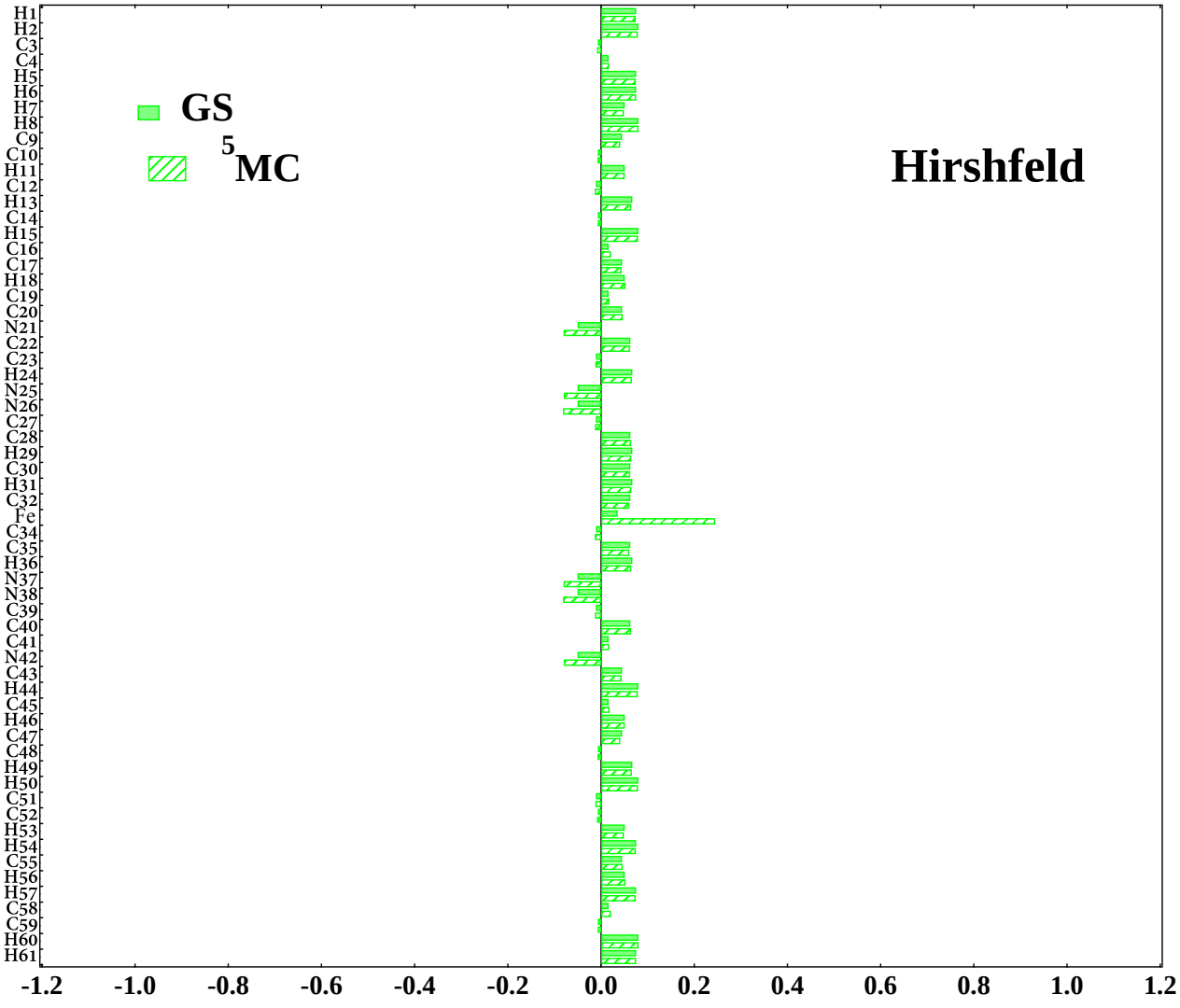
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Hirshfeld
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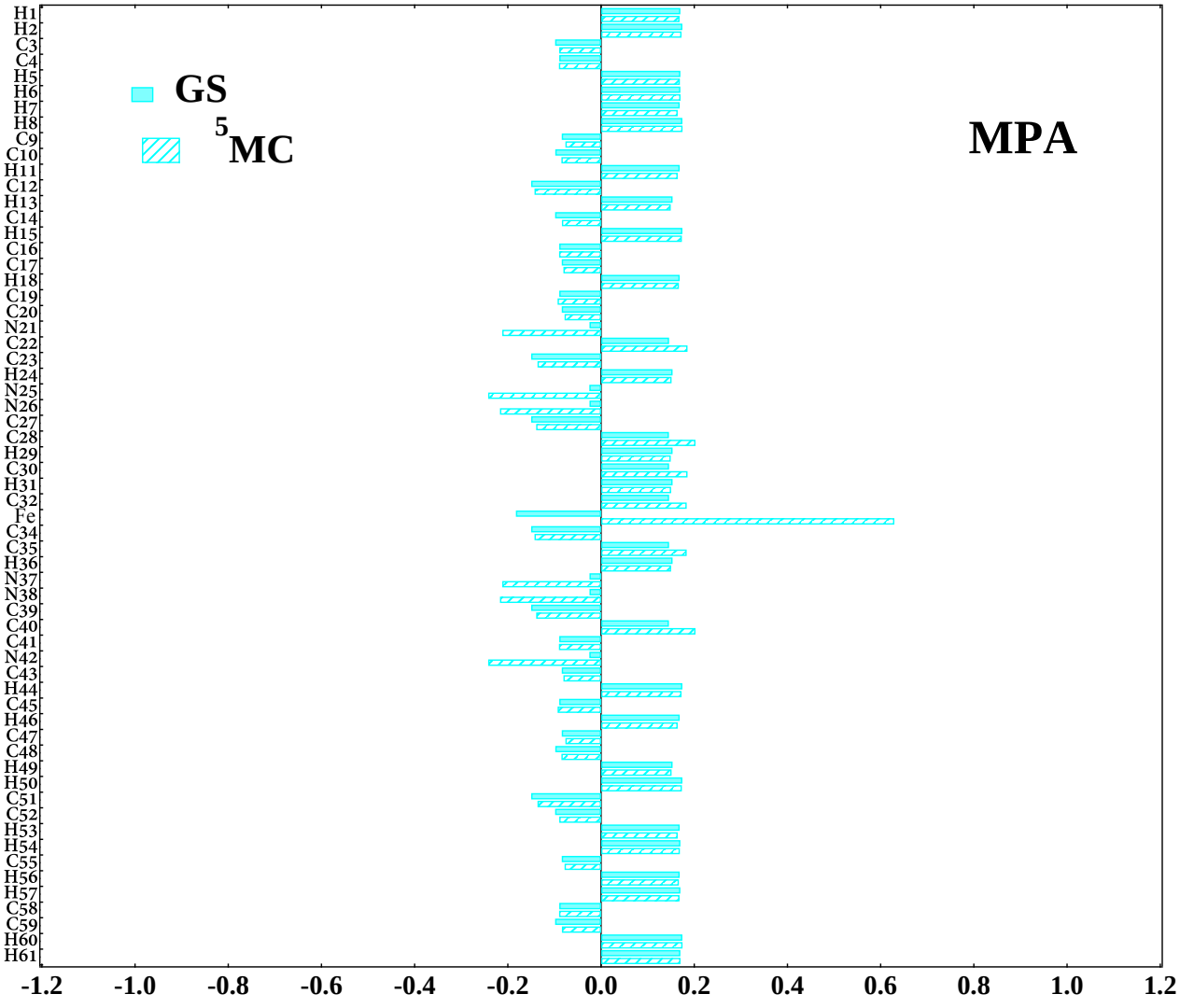
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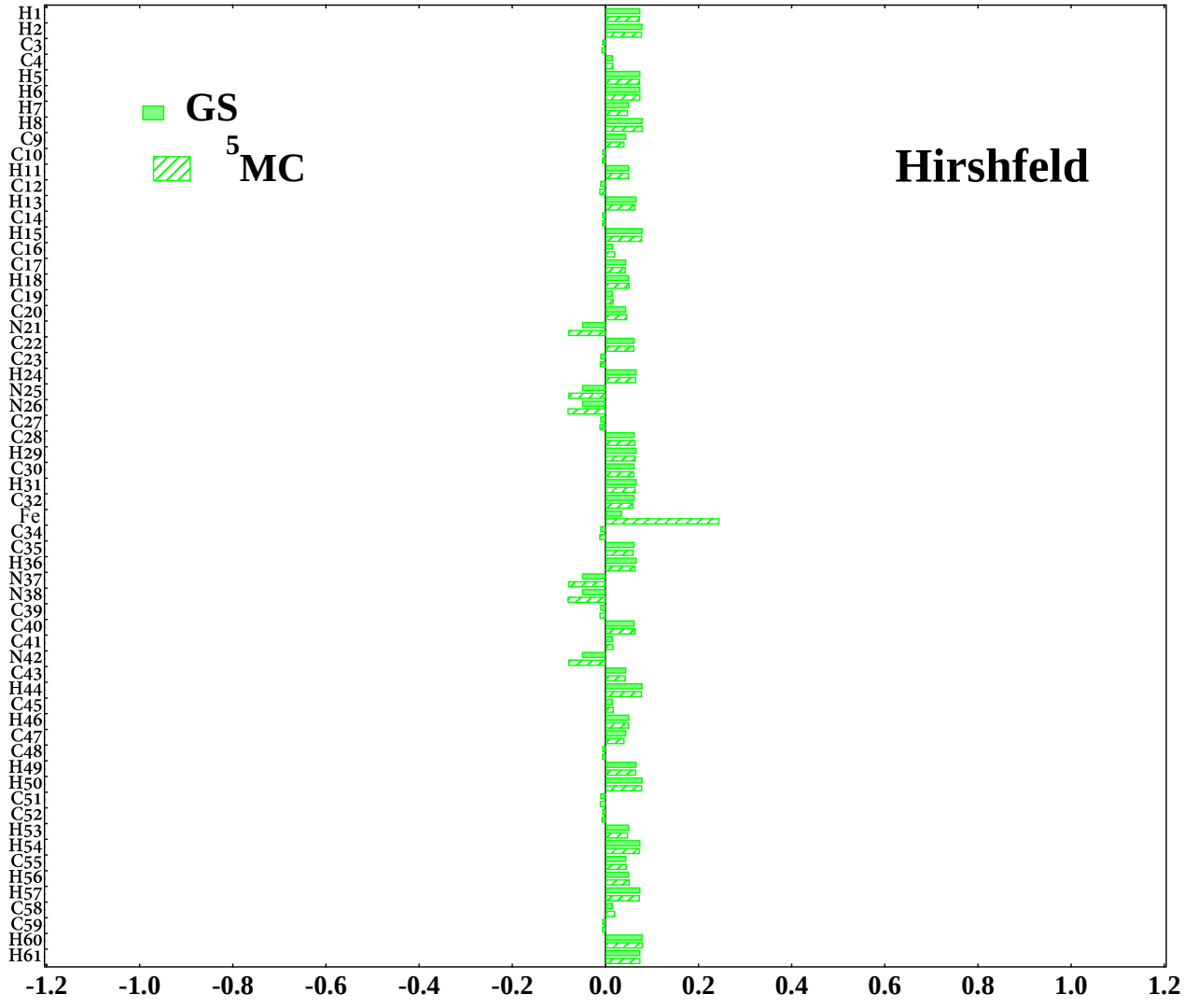
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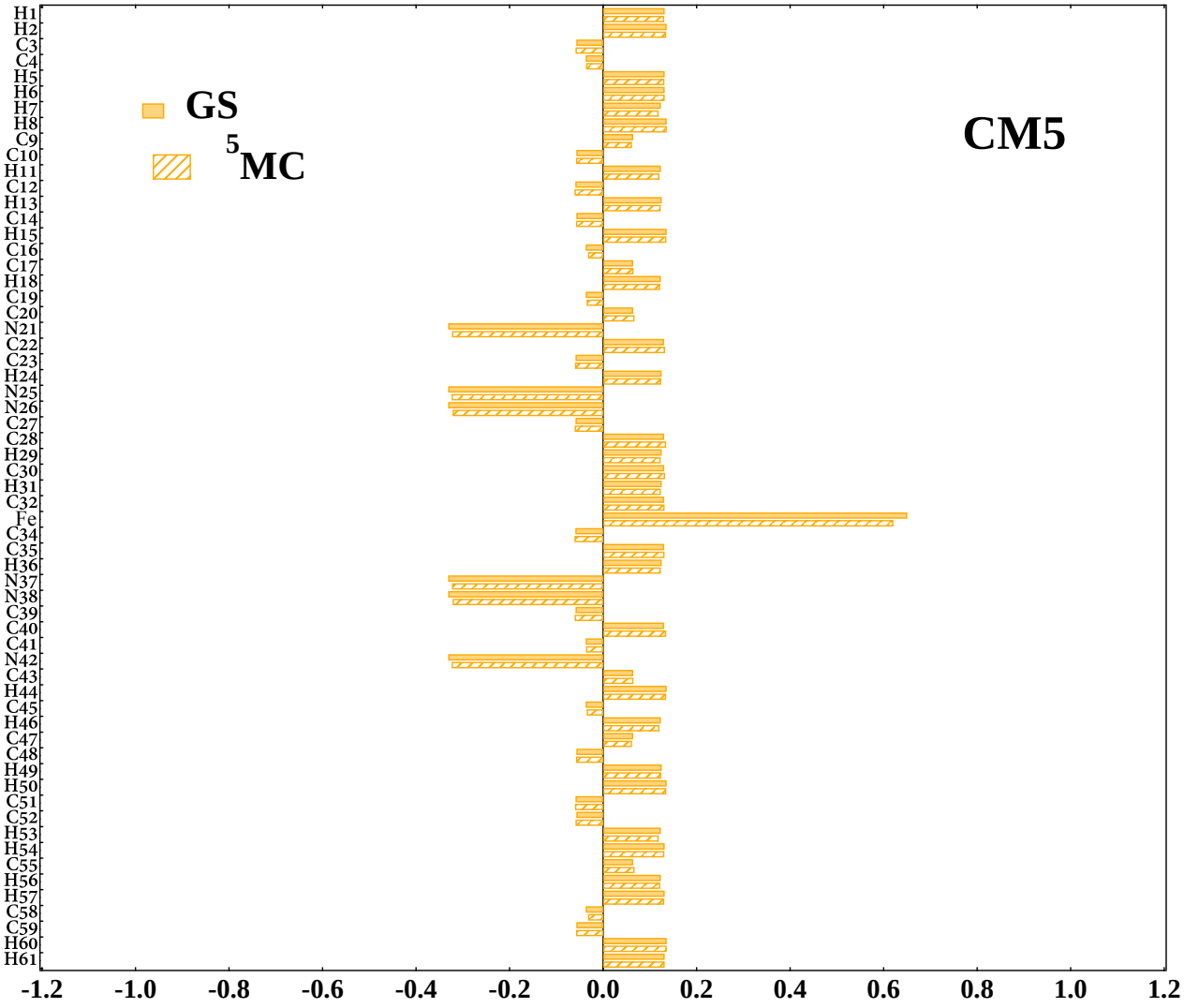
GS
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CM5
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H60
H61
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-1.0
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-0.6
-0.4
-0.2
0.0
0.2
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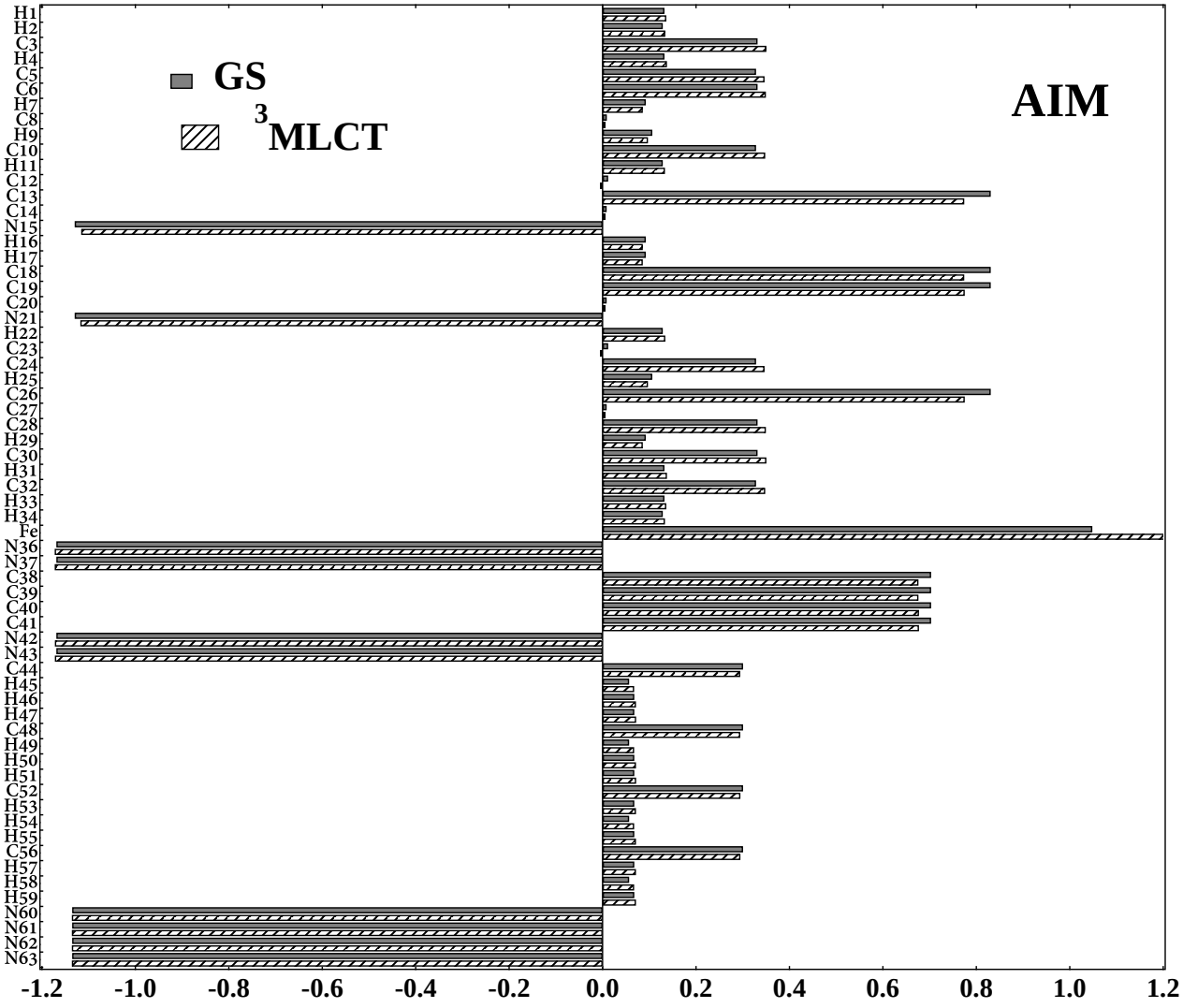
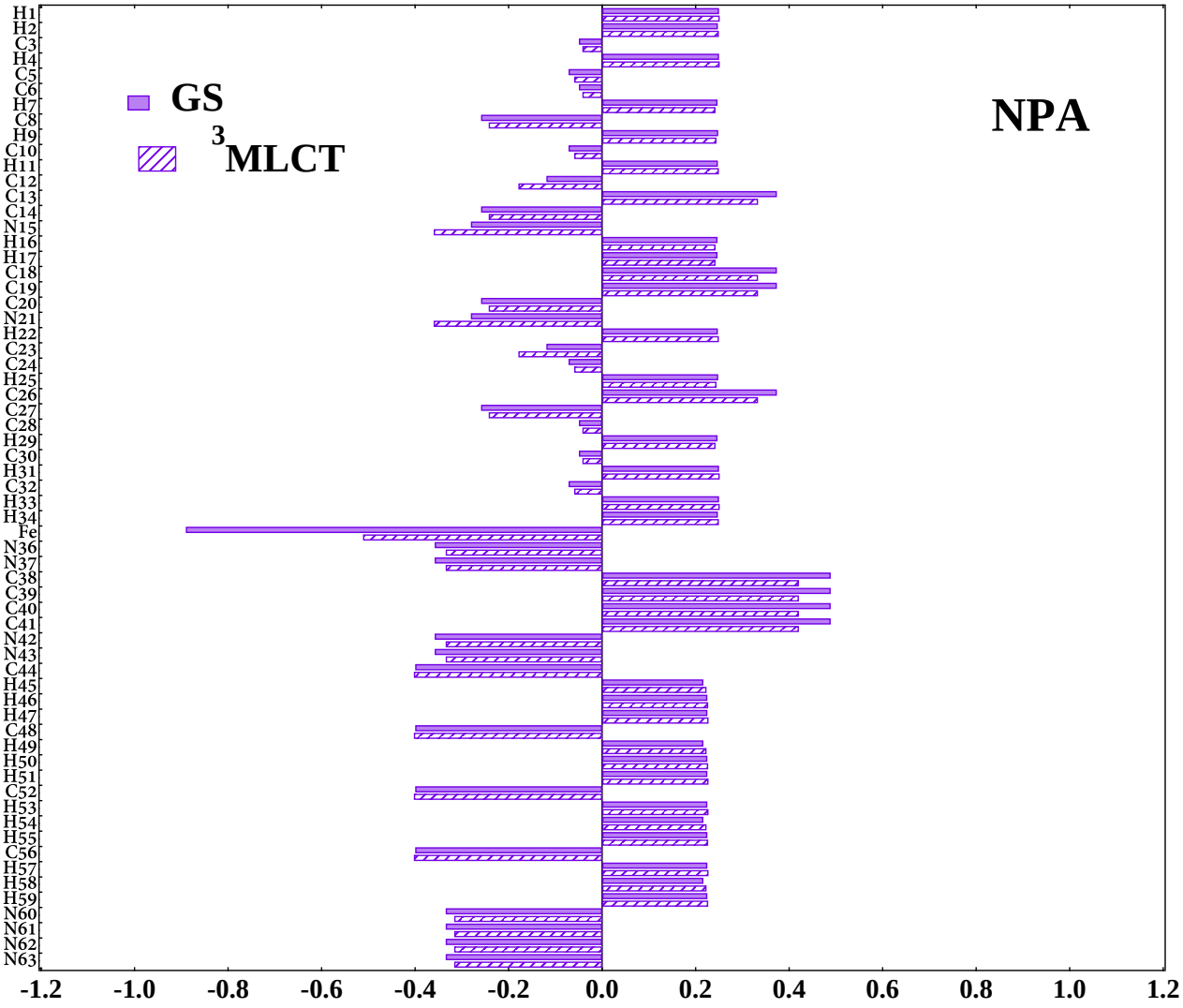
1.0
1.2

Fig. S3: Representation of PACs of $[Fe(bmip)_2]^{2+}$ in elementary charge unit (e) obtained from different methods.

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3MLCT
NPA
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C32
H33
H34
Fe
N36
N37
C38
C39
C40
C41
N42
N43
C44
H45
H46
H47
C48
H49
H50
H51
C52
H53
H54
H55
C56
H57
H58
H59
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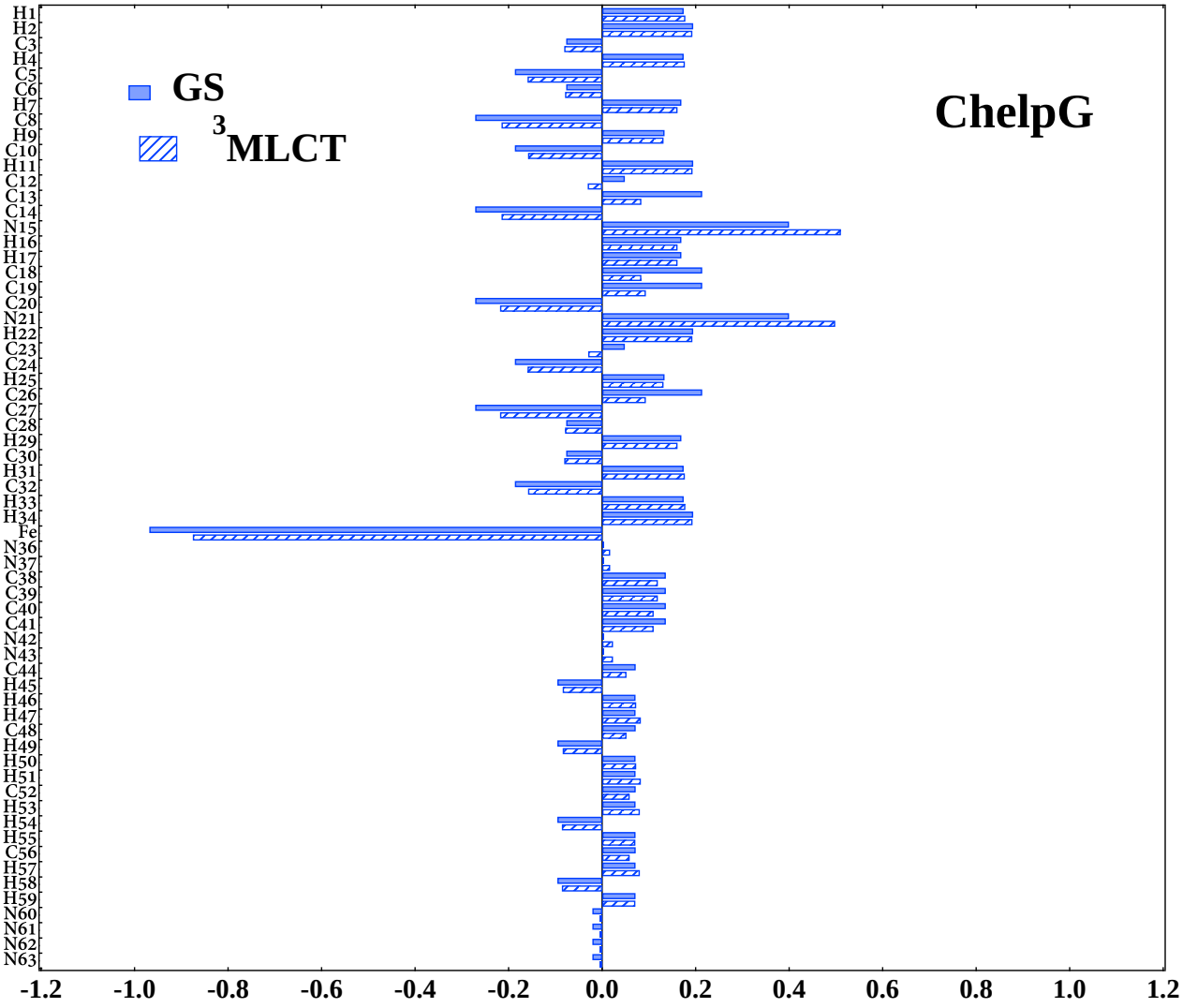
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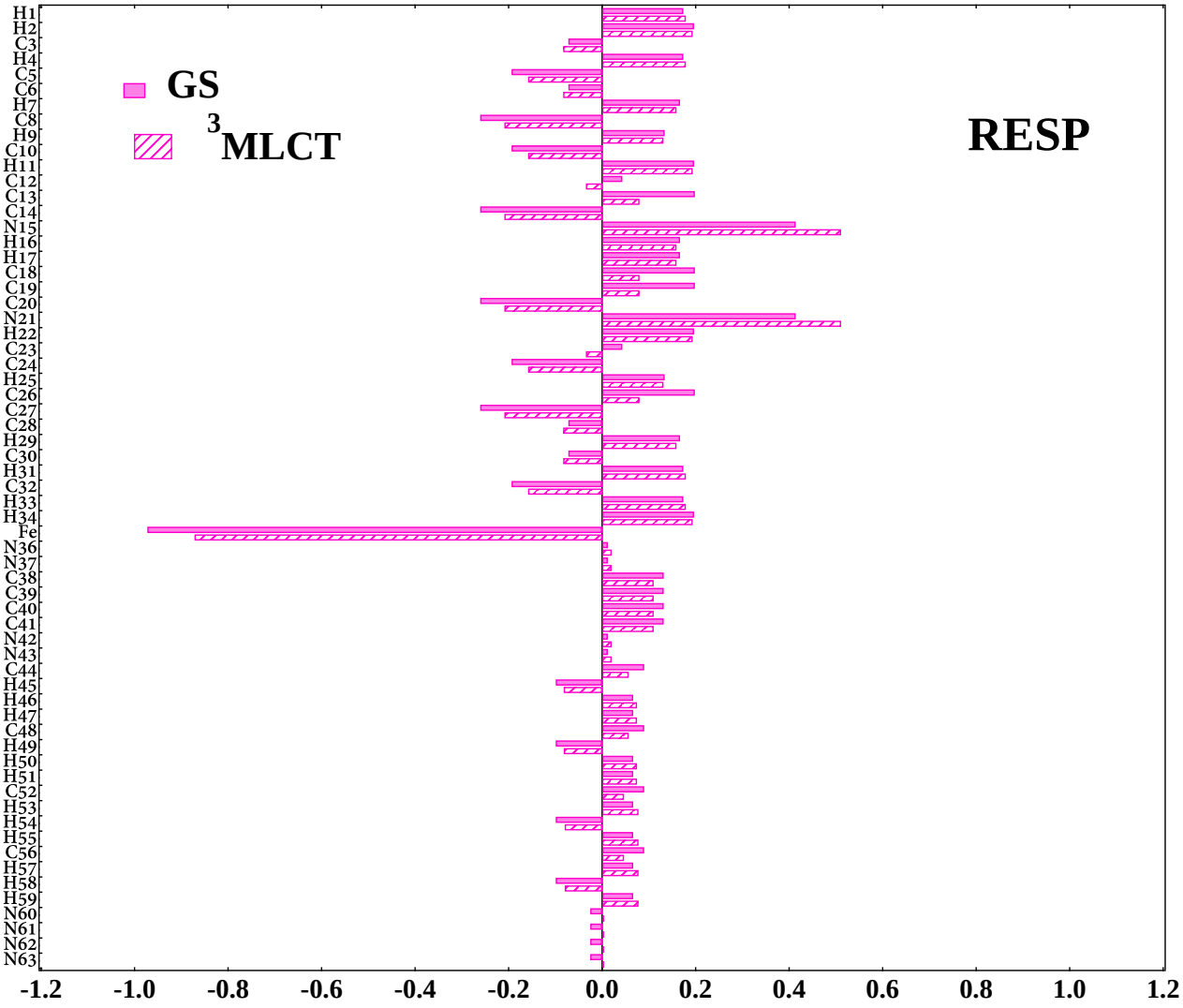
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H31
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N37
C38
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C40
C41
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N43
C44
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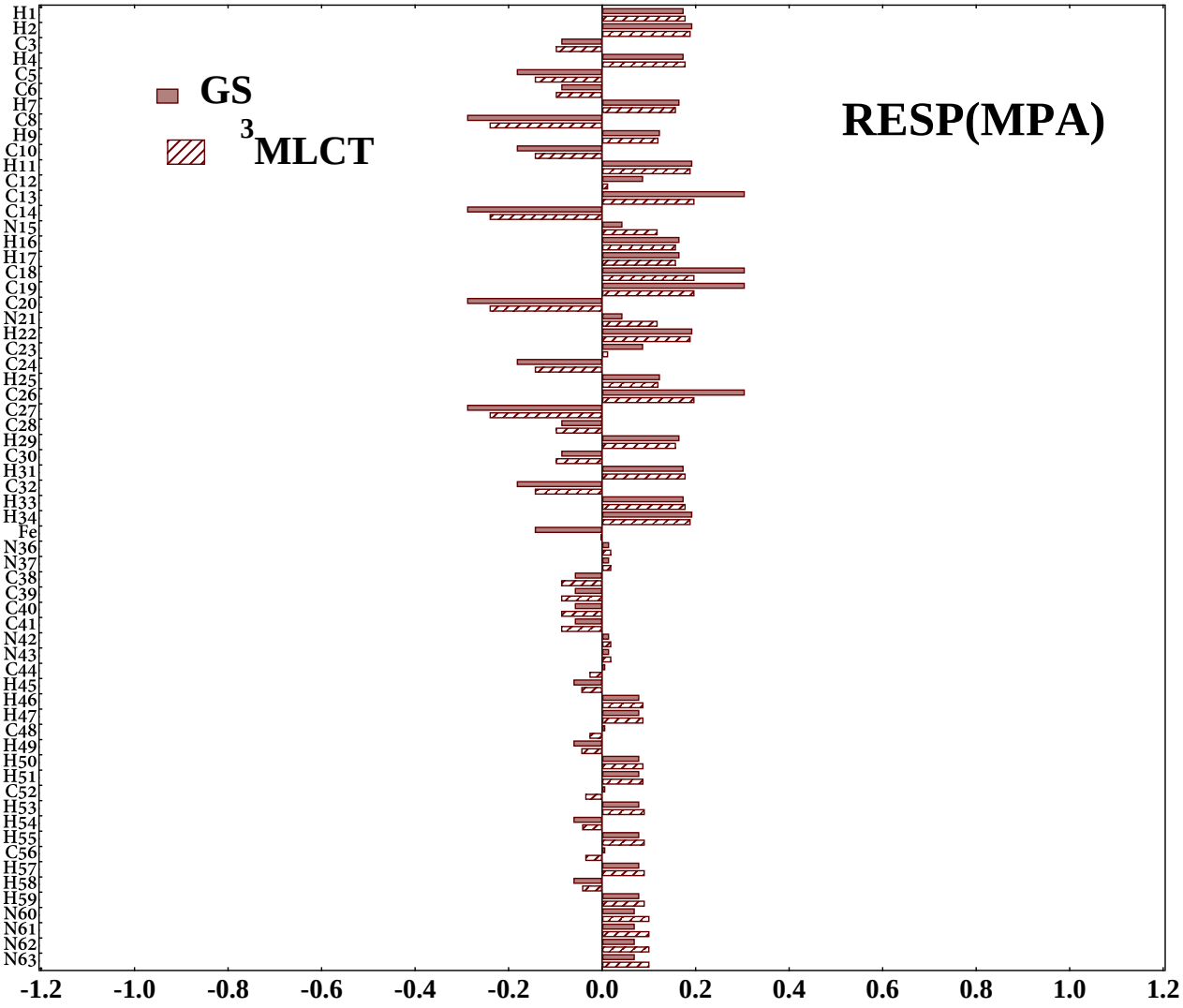
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H34
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C41
N42
N43
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H45
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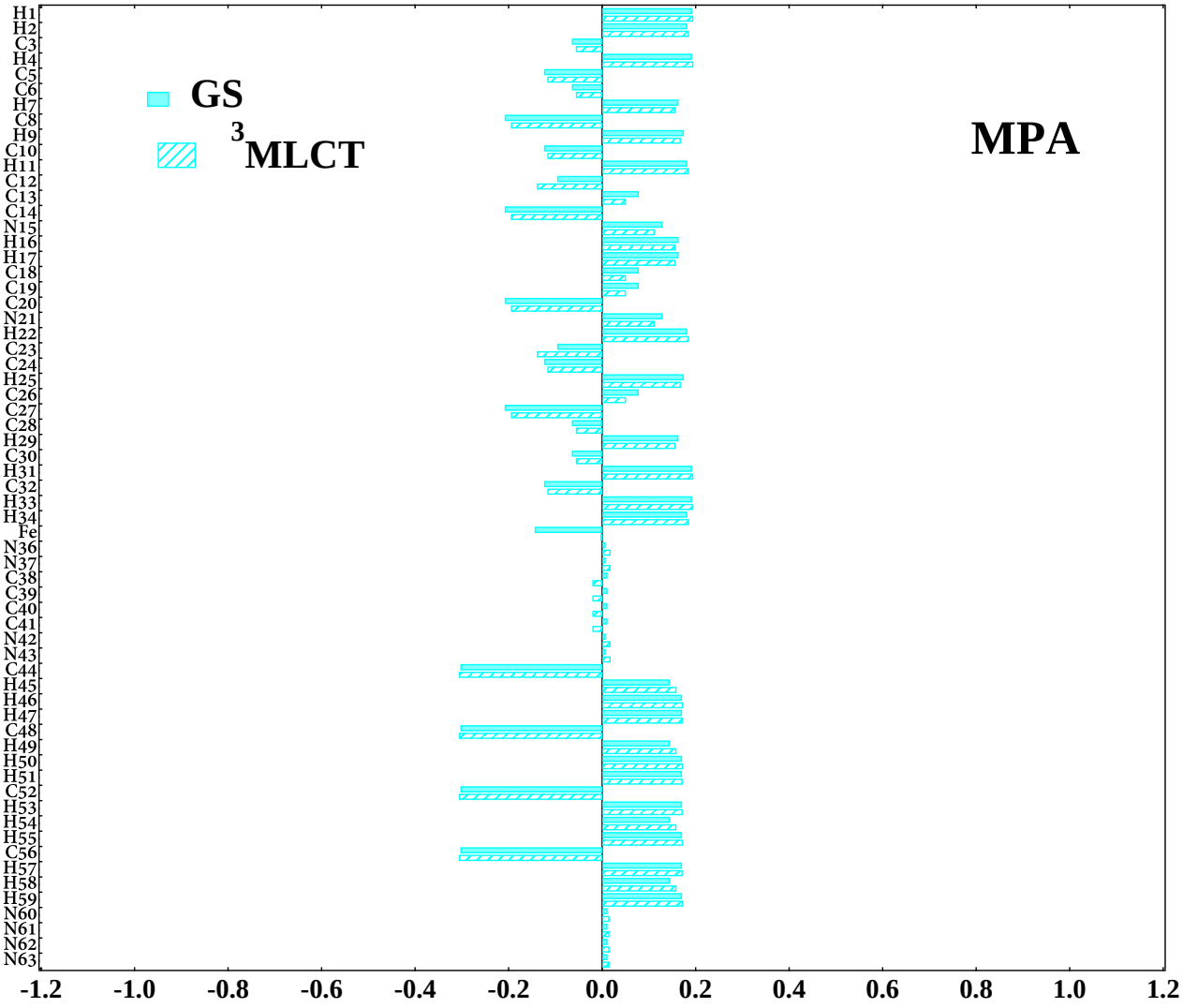
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H31
C32
H33
H34
Fe
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N37
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C41
N42
N43
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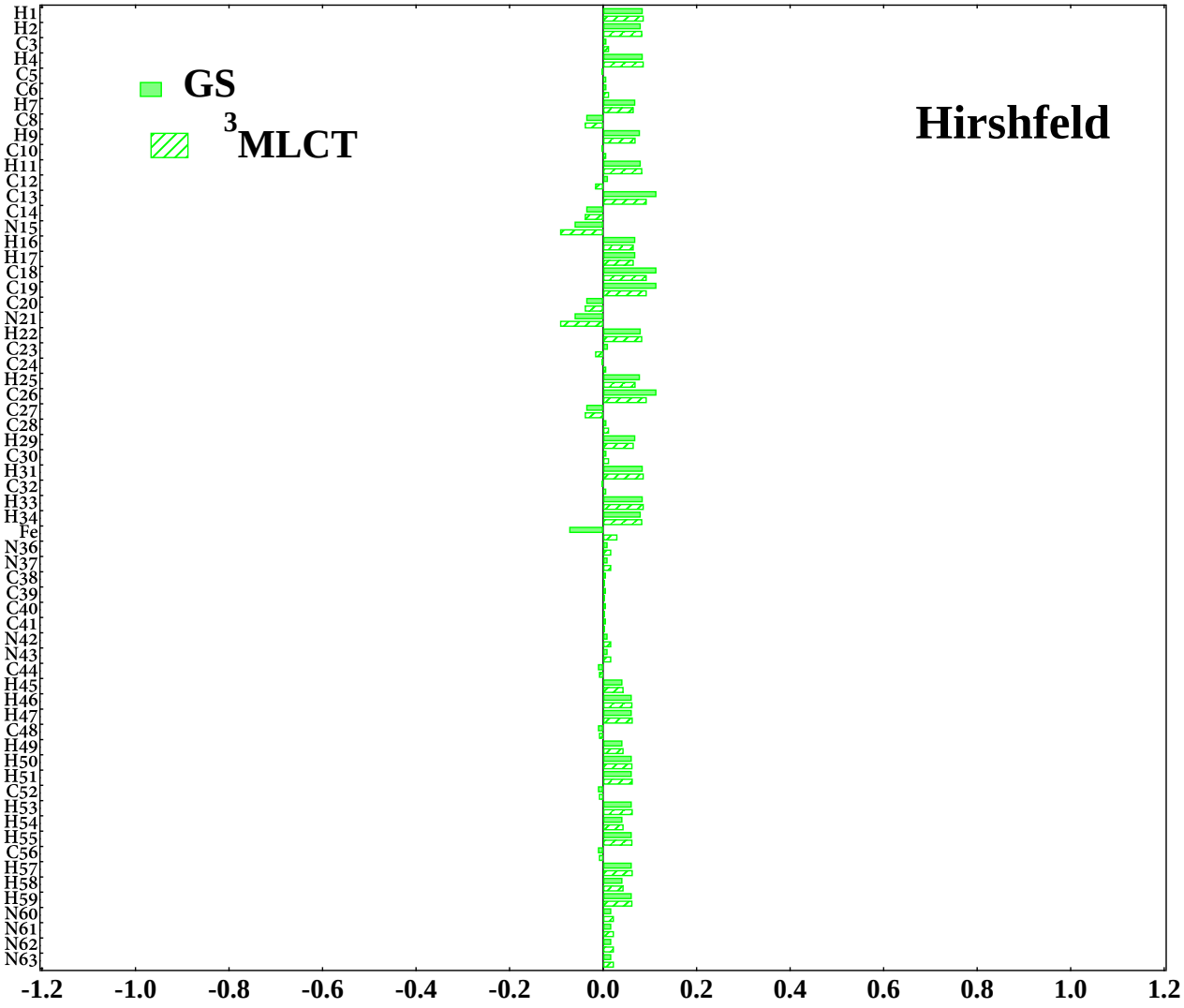
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Fe
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C38
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C41
N42
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C52
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H58
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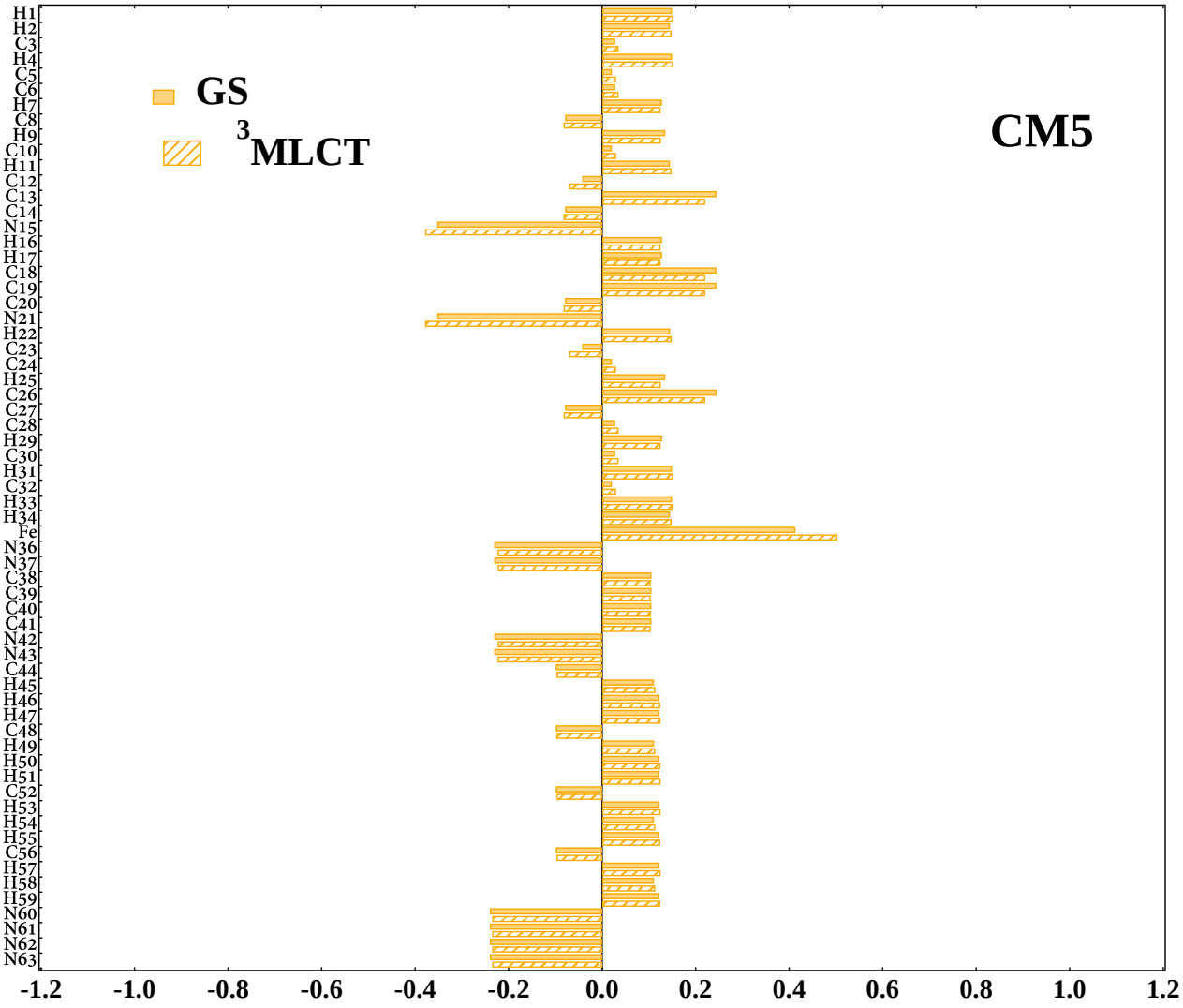
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H2
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H4
C5
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H7
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N15
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C18
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N21
H22
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C28
H29
C30
H31
C32
H33
H34
Fe
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N37
C38
C39
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C41
N42
N43
C44
H45
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C48
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C52
H53
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H55
C56
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H58
H59
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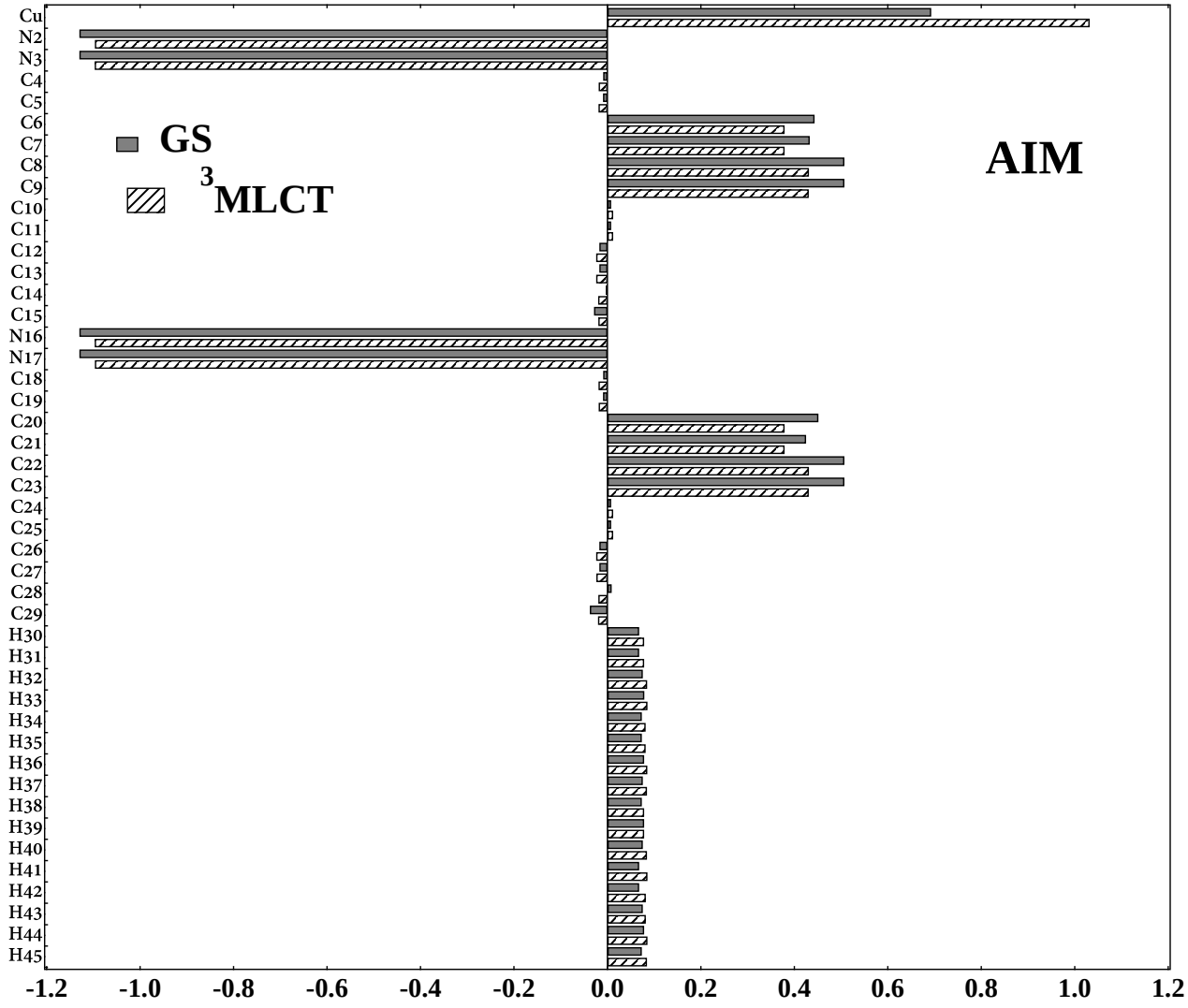
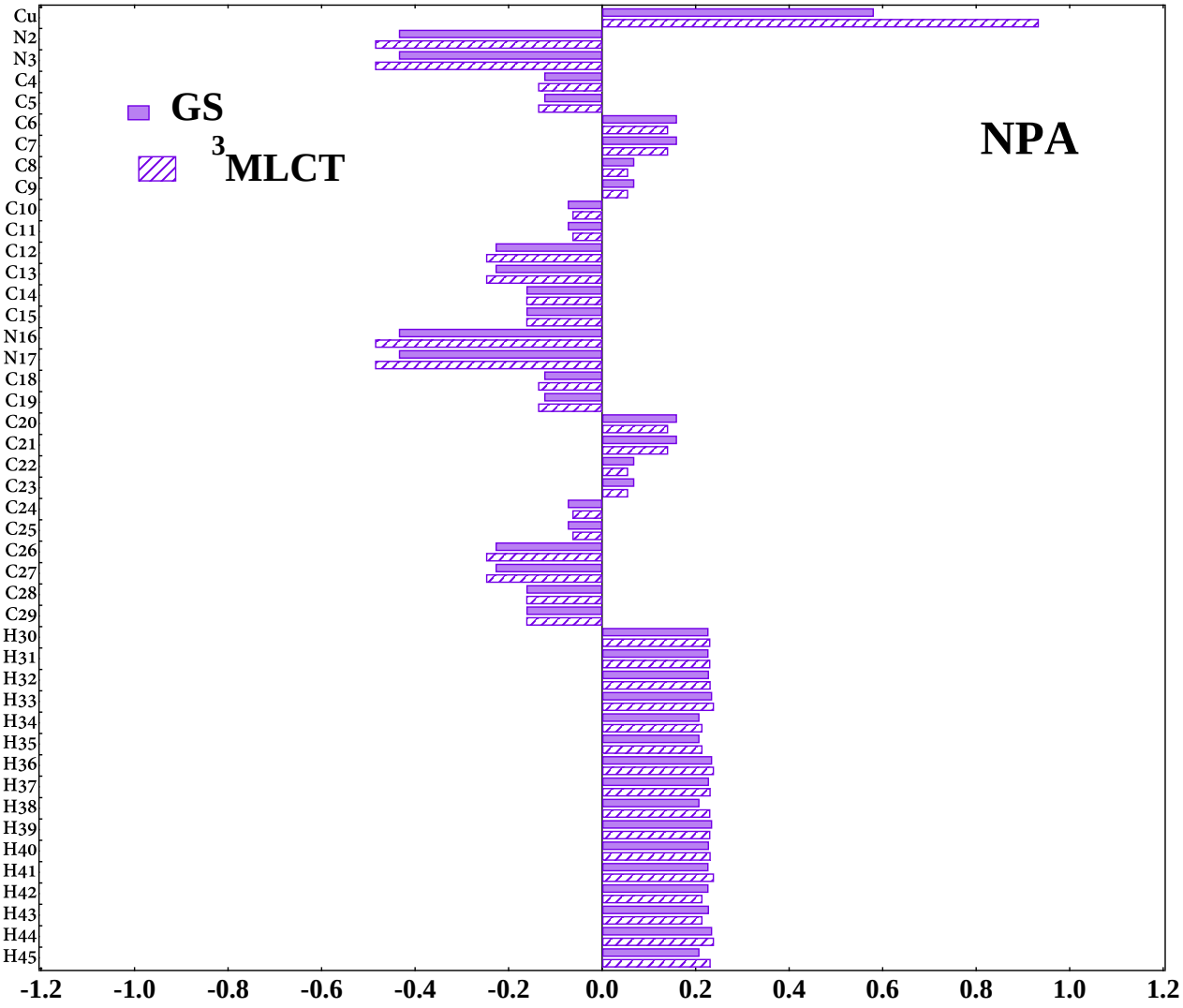
0.8
1.0
1.2

Fig. S4: Representation of PACs of $[Cu(phen)_2]^+$ in elementary charge unit (e) obtained from different methods.

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Cu
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C7
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C9
C10
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C15
N16
N17
C18
C19
C20
C21
C22
C23
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C25
C26
C27
C28
C29
H30
H31
H32
H33
H34
H35
H36
H37
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H39
H40
H41
H42
H43
H44
H45
-1.2
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0.4
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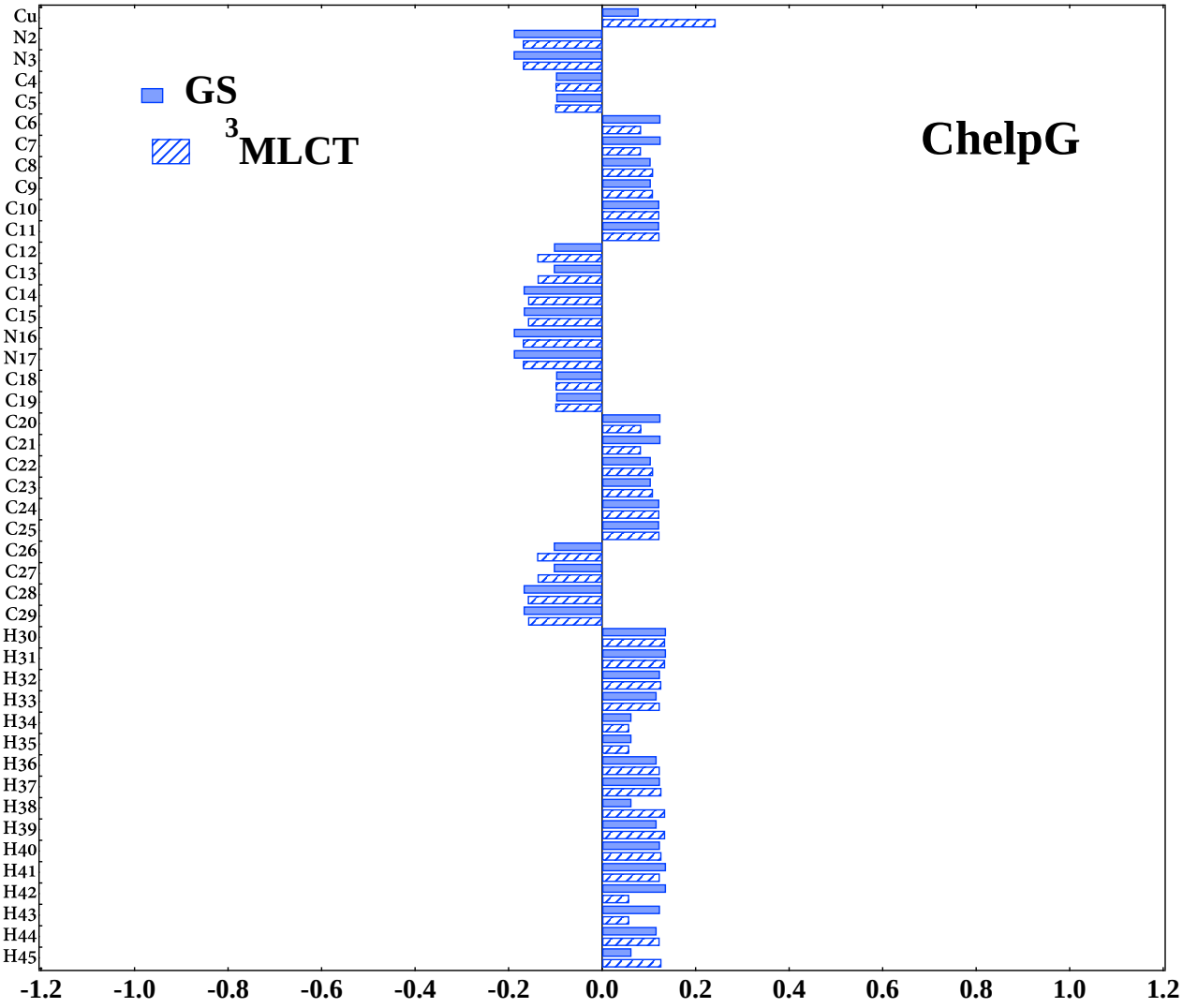
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H30
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H44
H45
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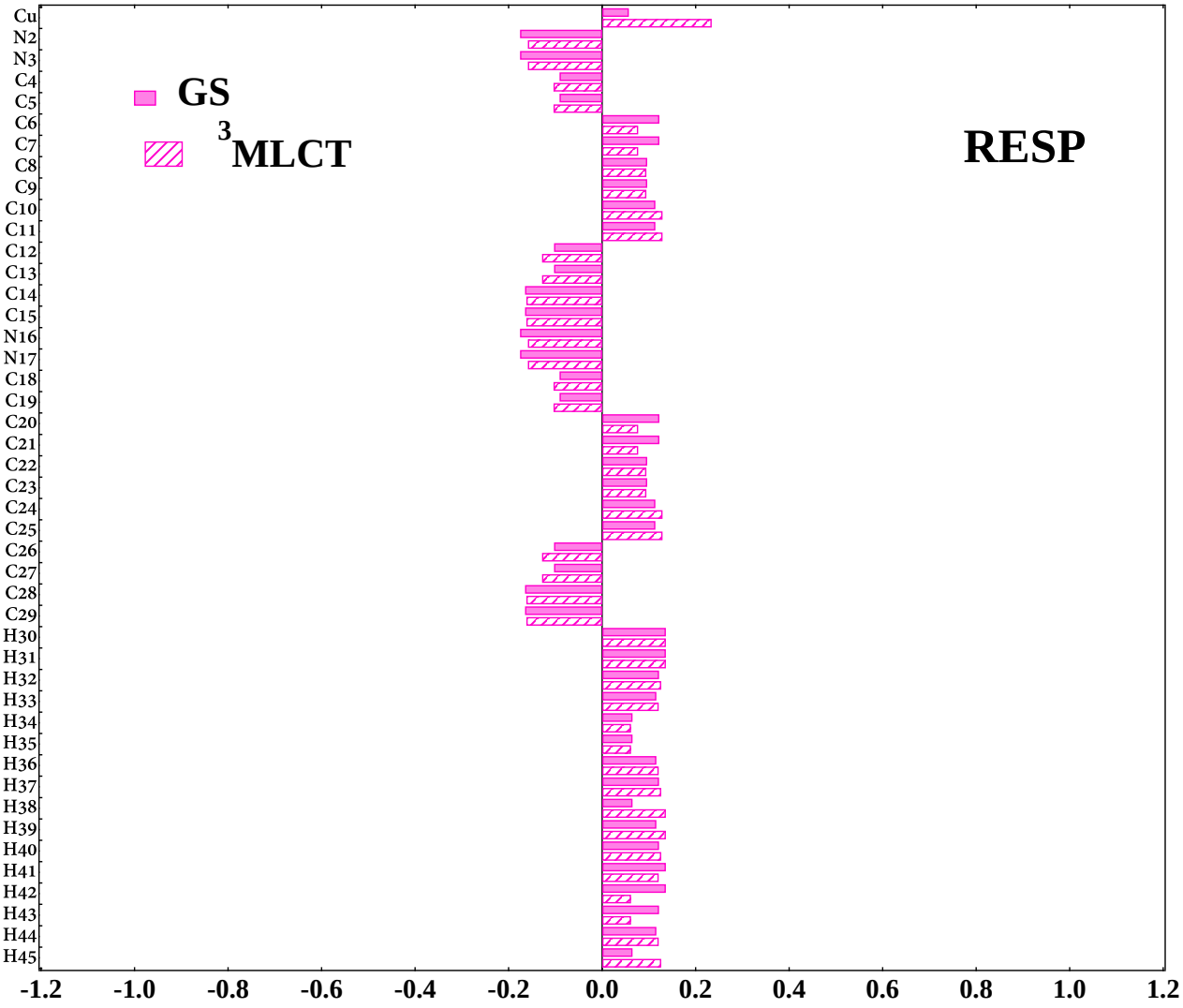
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RESP
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N16
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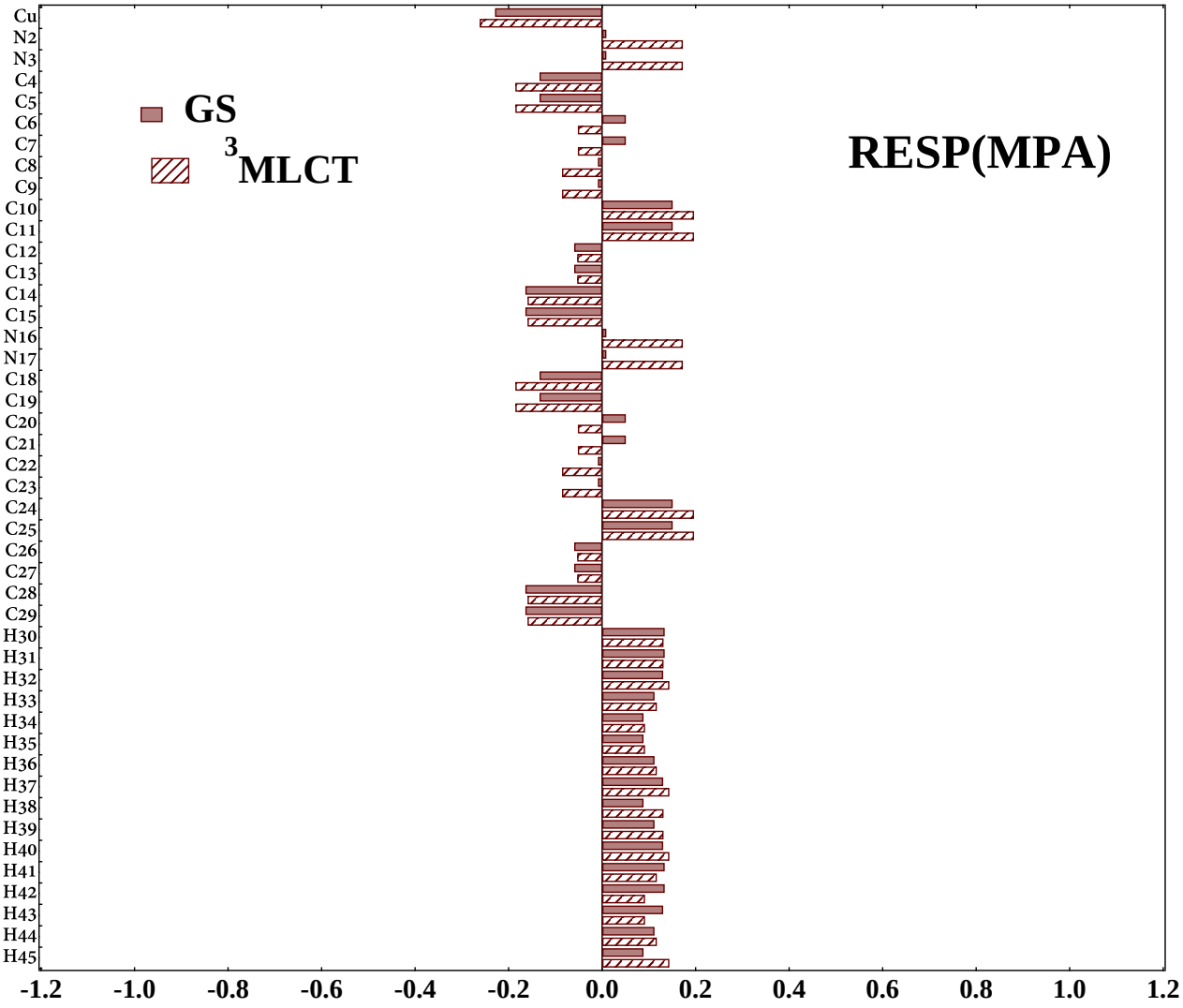
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RESP(MPA)
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C5
C6
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C8
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C11
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C14
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N17
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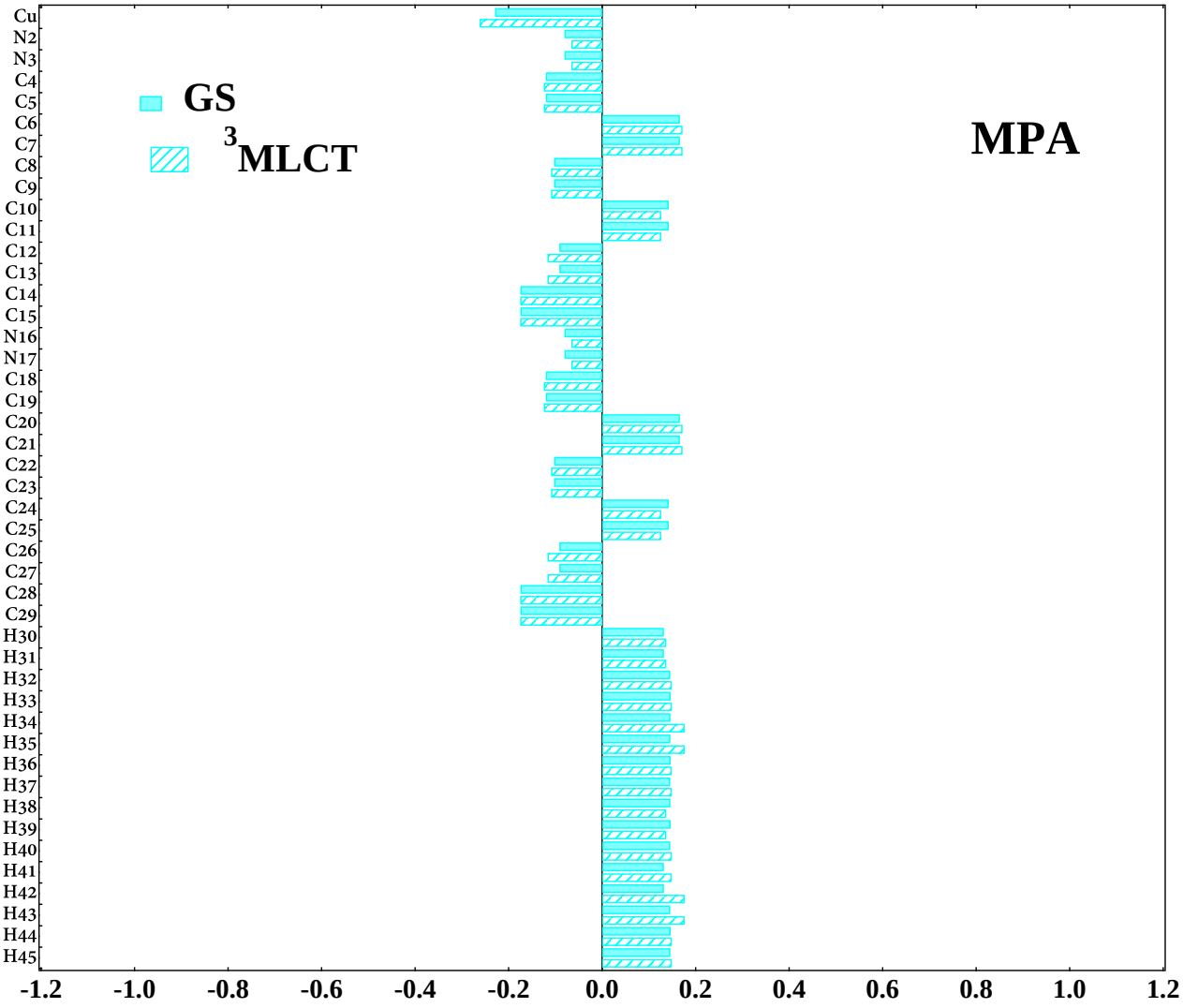
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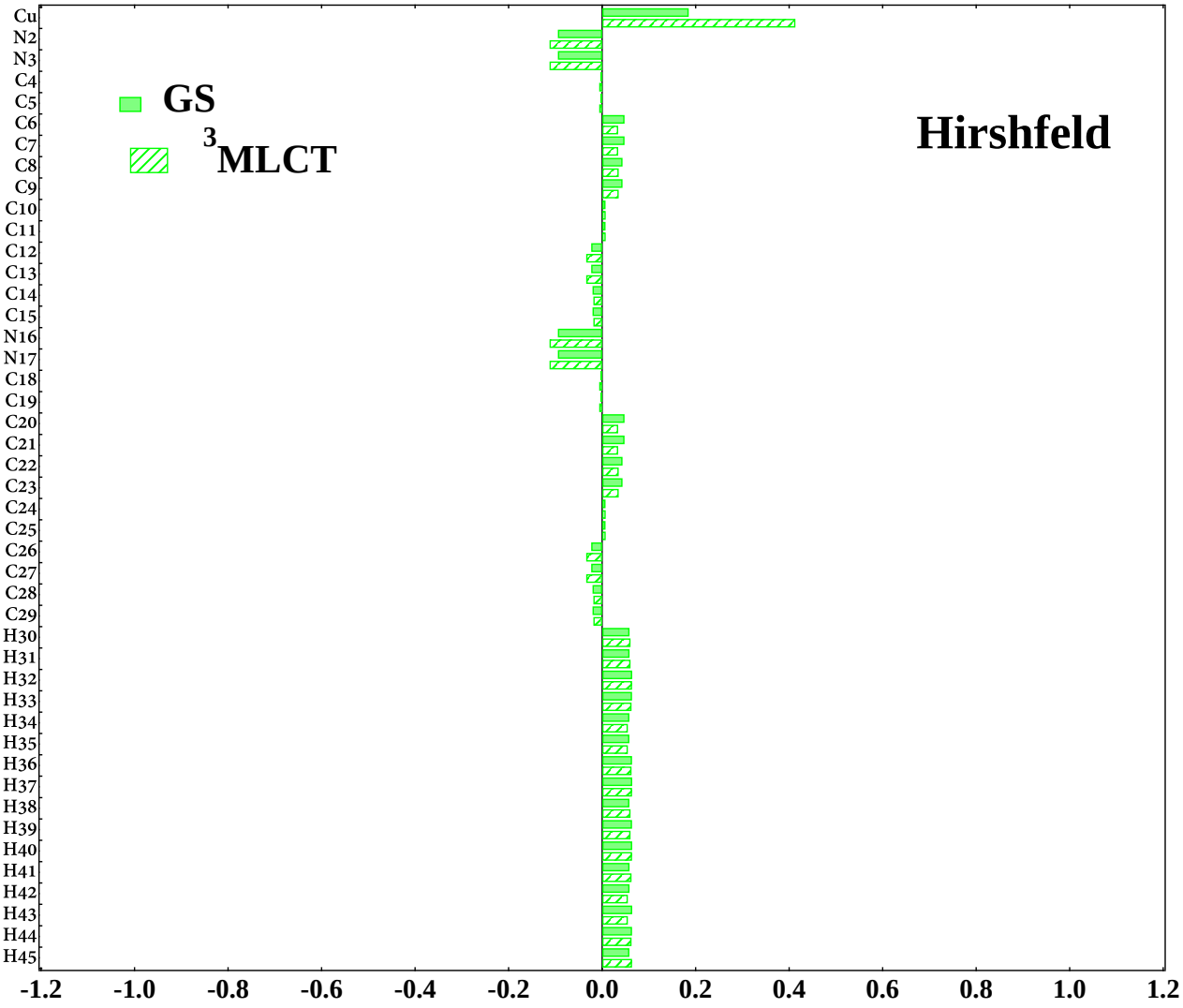
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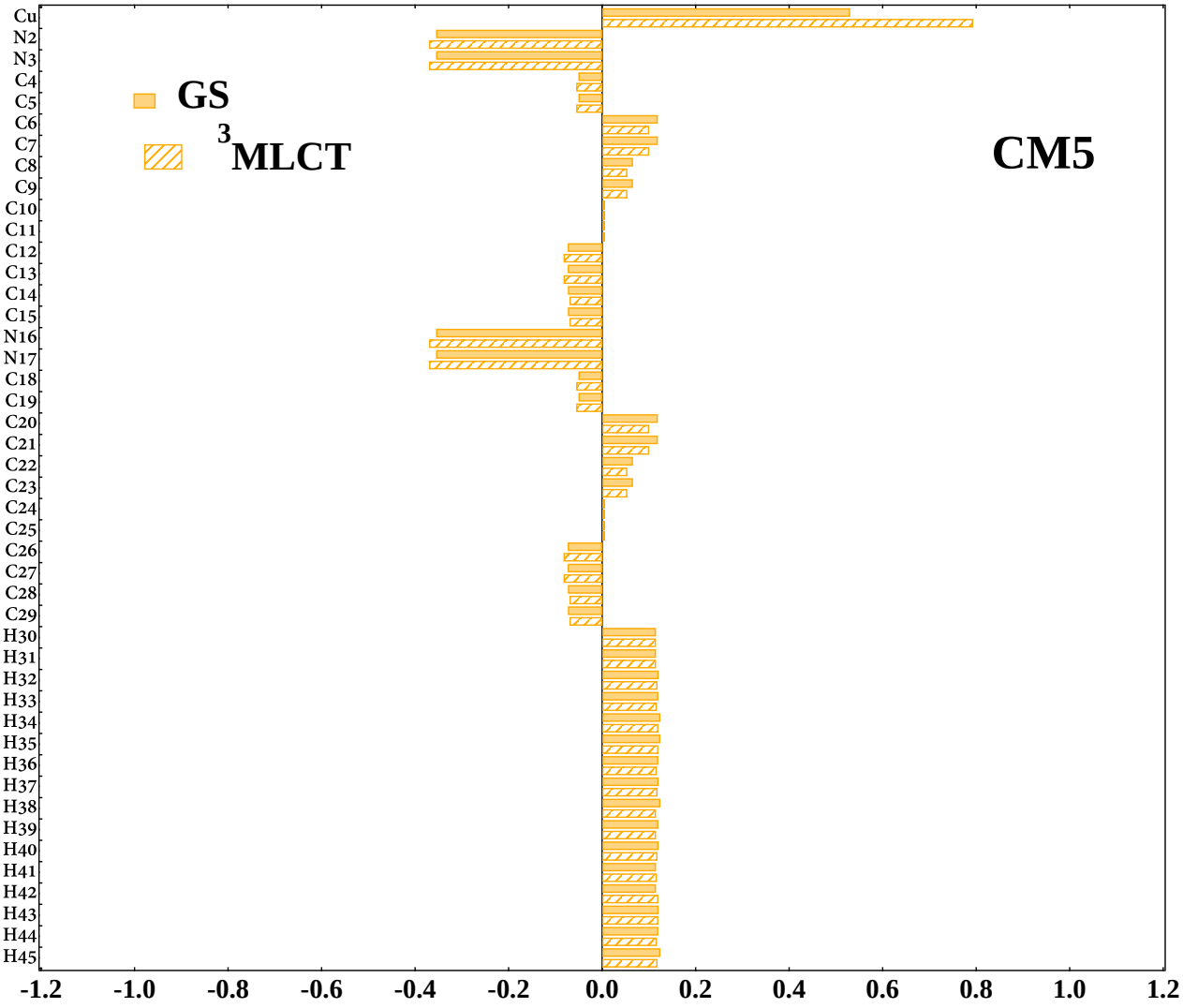
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Cu
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N3
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-0.2
0.0
0.2
0.4
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0.8
1.0
1.2

Fig. S5: Representation of spin densities calculated from different snapshots of a QM/MM MD trajectory of $[Ru(bpy)_3]^{2+}$ in the ^{3}MLCT state. Isosurfaces at 0.035 eV/Å^3.

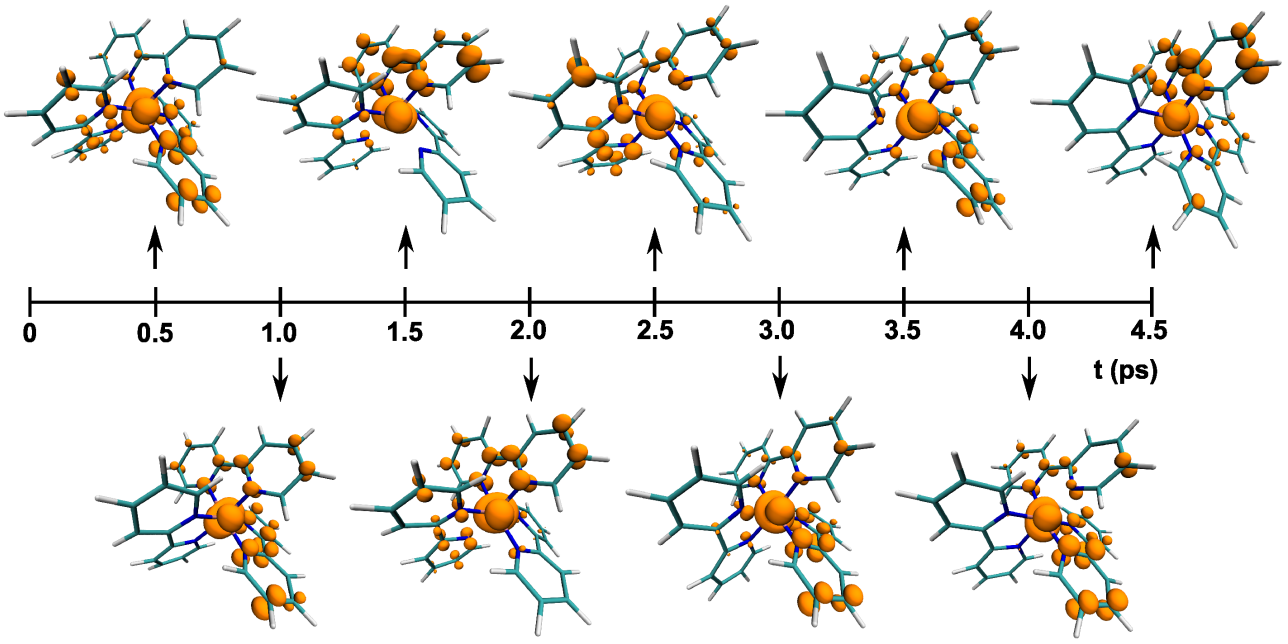


Fig. S6: Charge separation, in elementary charge unit (e), in the bpy ligand of $[Ru(bpy)_3]^{2+}$ for different PAC methods. The blue and red parts show the sum of the positive and negative partial charges on the three bpy ligands, respectively.

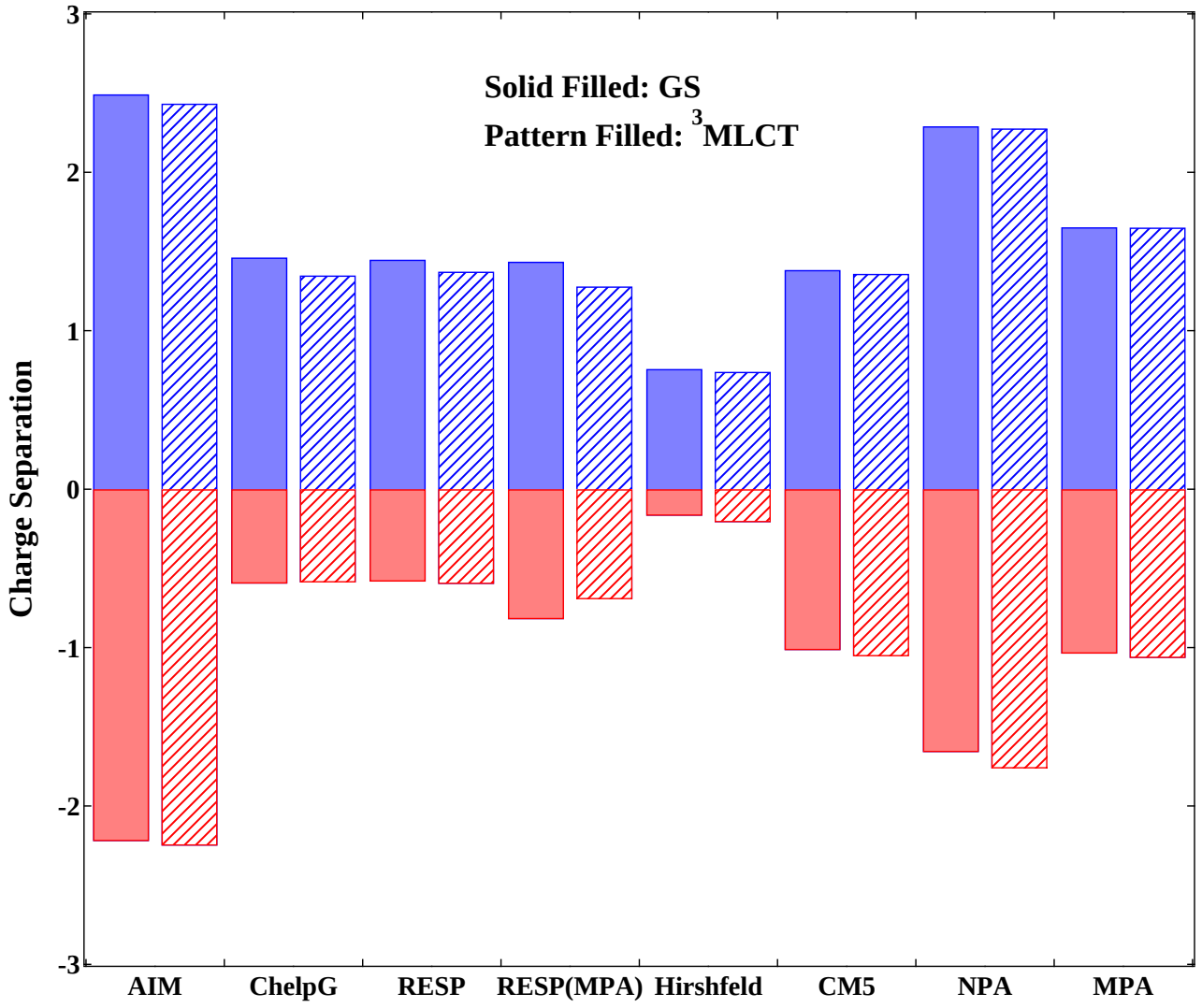


Fig. S7: The RDFs, $g(r)$, of $[Ru(bpy)_3]^{2+}$ in water for the Ru-O_w and Ru-H_w pairs obtained from the classical MD simulations using ChelpG PACs in the ^{3}MLCT state applying different vdW radii.

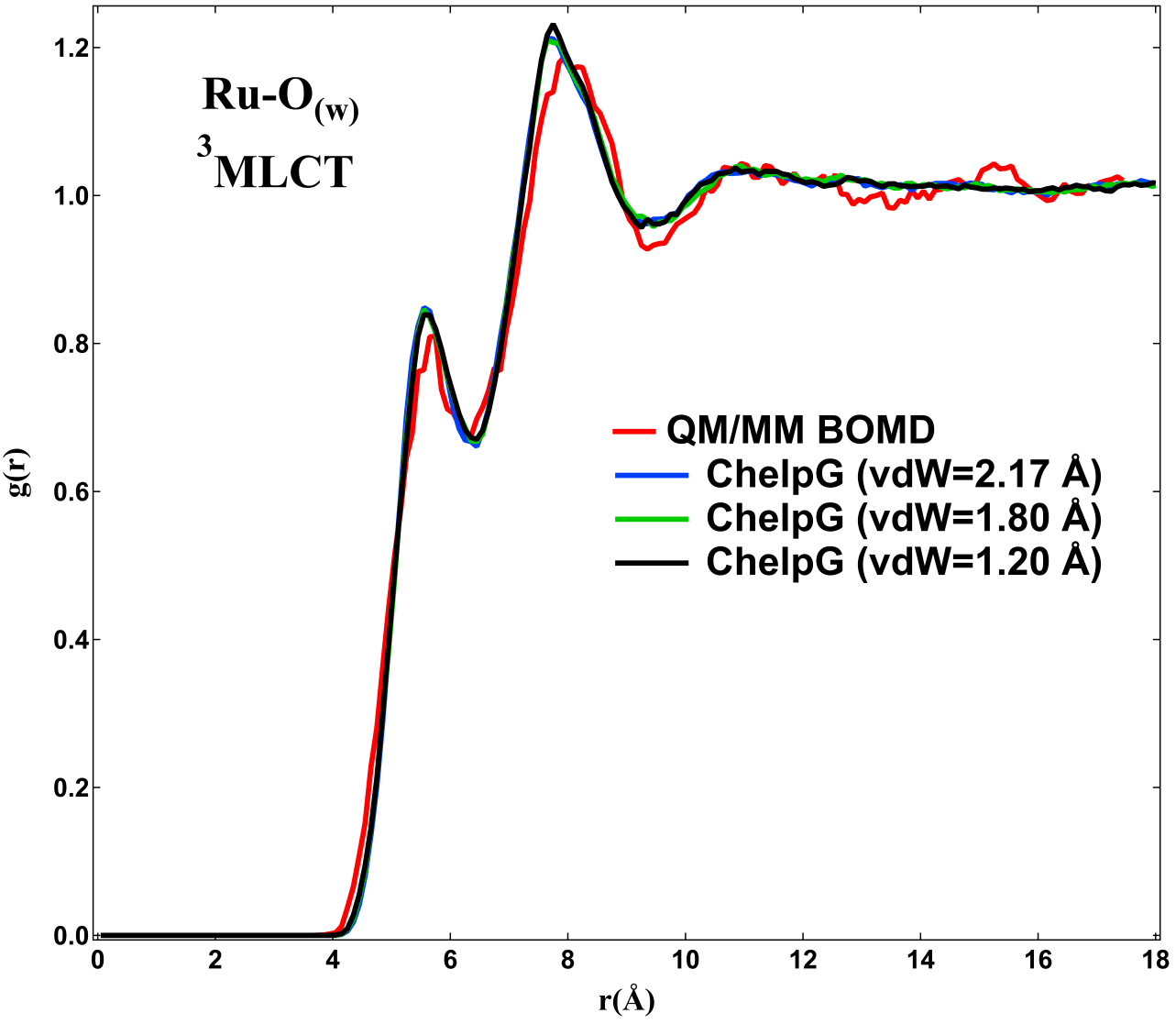


Fig. S8: Plot of the coordination number $cn_{\mathrm{Ru-O_w}}$ and $cn_{\mathrm{Ru-H_w}}$ obtained from the QM/MM MD simulations (top right panel) and the ratio $cn_{\mathrm{Ru-H_w}}/cn_{\mathrm{Ru-O_w}}$ as a function of the distance (R) from the Ru atom of $[\mathrm{Ru(bpy)_3}]^{2+}$.

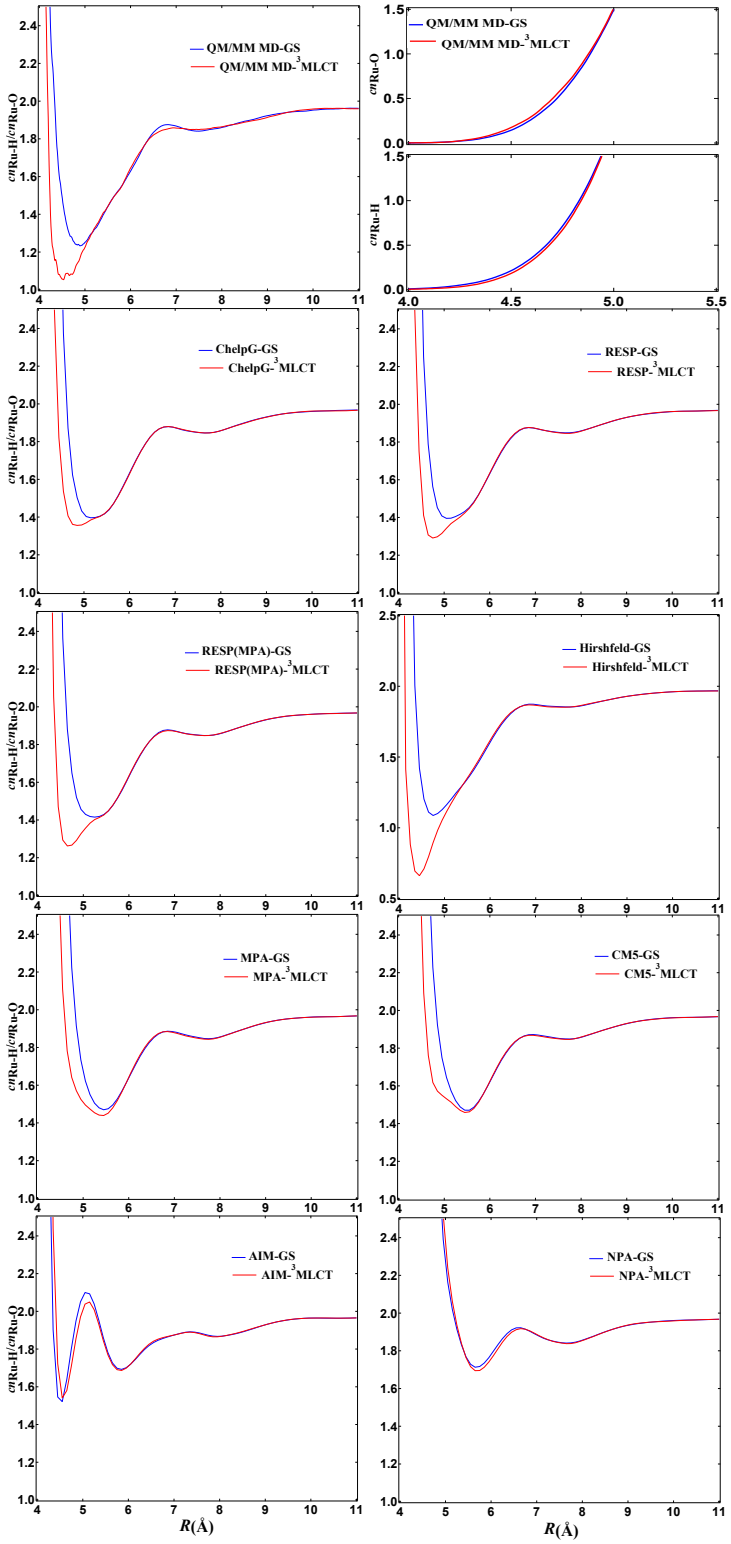


Fig. S9: The RDFs, $g(r)$, of $[Fe(bpy)_3]^{2+}$ in water for the Fe-O_w obtained from the classical MD using ChelpG PAC methods in the ^{5}MC state applying different vdW radii.

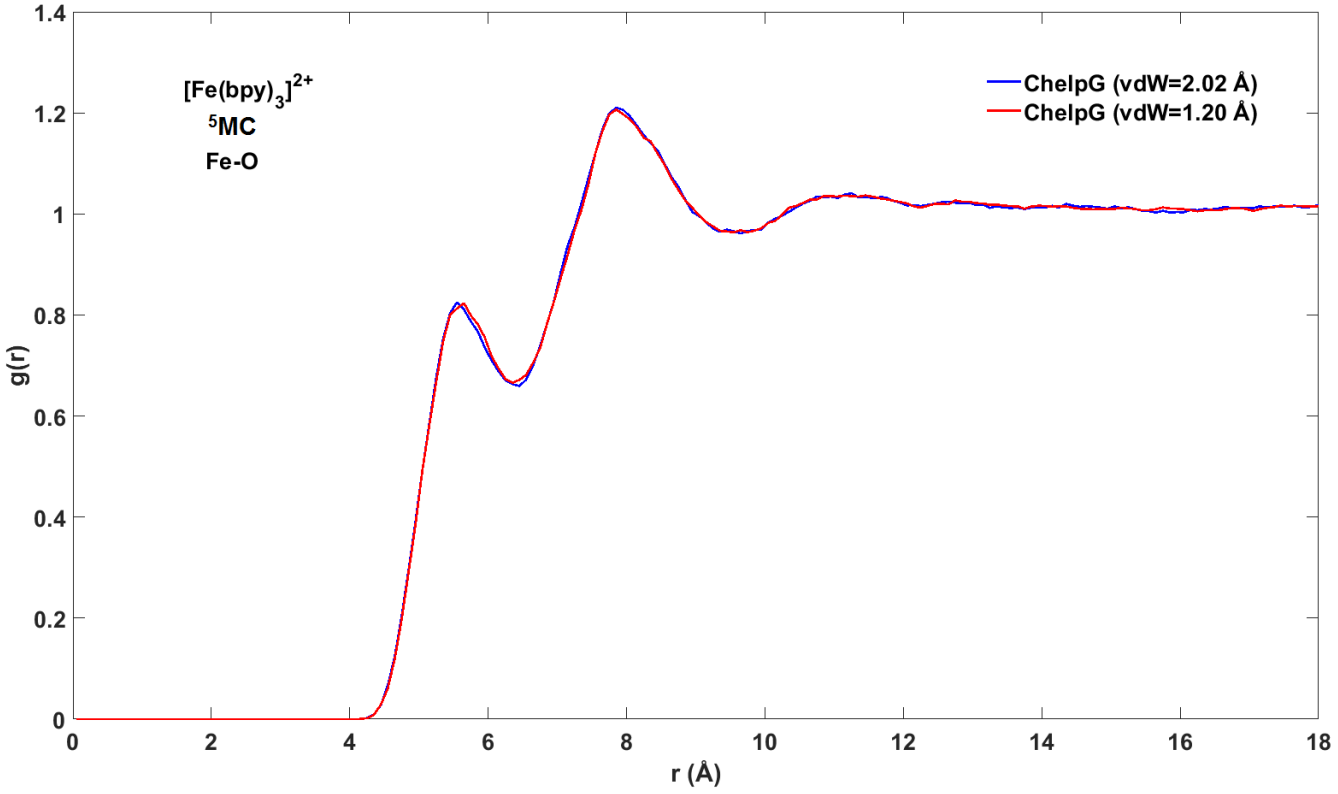


Fig. S10: The RDFs, $g(r)$, of $[Fe(bmip)_2]^{2+}$ in ACN for the Fe-$N_{(ACN)}$ and Fe- $Me_{(ACN)}$ paired obtained from the classical MD using the selected PAC methods in the ^{3}MLCT state.

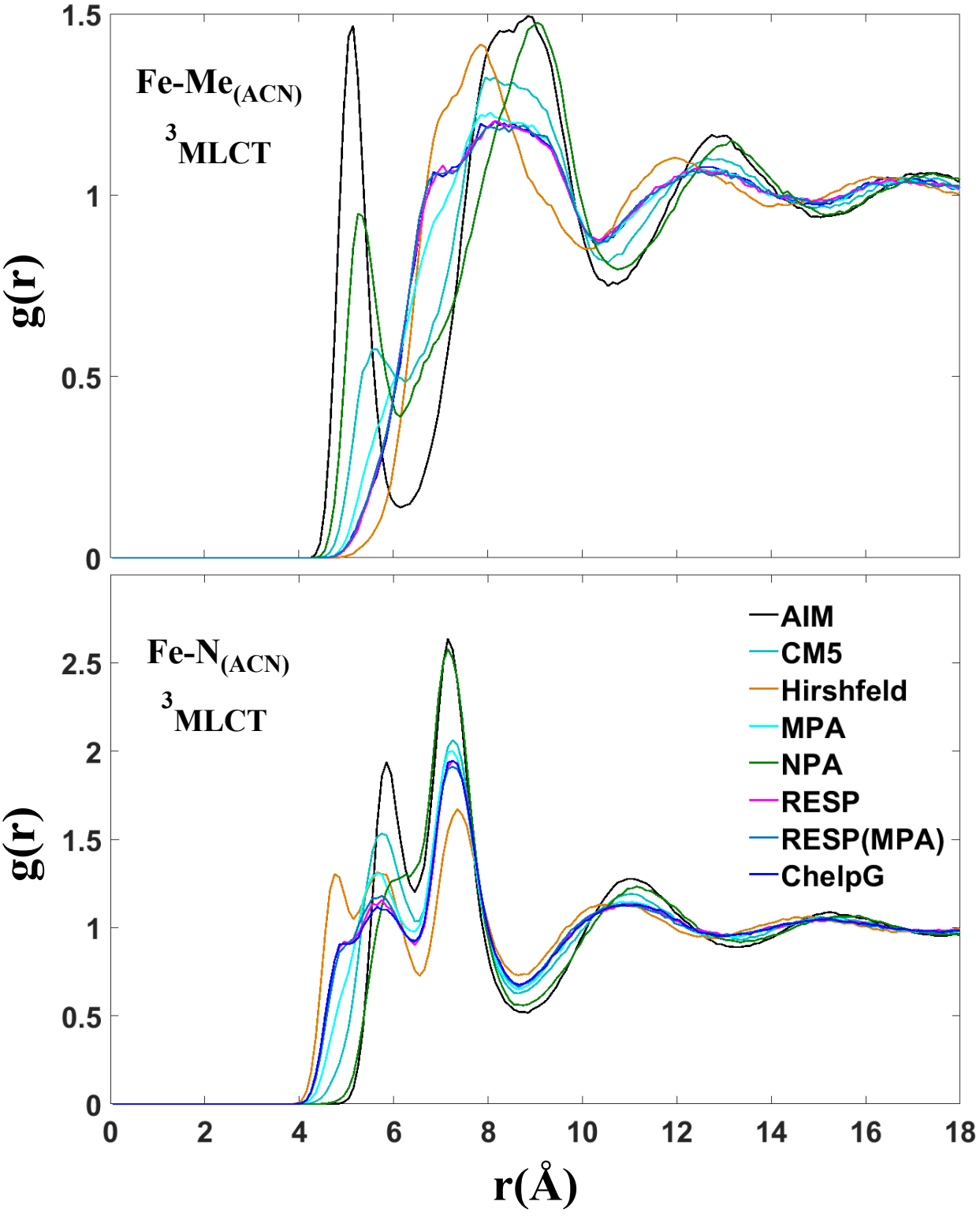


Fig. S11: The RDFs, $g(r)$, of $[Ru(bpy)_3]^{2+}$ in ACN for the Ru-$N_{(ACN)}$ and Ru- $Me_{(ACN)}$ paired obtained from the classical MD using the selected PAC methods in the GS and ^{3}MLCT state.

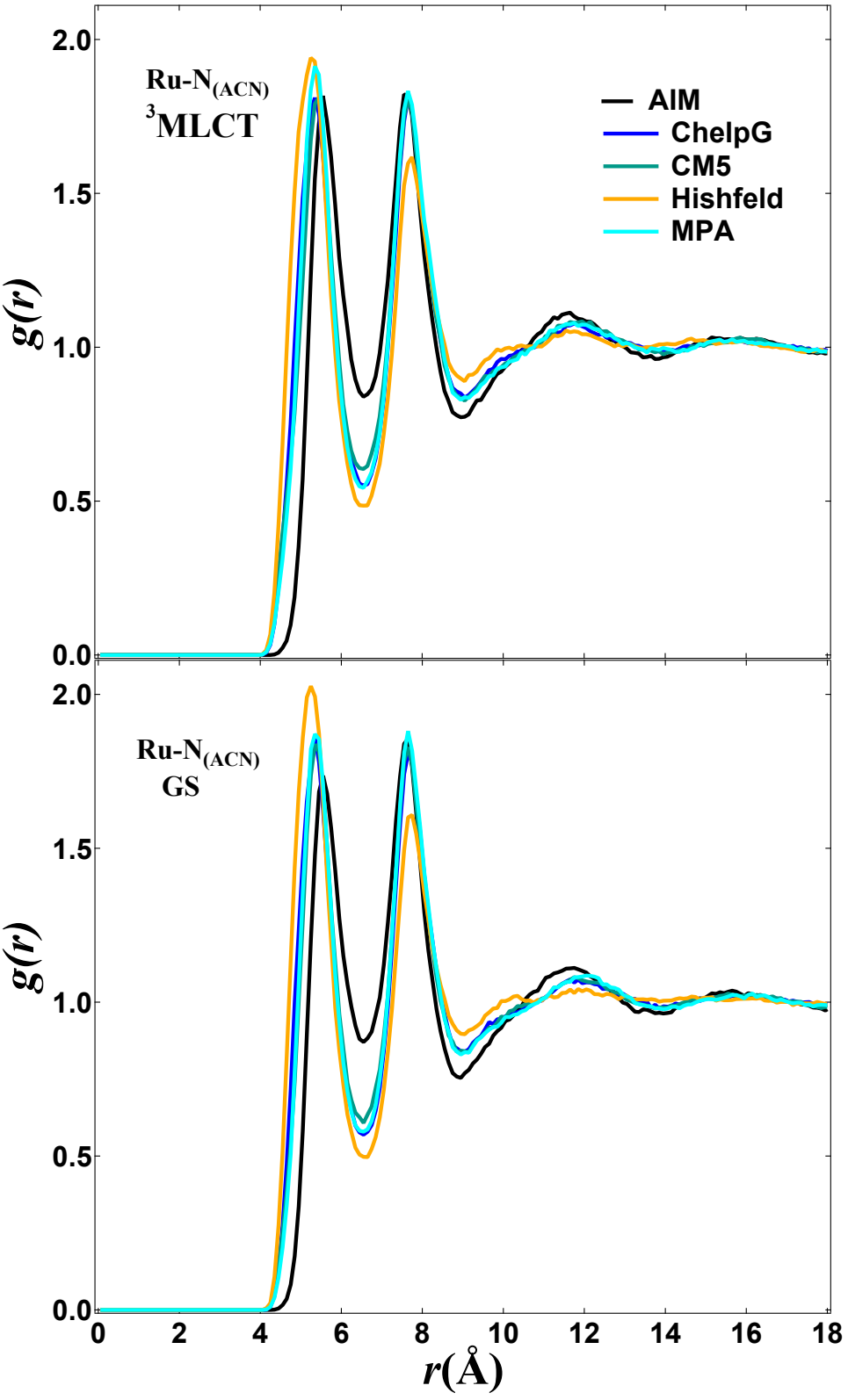


Fig. S12: The RDFs, $g(r)$, of $[Fe(bpy)_3]^{2+}$ in ACN for the Fe-$N_{(ACN)}$ and Fe- $Me_{(ACN)}$ paired obtained from the classical MD using the selected PAC methods in the GS and ^{5}MC state..

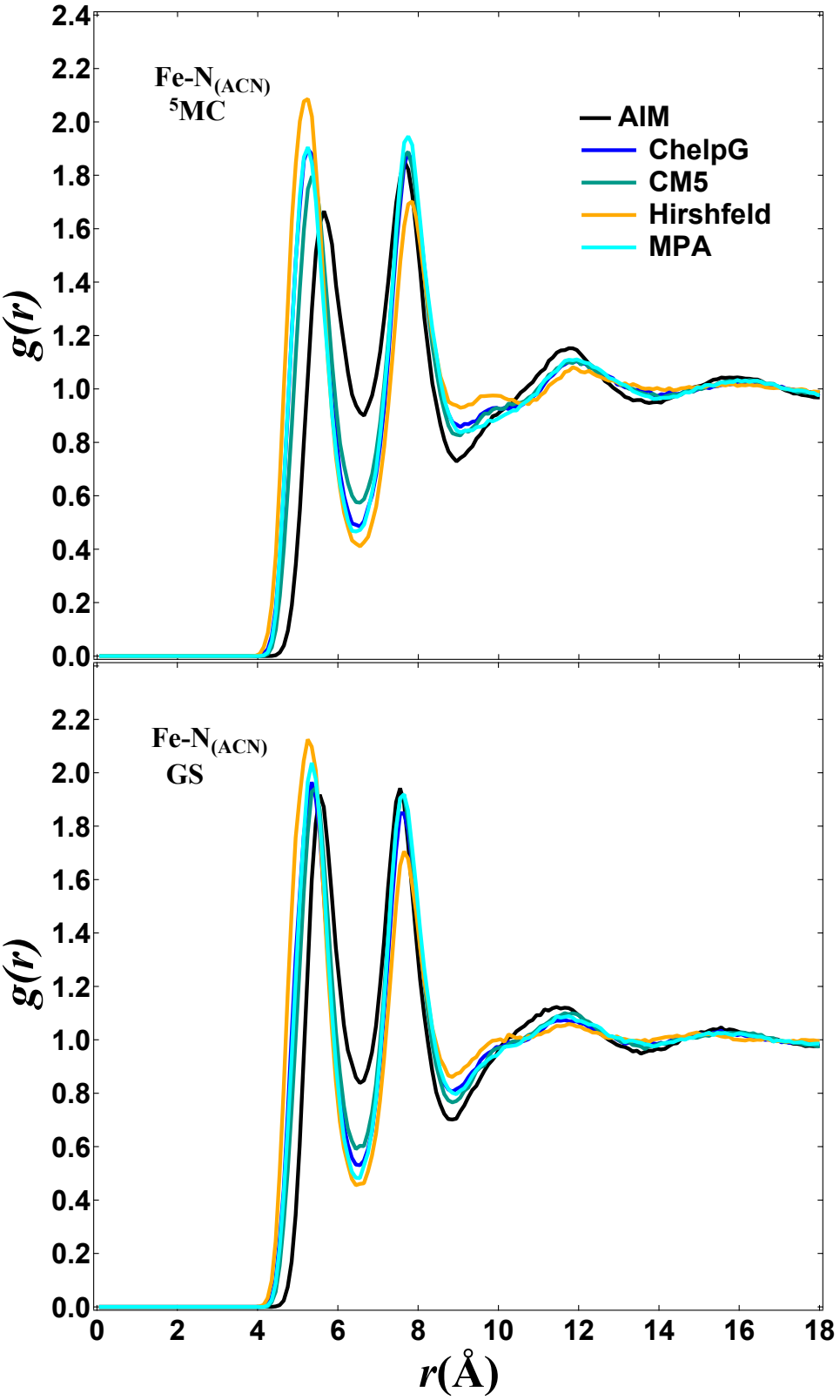


Fig. S13: The RDFs, $g(r)$, $[Fe(bmip)_2]^{2+}$ in water for the Fe-O_w pair obtained from the classical MD using the selected PAC methods in the GS.

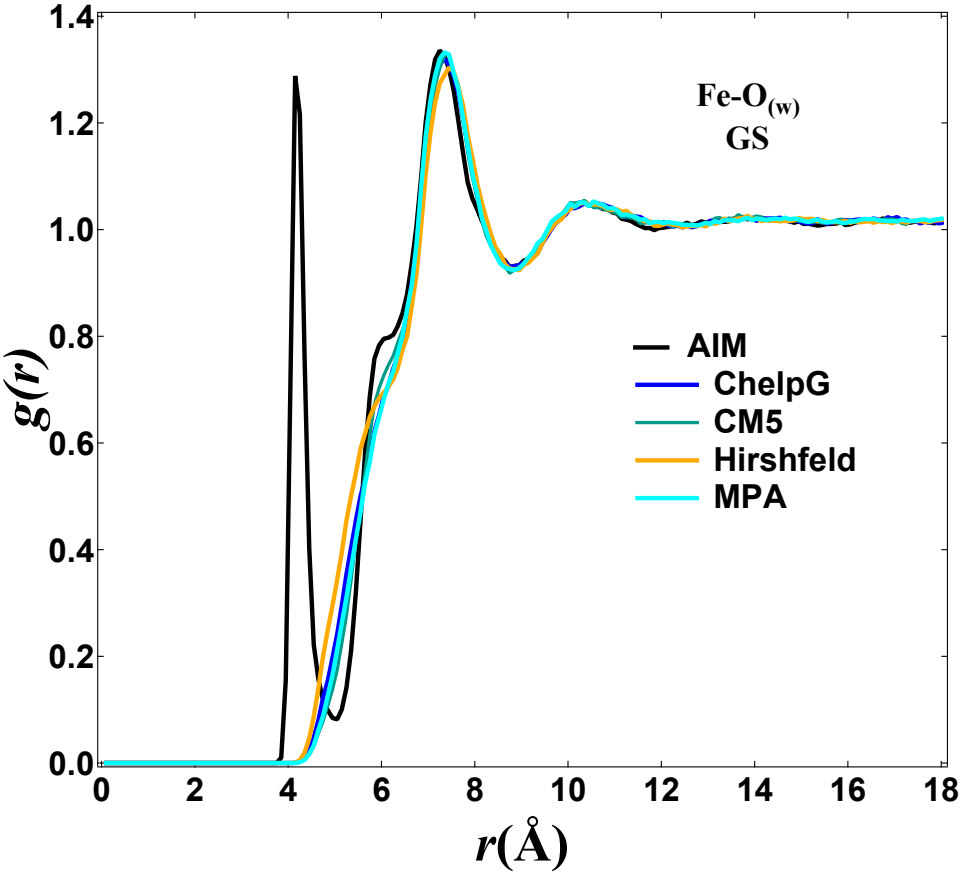
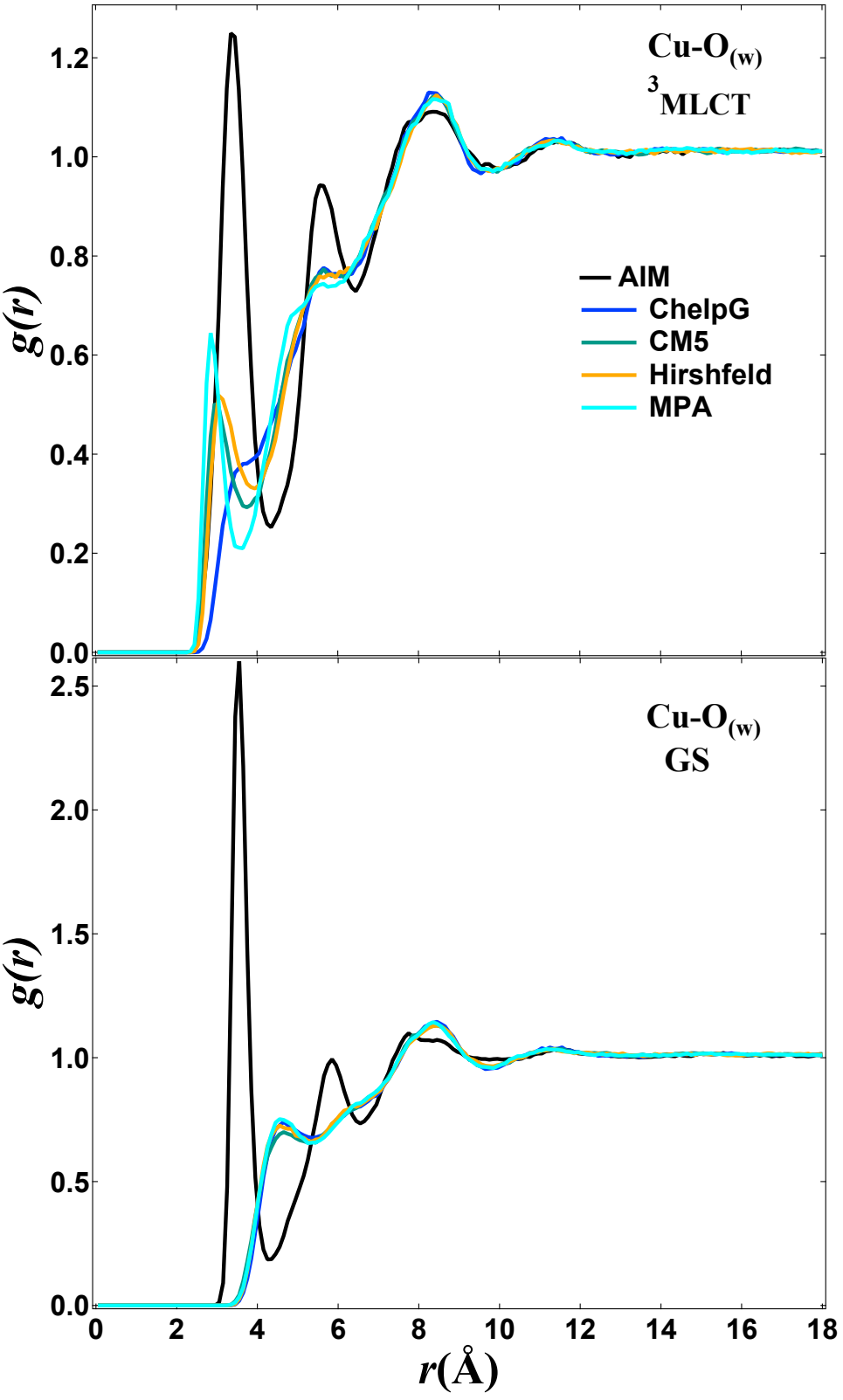


Fig. S14: The RDFs, $g(r)$, of $[Cu(phen)_2]^+$ for the Cu-O_w and Cu-H_w pairs obtained from the classical MD using the selected PAC methods in the GS and ^{3}MLCT state.



Figs. S11 and S12 show the ground- and excited-state RDFs obtained from classical MD simulations using AIM, ChelpG, CM5, Hirshfeld and MPA PACs in ACN for $[Ru(bpy)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$, respectively. As we discussed in the manuscript, in water all PACs methods provide very similar RDFs except AIM (see Figs. 2 and 3). However, the results in ACN indicate relatively different RDFs and more sensitivity of the choice of PAC method in ACN than in water. As seen in the main text, the RDFs obtained from the AIM method in water show very structured peaks centered at 4.3 and 3.3 Å in the $g_{\mathrm{Ru-O_w}}(r)$ and $g_{\mathrm{Ru-H_w}}(r)$, respectively, due to the predicted large positive charges for the metals and large negative charges for N atoms (see Figs. 2 and 3 and also Figs. S1 and S2 for the charges). This method in ACN provide qualitatively similar RDFs to those obtained by other applied PAC methods. This observation can be attributed to the bulky structure of ACN molecule compared to water. This prevents ACN molecules to approach the metal atoms and feel directly the positive (metals) and the negative (nitrogen atoms) parts of the complexes. For $[Fe(bmip)_2]^{2+}$ and $[Cu(phen)_2]^{+}$, we performed classical MD simulations in water using the same PAC methods and depict their corresponding RDFs in Figs. S13 and S14. The results show that, similar to the previous cases, the choice of PAC method is more sensitive in ACN than water. This sensitivity is more pronounced for $[Fe(bmip)_2]^{2+}$ and especially for $[Cu(phen)_2]^{+}$ due to the availability of more space between the ligands.

Fig. S15: The RDFs, g(r), of $[Cu(phen)_2]^+$ in water for the Cu-O_w and Cu-H_w (H_w) pairs obtained from the classical MD simulations using ChelpG PACs in the ^{3}MLCT state applying different vdW radii.

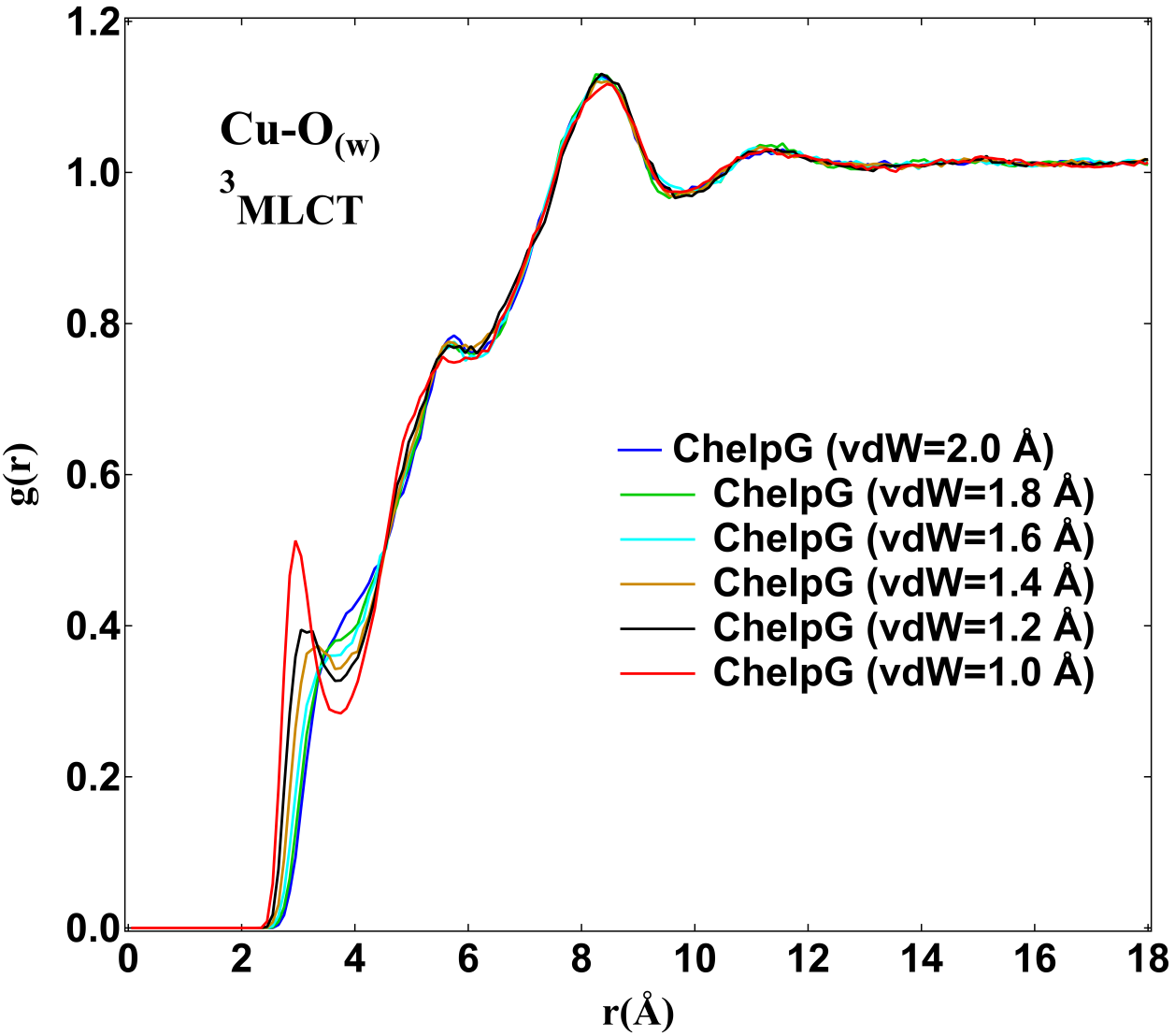
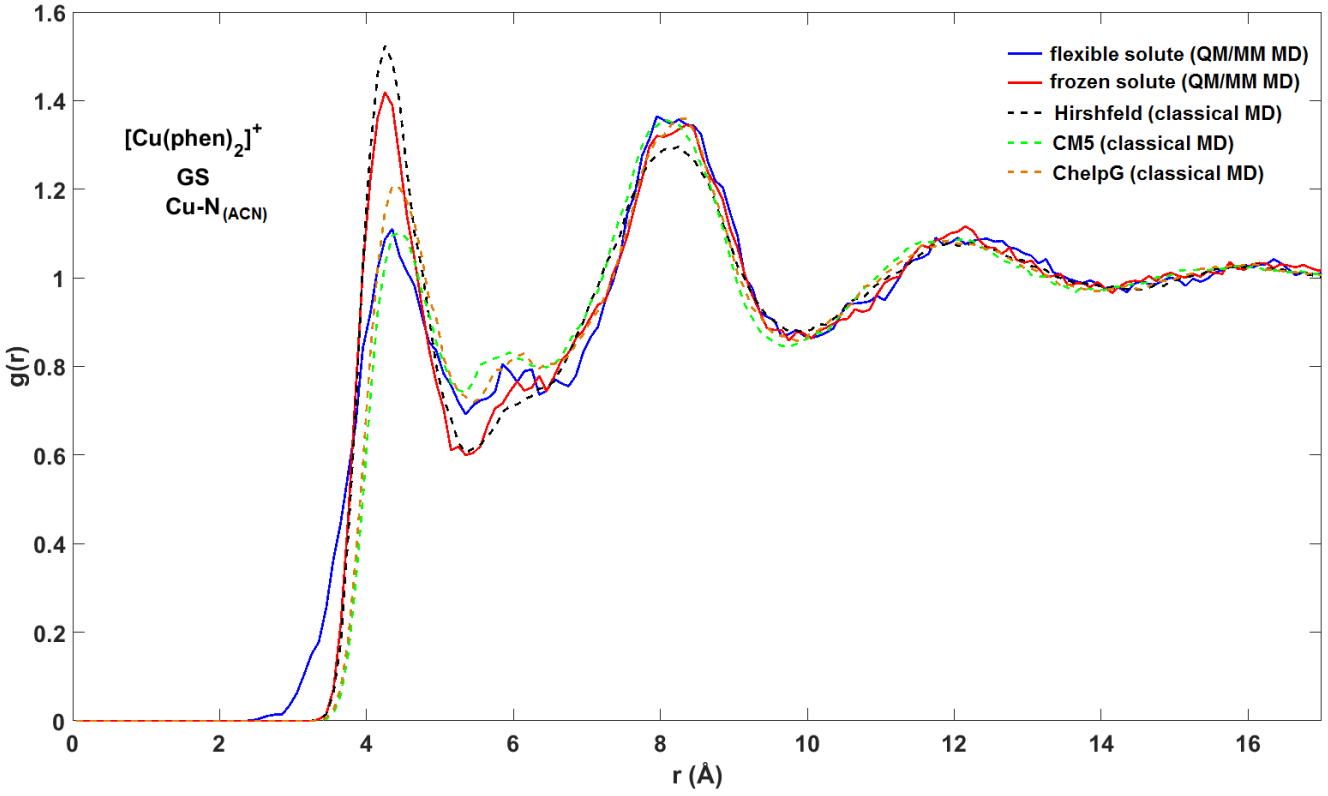


Fig. S16: The RDFs, g(r), of the ground state $[Cu(phen)_2]^+$ in ACN for the Cu-$N_{(ACN)}$ pair obtained from the classical MD simulations using Hirshfeld, CM5 and ChelpG PACs and QM/MM MD simulations with flexible and frozen solute.



We have performed additional QM/MM MD simulations of $[Cu(phen)_2]^+$ in the ground state in which the structure of the solute was kept frozen to the gas-phase BLYP optimized geometry. These simulations were aimed at investigating the impact of structural flexibility of the solute on the solvation structure. We chose $[Cu(phen)_2]^+$ because it is the most flexible of the studied systems (see standard deviations in Table S1). The QM/MM setup and MD protocol are the same as used to collect QM/MM MD data with flexible solute. To freeze the structure of the solute we applied harmonic restraints with a force constant of 1000 kcal/mol.Å^2 using the implementation of Hookean restraints in ASE. We collected a similar amount of data as for the QM/MM MD simulations with flexible solute. Fig. S16 shows the the Cu-$N_{(ACN)}$ RDFs of $[Cu(phen)_2]^+$ in ACN extracted from QM/MM MD simulations with frozen and flexibile solute as well as those obtained from classical MD simulations using Hirshfeld, CM5 and ChelpG PAC methods. These results show the impact of solute flexibility on the solvent structure in QM/MM MD simulations. For example, a tail at short distances (r<3.5 Å) is present in the RDF of the QM/MM MD simulations with flexible solute due to transient solute configurations for which the metal is more accessible to the solvent. This feature cannot be reproduced by QM/MM MD with frozen solute or any of the classical MD simulations. Among the classical MD RDFs, Hirshfeld is close to the one simulated by frozen-solute QM/MM MD, while CM5 is close to the RDF simulated by flexible-solute QM/MM MD. We stress that the purpose of this work is to assess the ability of classical MD with fixed PACs to provide RDFs close to those obtained from a reference as accurate as possible, in the present case QM/MM MD with a flexible solute.

Table S1: Selected internal coordinates obtained by averages from the QM/MM MD trajectories comparing with gas-phase DFT optimizations using the Gaussian 16 and GPAW programs for the investigated TMCs in ground and excited states. Standard deviations are reported in parentheses.

	$[Ru(bpy)_3]^{2+}$					
	Gaussian 16		GPAW		QM/MM MD	
	GS	ES	GS	ES	GS	ES
Ru-N Bonds (Å)	2.090	2.084	2.074	2.075	2.080 (0.018)	2.083 (0.019)
NRuN Angles (deg.)	78.05	78.43	78.8	79.1	78.7 (1.2)	79.0 (1.2)
NNRuNN Dihedrals (deg.)	87.7	86.3	88.9	87.9	88.7 (2.4)	87.2 (2.5)

	$[Fe(bpy)_3]^{2+}$					
	Gaussian 16		GPAW		QM/MM MD	
	GS	ES	GS	ES	GS	ES (t>1.5ps)
Fe-N Bonds (Å)	2.006	2.200	2.014	2.200	2.008 (0.020)	2.213 (0.026)
NFeN Angles (deg.)	80.7	75.0	81.0	75.6	81.2 (1.2)	75.4 (1.4)
NNFeNN Dihedrals (deg.)	88.5	92.0	88.7	90.9	89.2 (2.1)	91.5 (11.7)

	$[Fe(bmip)_2]^{2+}$					
	Gaussian 16		GPAW		QM/MM MD	
	GS	ES	GS	ES	GS	ES
Fe-N Bonds (Å)	1.949	-	1.963	-	1.951 (0.03)	-
Fe-C Bonds (Å)	1.991	-	2.007	-	1.993 (0.022)	-
NFeN Angles (deg.)	180.0	-	180.0	-	175.8 (2.2)	-
CFeC Angles (deg.)	157.74	-	157.2	-	157.8 (1.6)	-
CNC Angles (deg.)	117.6	-	102.9	-	102.3 (1.8)	-
CCFeCC Dihedrals (deg.)	90.0	-	90.0	-	89.9 (3.2)	-

	$[Cu(phen)_2]^{+}$					
	Gaussian 16		GPAW		QM/MM MD	
	GS	ES	GS	ES	GS	ES (t>4ps)
Cu-N Bonds (Å)	2.057	2.016	2.055	2.006	2.065 (0.033)	2.025 (.0025)
NCuN Angles (deg.)	81.89	83.23	82.05	83.5	82.2 (1.7)	83.1 (1.5)
NNCuNN Dihedrals (deg.)	90.0	38.4	89.9	39.3	84.0 (12.3)	37.5 (5.7)

Table S2: Cartesian Coordinates of the ground- and excited-state optimized structure of $[Ru(bpy)_3]^{2+}$.

	Gaussian 16 (B3LYP*/Def2TZVP)					
	GS			ES		
H	1.913103	3.228007	3.618873	-0.77289900	-3.67331400	-3.60420200
H	0.660248	5.232747	2.768660	-3.10438500	-4.21187700	-2.82109700
C	1.252369	3.158537	2.763642	-1.21513500	-3.16082100	-2.75957100
C	0.557715	4.265712	2.290824	-2.50962000	-3.45881400	-2.31797100
H	-3.751219	0.042631	3.619737	-2.79631800	2.50319500	-3.60427200
H	1.839345	-3.269742	3.619745	3.56278700	1.16824100	-3.60805900
H	1.614715	1.060694	2.460131	0.50482300	-1.92420800	-2.41005100
H	4.201871	-3.187177	2.769347	5.19826700	-0.57816400	-2.82418700
C	1.090879	1.943696	2.118786	-0.49617200	-2.18895800	-2.09541300
C	-3.361042	-0.494687	2.764245	-2.13147900	2.63042600	-2.75962900
H	-1.725146	0.867714	2.460634	-1.91805400	0.52271900	-2.41081000
C	-0.272198	4.110732	1.191251	-3.02023500	-2.78178500	-1.22891100
H	-0.819467	4.961214	0.807728	-4.01867900	-3.00342600	-0.87645500
C	2.109438	-2.663079	2.764277	3.34155800	0.52940000	-2.76274100
H	-4.861661	-2.044235	2.769159	-2.09959900	4.79218900	-2.82046600
C	3.415569	-2.615116	2.291361	4.24873600	-0.44074900	-2.32070500
C	-2.228291	-0.027195	2.119198	-1.64801900	1.52221000	-2.09586900
H	0.111412	-1.928219	2.460703	1.40929900	1.39770900	-2.41299900
C	-3.972925	-1.649593	2.291245	-1.74370800	3.90083000	-2.31766900
C	1.137991	-1.916109	2.119226	2.14053900	0.66474500	-2.09808900
N	0.287017	1.782495	1.052468	-0.98998300	-1.51080000	-1.04002500
C	-0.396515	2.862110	0.583138	-2.24924100	-1.80735100	-0.58084100
C	3.696171	-1.819166	1.191557	3.91945200	-1.22121900	-1.23093900
H	4.706336	-1.770406	0.808025	4.61190200	-1.97383900	-0.87835900
N	1.400151	-1.139701	1.052610	1.80199100	-0.10159000	-1.04183800
N	-1.687137	-0.642588	1.052607	-0.81388700	1.61138600	-1.04047200
C	-3.424066	-2.290720	1.191447	-0.90185700	4.00513300	-1.22886600
C	2.676890	-1.087488	0.583259	2.69001600	-1.04229900	-0.58252800
H	-2.061896	4.586329	-0.807449	-4.59846500	-2.00516200	0.87844300
C	-1.252905	2.603713	-0.583141	-2.68294700	-1.06061100	0.58255500
H	-3.887223	-3.189740	0.807838	-0.59546000	4.98084800	-0.87626400
C	-2.280560	-1.774206	0.583231	-0.44194800	2.85051400	-0.58127600
Ru	-0.000009	-0.000021	-0.000196	-0.00002700	-0.00040300	-0.00006400

C	-2.047194	3.575165	-1.191172	-3.91115700	-1.24780800	1.23093600
C	2.881241	-0.216837	-0.583182	2.26149500	-1.79179200	0.58104100
H	5.002694	-0.507738	-0.807585	4.03906100	-2.97572900	0.87677300
N	-1.224988	1.326301	-1.052698	-1.80140800	-0.11374200	1.04168100
N	1.760988	0.397636	-1.052805	1.00026500	-1.50378000	1.04023100
C	4.119663	-0.014882	-1.191326	3.03913500	-2.76087000	1.22922500
C	-1.628655	-2.386814	-0.583011	0.42243800	2.85339500	0.58142900
C	-2.824101	3.245353	-2.290935	-4.24580300	-0.46940900	2.32054600
N	-0.536175	-1.724154	-1.052572	0.80301400	1.61680200	1.04033500
C	1.871626	1.209358	-2.119619	0.51107400	-2.18517300	2.09567300
H	-3.444463	3.994280	-2.768698	-5.19441400	-0.61318900	2.82398400
C	4.222492	0.822618	-2.291259	2.53314800	-3.44123000	2.31837500
H	0.957569	1.676568	-2.461423	-0.49169500	-1.92717400	2.41027600
C	-1.983564	1.016095	-2.119251	-2.14524300	0.65048200	2.09776700
C	3.074014	1.446282	-2.764517	1.23665200	-3.15201200	2.75995100
H	-2.941405	-4.078563	-0.807112	0.56122100	4.98468700	0.87681300
H	5.181245	0.985251	-2.769106	3.13303300	-4.19016200	2.82159000
C	-2.072924	-3.560479	-1.190832	0.87444600	4.01105300	1.22916800
C	-2.790076	1.938862	-2.764080	-3.34531900	0.50702000	2.76241600
H	-1.931233	-0.009183	-2.460845	-1.41910800	1.38856000	2.41250600
H	3.102002	2.109547	-3.620153	0.79792900	-3.66741000	3.60464500
C	0.111857	-2.226416	-2.118895	1.63807700	1.53322300	2.09543900
H	0.973853	-1.668855	-2.460550	1.91520100	0.53556500	2.41003900
H	-3.378704	1.631378	-3.619525	-3.57096000	1.14449800	3.60759700
C	-1.398773	-4.068769	-2.290370	1.71724800	3.91239600	2.31776800
C	-0.284111	-3.386383	-2.763450	2.11399300	2.64462300	2.75932800
H	-1.737268	-4.980530	-2.767978	2.06705500	4.80610100	2.82066900
H	0.276602	-3.742725	-3.618691	2.77997100	2.52182300	3.60373000

Table S3: Cartesian Coordinates of the ground- and excited-state optimized structure of $[Ru(bpy)_3]^{2+}$.

	GPAW (BP86/TZP(Ru)DZP)					
	GS			ES		
H	12.98731224	11.77201420	12.35615050	13.06902249	11.79990140	12.36556773
H	12.36702936	14.10353885	11.50250738	12.39018289	14.13280035	11.54994364
C	12.32212484	11.90789924	11.48230106	12.40050577	11.93401015	11.49527724
C	11.98012987	13.19155111	11.00865368	12.02105109	13.22346263	11.03892901
H	6.64738053	10.38190053	12.35006550	6.69193962	10.45145475	12.36898796
H	11.00020833	5.61343868	12.35921653	11.02803381	5.64221179	12.38523054
H	12.05610221	9.75870185	11.16437038	12.17729023	9.78716209	11.14393587
H	13.31476834	4.95713148	11.49159807	13.37650298	5.03520167	11.55510265
C	11.81026248	10.78114807	10.82149243	11.91311824	10.81133609	10.81960801
C	6.86596932	9.74322676	11.47357995	6.91705907	9.80329777	11.50127208
H	8.85127254	10.60862483	11.15486602	8.88865776	10.68392096	11.16431898
C	11.14172627	13.29014025	9.88564956	11.17371361	13.33037322	9.93036415
H	10.86324894	14.28356018	9.48826548	10.86816257	14.32585441	9.55914186
C	11.44827295	6.11190074	11.47891209	11.48048574	6.15203569	11.51440589
H	4.95483291	8.66386779	11.50017955	5.01225073	8.70118740	11.54533759
C	12.72389848	5.75238943	10.99829296	12.78000378	5.81840491	11.04972164
C	8.09555151	9.87786816	10.81057350	8.13810865	9.94022140	10.83497050
H	9.72950917	7.42944678	11.16667466	9.74622503	7.43826223	11.17884723
C	5.93381665	8.79706187	11.00149244	5.98797996	8.83315738	11.03950037
C	10.73298519	7.12165849	10.81860211	10.75879214	7.14499813	10.84570722
N	10.98943301	10.86318938	9.73130607	11.07066878	10.90006850	9.74483451
C	10.66053642	12.12145639	9.25790558	10.70138452	12.16151985	9.28003536
C	13.23378227	6.42688625	9.87635654	13.29536956	6.49330193	9.93793153
H	14.22997086	6.16107626	9.47695840	14.30213359	6.24321683	9.55580949
N	11.21615048	7.78712068	9.72647926	11.25624523	7.82340480	9.76577768
N	8.44193060	9.12607721	9.72288608	8.49103899	9.16756148	9.76137164
C	6.27408311	8.02362003	9.87912947	6.32597553	8.04593142	9.93397345
C	12.47070924	7.43794493	9.25417764	12.52639493	7.49489342	9.29174495
H	9.58367421	14.28456105	7.83648018	9.66480779	14.32484801	7.83040416
C	9.78545978	12.12218133	8.06820425	9.83272624	12.16137813	8.10740571
H	5.55979253	7.27772267	9.48429854	5.61648729	7.28590485	9.55700753
C	7.52686026	8.20055757	9.25286653	7.57854575	8.22045291	9.28905662
Ru	10.22385292	9.26169602	8.6623253	10.26760756	9.29557103	8.69652674

C	9.30463869	13.29099074	7.44012629	9.35831717	13.32977519	7.45873722
C	12.92251048	8.20275422	8.07322581	12.96101402	8.24069495	8.11550499
H	14.89094304	7.28010296	7.84220476	14.92515822	7.31100891	7.85604528
N	9.45699990	10.86501340	7.59493711	9.46749498	10.89967891	7.64031351
N	12.00693431	9.12660650	7.60197075	12.04712448	9.17954229	7.63721552
C	14.17606678	8.02601418	7.44760067	14.21486644	8.06736580	7.47432270
C	7.97807833	7.43574550	8.07181920	8.01278209	7.47735339	8.11233553
C	8.46650859	13.19192034	6.31713317	8.51138639	13.22362701	6.35033113
N	9.23105240	7.78722979	7.59759006	9.28203536	7.81203607	7.63572928
C	12.35339502	9.87665264	6.51242685	12.39961540	9.95328629	6.56467419
H	8.08125594	14.10387300	5.82204524	8.14116753	14.13353932	5.84068770
C	14.51649614	8.79860465	6.32453000	14.55072087	8.84829149	6.36423437
H	11.59726566	10.60582513	6.16596377	11.64743943	10.69340625	6.23319195
C	8.63566164	10.78213787	6.50492285	8.62605382	10.81086223	6.56515258
C	13.58372745	9.74372555	5.85046759	13.62191773	9.81606041	5.89929724
H	6.22065459	6.15554431	7.85060792	6.23716366	6.22403193	7.84477018
H	15.49610265	8.66559778	5.82636340	15.52571643	8.71283975	5.85845988
C	7.21648063	6.42278332	7.45095257	7.24390801	6.47662272	7.46274634
C	8.12380523	11.90838615	5.84370506	8.13470608	11.93415698	5.89245183
H	8.39108556	9.75958030	6.16182955	8.36289158	9.78700894	6.23880443
H	13.80228614	10.38150038	4.97323685	13.84607850	10.46070017	5.02975879
C	9.71451038	7.12235147	6.50501657	9.77865587	7.13609499	6.55373460
H	10.71691351	7.43274804	6.15526264	10.79032751	7.43252623	6.22034243
H	7.45968345	11.77234653	4.96947709	7.46700436	11.80055372	5.02130963
C	7.72606374	5.74940318	6.32829318	7.75887501	5.80733024	6.34846281
C	9.00077314	6.11059669	5.84636022	9.05842186	6.14391690	5.88320517
H	7.13639176	4.95292976	5.83587015	7.16135501	5.02649271	5.83894600
H	9.44907769	5.61253213	4.96635151	9.51007330	5.63768230	5.01010868

Table S4: Cartesian Coordinates of the ground- and excited-state by averages from the QM/MM MD trajectories of $[Ru(bpy)_3]^{2+}$.

	QM/MM MD (BP86/TZP(Ru)DZP)					
	GS			ES		
C	2.23025965	3.08420881	2.18774867	1.36719754	3.15401147	2.72676035
C	1.62234536	4.26020016	1.74775866	0.61301754	4.25528728	2.30056615
C	1.77855113	1.86555334	1.68861728	1.20918605	1.94295132	2.06732008
C	-2.78014300	0.32797599	3.37071808	-3.29334395	-0.40821800	2.85221316
C	0.58586112	4.17456869	0.81751259	-0.26027532	4.10342808	1.22897107
C	2.18766606	-2.68091799	2.69356241	2.16377026	-2.65330905	2.74377133
C	3.37074257	-2.91278699	1.99425430	3.47173737	-2.59252724	2.24669032
C	-1.73219918	0.54633163	2.47910705	-2.17424725	0.04919219	2.17143925
C	-3.64874429	-0.74099158	3.14724623	-3.92011125	-1.58033631	2.41127144
C	1.22068295	-1.85396230	2.12635286	1.17191144	-1.92266024	2.10433789
N	0.76586259	1.76344987	0.78968954	0.34701908	1.77252483	1.03217148
C	0.17185942	2.92289794	0.34721931	-0.38852417	2.85997071	0.58945339
C	3.54503698	-2.30792390	0.74858569	3.73539623	-1.81057591	1.12684019
N	1.37682328	-1.25329386	0.91872448	1.41630936	-1.14146210	1.02153532
N	-1.50847810	-0.24008643	1.39364157	-1.65006704	-0.59783826	1.09849285
C	-3.43669237	-1.55577677	2.03335964	-3.40497534	-2.24662287	1.30405772
C	2.54132793	-1.48436943	0.22506691	2.70150254	-1.09005745	0.51108937
C	-0.91197548	2.73072761	-0.63197934	-1.25683330	2.60385846	-0.54870823
C	-2.36659074	-1.29139106	1.16750497	-2.27034716	-1.74835252	0.64515995
Ru	0.00846056	0.00245118	-0.00671504	0.01147168	0.00256808	-0.00000508
C	-1.64745845	3.77959205	-1.19860033	-2.07659799	3.56842435	-1.15730341
C	2.63631405	-0.79396194	-1.07347962	2.86990855	-0.25685263	-0.67179044
N	-1.16145097	1.42060647	-0.97039660	-1.24185364	1.30345775	-1.02635573
N	1.54740712	-0.01990901	-1.39939285	1.72732884	0.39314774	-1.10555847
C	3.73270616	-0.90394608	-1.93846217	4.08342336	-0.09067912	-1.35922064
C	-2.06422902	-2.09346407	-0.03125276	-1.66452979	-2.36444362	-0.52736348
C	-2.65565718	3.50446046	-2.12185429	-2.88178929	3.22605294	-2.23653246
N	-0.98005841	-1.66193532	-0.76080138	-0.54254218	-1.72195723	-1.02166437
C	1.56706891	0.64846975	-2.58368065	1.81132012	1.21683597	-2.18254090
C	3.73253391	-0.21763734	-3.15496746	4.14813796	0.74090174	-2.47271389
C	-2.14793163	1.16977317	-1.86938825	-2.04552260	0.98183638	-2.07209924
C	2.63004450	0.57251902	-3.47964503	2.99023837	1.41184614	-2.88917956
C	-2.80951935	-3.20908752	-0.43103908	-2.14125533	-3.53026058	-1.14552673

C	-2.90740713	2.17537552	-2.46254565	-2.86637869	1.90497593	-2.70407189
C	-0.64531599	-2.35584355	-1.87996986	0.09969238	-2.25920041	-2.09002330
C	-2.45500254	-3.90699470	-1.58667004	-1.48167798	-4.05839787	-2.24993300
C	-1.35265297	-3.47006517	-2.32243587	-0.33587523	-3.41087382	-2.72997722

Table S5: Cartesian Coordinates of the ground- and excited-state optimized structure of $[Fe(bpy)_3]^{2+}$.

	Gaussian 16 (B3LYP*/Def2TZVP)					
	GS			ES		
H	2.75557400	2.41523500	3.61363000	2.66886000	-2.67246000	-3.70662100
H	2.17242500	4.70478000	2.76182700	2.09652800	-4.93231800	-2.77205400
C	2.10556400	2.54914500	2.75784400	2.04109600	-2.77794800	-2.83051600
C	1.78040100	3.81432300	2.28467000	1.72105800	-4.02619400	-2.31091700
H	-3.46944200	1.17878000	3.61363000	-3.71288200	-1.03882700	-3.66948000
H	0.71386800	-3.59401500	3.61363000	1.01314000	3.74147400	-3.63348600
H	1.81624000	0.44221100	2.45828900	1.77050500	-0.66106300	-2.56381600
H	2.98824600	-4.23376500	2.76182700	3.24319200	4.37692900	-2.67204600
C	1.58257600	1.43972200	2.11185600	1.53880800	-1.65351800	-2.19462100
C	-3.26040700	0.54890000	2.75784400	-3.49267900	-0.43511500	-2.79777200
H	-1.29108600	1.35180400	2.45828900	-1.48026400	-1.16970700	-2.58798600
C	0.94197200	3.91772500	1.18487600	0.91255500	-4.09776700	-1.18622700
H	0.67837000	4.89284300	0.79773500	0.66440700	-5.06443000	-0.77027500
C	1.15484200	-3.09804500	2.75784400	1.42476600	3.22508700	-2.77525600
H	-5.16067200	-0.47101400	2.76182700	-5.43331300	0.49428900	-2.67366600
C	2.41310000	-3.44903400	2.28467000	2.65956700	3.57160100	-2.24099300
C	-2.03812400	0.65068900	2.11185600	-2.24411300	-0.50666500	-2.19763100
H	-0.52515400	-1.79401600	2.45828900	-0.25051800	1.88962700	-2.55758800
C	-4.19350100	-0.36528900	2.28467000	-4.44064900	0.41659800	-2.24546800
C	0.45554800	-2.09041200	2.11185600	0.71869100	2.19252300	-2.17760100
N	0.76906700	1.52815500	1.04711200	0.75500500	-1.71361300	-1.10879300
C	0.44741300	2.76211900	0.58259800	0.43446500	-2.92429700	-0.59976700
C	2.92186400	-2.77463400	1.18487600	3.13809400	2.87529200	-1.13971800
H	3.89814200	-3.03390700	0.79773500	4.09116200	3.14899500	-0.70829600
N	0.93888800	-1.43010900	1.04711200	1.17639100	1.51378300	-1.11695600
N	-1.70795500	-0.09804600	1.04711200	-1.90632200	0.21743600	-1.12325900
C	-3.86383500	-1.14309100	1.18487600	-4.10036700	1.16757500	-1.12886400
C	2.16835800	-1.76853100	0.58259800	2.37774400	1.84136100	-0.59231900
H	-0.67837000	4.89284300	-0.79773500	-0.66445400	-5.06442400	0.77027500
C	-0.44741300	2.76211900	-0.58259800	-0.43449300	-2.92429300	0.59976700
H	-4.57651200	-1.85893600	0.79773500	-4.83544200	1.82335900	-0.68255900
C	-2.61577200	-0.99358800	0.58259800	-2.81843600	1.05825800	-0.58883000
Fe	0.00000000	0.00000000	0.00000000	0.00000000	0.02924200	0.00000000

C	-0.94197200	3.91772500	-1.18487600	-0.91259300	-4.09775800	1.18622700
C	2.61577200	-0.99358800	-0.58259800	2.81844600	1.05823300	0.58883100
H	4.57651200	-1.85893600	-0.79773500	4.83545800	1.82331600	0.68256100
N	-0.76906700	1.52815500	-1.04711200	-0.75502100	-1.71360600	1.10879300
N	1.70795500	-0.09804600	-1.04711200	1.90632400	0.21741800	1.12325900
C	3.86383500	-1.14309100	-1.18487600	4.10037800	1.16753800	1.12886500
C	-2.16835800	-1.76853100	-0.58259800	-2.37772600	1.84138200	0.59231900
C	-1.78040100	3.81432300	-2.28467000	-1.72109500	-4.02617800	2.31091800
N	-0.93888800	-1.43010900	-1.04711200	-1.17637700	1.51379400	1.11695500
C	2.03812400	0.65068900	-2.11185600	2.24410800	-0.50668500	2.19763000
H	-2.17242500	4.70478000	-2.76182700	-2.09657300	-4.93229900	2.77205400
C	4.19350100	-0.36528900	-2.28467000	4.44065200	0.41655800	2.24546900
H	1.29108600	1.35180400	-2.45828900	1.48025300	-1.16972100	2.58798500
C	-1.58257600	1.43972200	-2.11185600	-1.53882400	-1.65350400	2.19462100
C	3.26040700	0.54890000	-2.75784400	3.49267500	-0.43514700	2.79777300
H	-3.89814200	-3.03390700	-0.79773500	-4.09113300	3.14903300	0.70829600
H	5.16067200	-0.47101400	-2.76182700	5.43331700	0.49424100	2.67366700
C	-2.92186400	-2.77463400	-1.18487600	-3.13806700	2.87532000	1.13971900
C	-2.10556400	2.54914500	-2.75784400	-2.04112200	-2.77792900	2.83051600
H	-1.81624000	0.44221100	-2.45828900	-1.77051100	-0.66104700	2.56381600
H	3.46944200	1.17878000	-3.61363000	3.71287200	-1.03886100	3.66948000
C	-0.45554800	-2.09041200	-2.11185600	-0.71867000	2.19252900	2.17760000
H	0.52515400	-1.79401600	-2.45828900	0.25053600	1.88962500	2.55758800
H	-2.75557400	2.41523500	-3.61363000	-2.66888500	-2.67243600	3.70662100
C	-2.41310000	-3.44903400	-2.28467000	-2.65953300	3.57162500	2.24099300
C	-1.15484200	-3.09804500	-2.75784400	-1.42473500	3.22510000	2.77525600
H	-2.98824600	-4.23376500	-2.76182700	-3.24315100	4.37695900	2.67204600
H	-0.71386800	-3.59401500	-3.61363000	-1.01310400	3.74148400	3.63348500

Table S6: Cartesian Coordinates of the ground- and excited-state optimized structure of $[Fe(bpy)_3]^{2+}$.

	GPAW (BP86/TZP(Fe)DZP)					
	GS			ES		
Fe	10.22904573	9.29925159	8.65401813	10.23343516	9.30815693	8.66264232
N	10.99357237	10.83245891	9.71203179	11.01110365	11.05063092	9.77987488
N	11.16379428	7.86212752	9.71067613	11.34581004	7.79424195	9.76916748
N	8.51592261	9.20124949	9.70759603	8.34125438	9.08413027	9.77657584
N	9.46333606	10.83221463	7.59483435	9.49978728	11.05362623	7.54803571
N	11.94320613	9.20397462	7.60093912	12.11896353	9.12084812	7.55965482
N	9.29528219	7.86008882	7.59659963	9.12173200	7.74343826	7.55842619
H	13.02904805	11.73372227	12.31452619	13.03663307	12.01416375	12.36979584
H	12.45047941	14.06563912	11.44579570	12.49987286	14.31580448	11.40268737
C	12.36305389	11.87352850	11.44432009	12.38047474	12.12785435	11.48822731
C	12.04190288	13.15991067	10.96212005	12.08252663	13.39718759	10.95045867
H	6.70245085	10.50829359	12.30332626	6.45681017	10.39829609	12.31873001
H	10.94338556	5.64265066	12.31002911	11.16482153	5.53792868	12.34548374
H	12.06114722	9.73208954	11.15284240	12.04995127	9.97813282	11.25494700
H	13.25745063	4.99295169	11.44096728	13.44732457	4.88231569	11.40180340
C	11.82592103	10.74797050	10.79656437	11.83192555	10.99075820	10.86969355
C	6.92029232	9.86178692	11.43468360	6.70239682	9.75764691	11.45384212
H	8.91990713	10.68687081	11.14166747	8.72605663	10.55656943	11.22404259
C	11.18977720	13.26569744	9.84866586	11.24179559	13.47548141	9.82418994
H	10.92478894	14.25818157	9.44757249	11.00942655	14.46063199	9.38599493
C	11.39314678	6.15264242	11.44010375	11.59621934	6.05886264	11.47250998
H	4.98832699	8.82194002	11.44156391	4.76966951	8.72698488	11.38210278
C	12.67019858	5.79490830	10.95766336	12.85564378	5.69761309	10.94785929
C	8.16320230	9.96836136	10.78685242	7.96608738	9.84946313	10.84415976
H	9.68208849	7.47674464	11.15272262	9.89391225	7.40738471	11.23855306
C	5.97514209	8.93017765	10.95656935	5.77309534	8.83450622	10.93081308
C	10.67948117	7.17639373	10.79223448	10.88368276	7.10024794	10.85511375
C	10.67799435	12.09690208	9.23998180	10.71251133	12.29181013	9.25798008
C	13.18338926	6.48584709	9.84634443	13.34612789	6.39790106	9.83176674
H	14.17692438	6.22367830	9.44448679	14.32384854	6.12175010	9.40323143
C	6.31735767	8.13733324	9.84687023	6.14166394	8.04684311	9.82458133
C	12.42033371	7.50855936	9.23913536	12.57945503	7.44009200	9.25608849
H	9.53750080	14.25828990	7.85078303	9.51660451	14.46057794	7.92932478

C	9.78011808	12.09669892	8.06525338	9.80552047	12.29270939	8.06827071
H	5.59362543	7.40572715	9.44928348	5.41732708	7.33308254	9.39935078
C	7.58496516	8.28654177	9.23938596	7.43241100	8.18538704	9.26026125
C	9.27015005	13.26486997	7.45289678	9.26992663	13.47426435	7.50210728
C	12.87523857	8.29060809	8.07054404	13.03507272	8.22098305	8.07204211
H	14.86624865	7.40776051	7.85909531	15.04493787	7.35884094	7.92831023
C	14.14248798	8.13939272	7.46130430	14.32147821	8.07094512	7.49842697
C	8.04059385	7.50356884	8.07032154	7.89401004	7.39176634	8.07686453
C	8.41825774	13.15826805	6.33978923	8.40762428	13.39146988	6.39269246
C	12.29662528	9.96868603	6.51999839	12.49667908	9.87028371	6.47878978
H	8.01016682	14.06364933	5.85505857	7.98469902	14.31029527	5.94572574
C	14.48473173	8.93009815	6.35081613	14.68651414	8.84164949	6.38123948
H	11.54076475	10.68750422	6.16357230	11.74485212	10.58598597	6.09980673
C	8.63381055	10.74720201	6.50831737	8.66304578	10.98776562	6.47093227
C	13.53950118	9.86196743	5.87169745	13.75289505	9.76148947	5.85817427
H	6.28669078	6.21395013	7.86405899	6.15244120	6.06657471	7.94139483
H	15.47197025	8.82161066	5.86634022	15.68698571	8.72789109	5.92568339
C	7.27885536	6.48001318	7.46204980	7.12508305	6.34933058	7.50600459
C	8.09690385	11.87129172	5.85838140	8.09541372	12.12165833	5.86409533
H	8.40025773	9.73062230	6.15175307	8.45053580	9.97495244	6.08332750
H	13.75849889	10.50907344	5.00426320	13.99472841	10.39610712	4.98736385
C	9.78089769	7.17600689	6.51421471	9.58060451	7.06200460	6.46732889
H	10.77827468	7.47740561	6.15483798	10.56679579	7.37710539	6.08026682
H	7.43265147	11.73104273	4.98710563	7.42507660	12.00785420	4.99376971
C	7.79198543	5.79306915	6.34717856	7.61038559	5.65901346	6.37974105
C	9.06783751	6.15277815	5.86489006	8.86214152	6.02559404	5.84292098
H	7.20566282	4.99182346	5.86253339	7.01610012	4.84468286	5.92607084
H	9.51890198	5.64361661	4.99437130	9.28451220	5.51451666	4.96013053

Table S7: Cartesian Coordinates of the ground- and excited-state by averages from the QM/MM MD trajectories of $[Fe(bpy)_3]^{2+}$.

	QM/MM MD (BP86/TZP(Fe)DZP)					
	GS			ES (t>1.5ps)		
Fe	0.00095397	0.00717954	-0.00067571	-0.00507592	0.01804232	0.00366408
N	0.67732896	1.70634805	0.81999759	0.19486457	2.14306951	0.54742711
N	1.42950050	-1.14811895	0.80009465	1.86094622	-0.66825717	0.96036563
N	-1.33646390	-0.35042114	1.45015847	-1.32562930	-0.53771120	1.67756392
N	-1.28337701	1.28989947	-0.85069599	-1.60586269	1.02846943	-1.12084100
N	1.37437073	0.16885219	-1.45123447	1.51359725	0.14271323	-1.58835488
N	-0.85861754	-1.63341282	-0.77156460	-0.65297983	-2.03727903	-0.46056672
C	2.12577698	3.07899089	2.20196547	1.26646013	4.01980071	1.62776523
C	1.43131025	4.23250475	1.82964399	0.37923888	4.89373065	1.00729525
C	1.72578843	1.84691084	1.68059943	1.14309975	2.66219828	1.36702427
C	-2.52531510	0.07311236	3.52140398	-2.54664410	-0.11355823	3.71488200
C	0.36001067	4.11195024	0.93882391	-0.59969968	4.37715205	0.15558217
C	2.42307915	-2.61981229	2.45558025	3.15688005	-1.60227507	2.77023888
C	3.57628848	-2.75326466	1.68226022	4.27372288	-1.65747479	1.94869152
C	-1.54415680	0.38456500	2.57848427	-1.66692849	0.26634727	2.71305532
C	-3.34431327	-1.03789105	3.31105484	-3.11515420	-1.37827384	3.64742626
C	1.38025433	-1.81881004	1.98648883	1.97764577	-1.10625344	2.23857173
C	-0.00137534	2.84765559	0.44636701	-0.68089033	3.00093358	-0.05850979
C	3.64394531	-2.08083798	0.45837556	4.17148426	-1.21572286	0.62890321
C	-3.14865082	-1.80502635	2.15997806	-2.78016789	-2.21713914	2.58474328
C	2.56661803	-1.28733366	0.03430412	2.95963849	-0.72398576	0.15179771
C	-1.11708311	2.60994775	-0.48973486	-1.70347957	2.38055208	-0.94177229
C	-2.14547716	-1.44776589	1.24416065	-1.88259636	-1.78224540	1.61117354
C	-1.94846967	3.61941629	-0.99847707	-2.71895462	3.11401743	-1.55781881
C	2.54046756	-0.53247676	-1.23359780	2.77902484	-0.23848706	-1.24151708
C	3.59317251	-0.51304200	-2.16335526	3.82913407	-0.16363333	-2.16005890
C	-1.85347929	-2.19104858	0.00387999	-1.47501370	-2.62491077	0.45753038
C	-2.97267818	3.29329370	-1.89316591	-3.65144804	2.46599379	-2.37036522
C	1.27847566	0.89719642	-2.60061714	1.30186711	0.60265713	-2.84634107
C	3.47065843	0.23496565	-3.33865397	3.59100563	0.30614985	-3.45203541
C	-2.29386211	0.99178074	-1.71717963	-2.52278448	0.41432269	-1.90921366
C	2.29431318	0.95326698	-3.55684125	2.30390019	0.69844576	-3.80264424
C	-2.51498562	-3.36555676	-0.38448853	-1.89110840	-3.94481240	0.30306910

C	-3.14690494	1.95616243	-2.25539177	-3.55276382	1.08963281	-2.54988087
C	-0.53579711	-2.26375768	-1.93711536	-0.24744179	-2.77077381	-1.52498675
C	-2.16712630	-3.99630993	-1.58269454	-1.46657328	-4.68331388	-0.80083103
C	-1.16338149	-3.43123314	-2.37193127	-0.62998315	-4.08579643	-1.73392741

Table S8: Cartesian Coordinates of the ground-state optimized structure of $[Fe(bmip)_2]^{2+}$.

	Gaussian 16 (B3LYP*/Def2TZVP)		
	GS		
H	-5.23508400	0.00000000	0.51016900
H	0.00000000	-4.03198700	-2.97722100
C	-4.19105200	0.00000000	0.77799900
H	0.00000000	-5.23508400	-0.51016900
C	0.00000000	-3.60326900	-1.98983400
C	0.00000000	-4.19105200	-0.77799900
H	0.00000000	-2.15437100	-4.54092800
C	0.00000000	-1.21137200	-4.01093200
H	0.00000000	0.00000000	-5.78230200
C	-3.60326900	0.00000000	1.98983400
H	-4.03198700	0.00000000	2.97722100
C	0.00000000	0.00000000	-4.69887600
C	0.00000000	-1.15961400	-2.62437000
C	0.00000000	1.21137200	-4.01093200
N	0.00000000	0.00000000	-1.94877800
H	0.00000000	2.15437100	-4.54092800
H	-2.15437100	0.00000000	4.54092800
C	0.00000000	1.15961400	-2.62437000
C	-1.15961400	0.00000000	2.62437000
C	-1.21137200	0.00000000	4.01093200
N	0.00000000	0.00000000	1.94877800
H	0.00000000	4.03198700	-2.97722100
C	0.00000000	0.00000000	4.69887600
C	0.00000000	3.60326900	-1.98983400
H	0.00000000	0.00000000	5.78230200
C	1.15961400	0.00000000	2.62437000
C	1.21137200	0.00000000	4.01093200
C	0.00000000	4.19105200	-0.77799900
H	2.15437100	0.00000000	4.54092800
C	4.19105200	0.00000000	0.77799900
H	0.00000000	5.23508400	-0.51016900
C	3.60326900	0.00000000	1.98983400
H	5.23508400	0.00000000	0.51016900

H	4.03198700	0.00000000	2.97722100
Fe	0.00000000	0.00000000	0.00000000
N	-2.23471800	0.00000000	1.74219900
N	2.23471800	0.00000000	1.74219900
C	1.95378600	0.00000000	0.38435800
C	-1.95378600	0.00000000	0.38435800
C	0.00000000	-1.95378600	-0.38435800
C	0.00000000	1.95378600	-0.38435800
N	0.00000000	-2.23471800	-1.74219900
N	0.00000000	2.23471800	-1.74219900
C	-3.47201700	0.00000000	-1.61188500
H	-2.53972600	0.00000000	-2.16667700
H	-4.04884800	-0.88872900	-1.87441200
H	-4.04884800	0.88872900	-1.87441200
C	3.47201700	0.00000000	-1.61188500
H	2.53972600	0.00000000	-2.16667700
H	4.04884800	0.88872900	-1.87441200
H	4.04884800	-0.88872900	-1.87441200
C	0.00000000	-3.47201700	1.61188500
H	0.88872900	-4.04884800	1.87441200
H	0.00000000	-2.53972600	2.16667700
H	-0.88872900	-4.04884800	1.87441200
C	0.00000000	3.47201700	1.61188500
H	-0.88872900	4.04884800	1.87441200
H	0.00000000	2.53972600	2.16667700
H	0.88872900	4.04884800	1.87441200
N	0.00000000	3.17913600	0.18265100
N	0.00000000	-3.17913600	0.18265100
N	-3.17913600	0.00000000	-0.18265100
N	3.17913600	0.00000000	-0.18265100

Table S9: Cartesian Coordinates of the ground-state optimized structure of $[Fe(bmip)_2]^{2+}$.

	GPAW (BP86/TZP(Fe)DZP)		
	GS		
Fe	10.31124468	10.31023078	10.85603539
N	10.31056984	10.31142358	12.81909054
N	10.31258624	10.31012938	8.89219628
C	12.27762240	10.31159851	11.25271539
C	8.34316980	10.31154588	11.25315873
C	10.31180856	8.34253794	10.45914783
C	10.31171731	12.27746081	10.46056986
H	4.99914685	10.31205690	11.37117916
H	10.31265865	6.20789638	7.82797833
C	6.06299319	10.31227309	11.64660128
H	10.31161808	4.99897940	10.34259166
C	10.31203198	6.65285692	8.83131411
C	10.31183298	6.06252041	10.06662640
H	10.31090318	8.12217788	6.24221568
C	10.31124379	9.08560670	6.77914249
H	10.31061832	10.31242797	4.97207890
C	6.65320885	10.31218833	12.88203354
H	6.20863368	10.31262584	13.88488788
C	10.31089897	10.31123299	6.07618965
C	10.31193974	9.13352077	8.18462776
C	10.31118318	11.53729029	6.78002775
H	10.31086304	12.50073657	6.24404419
H	8.12166637	10.31098694	15.46937306
C	10.31191314	11.48738226	8.18602254
C	9.13382429	10.31128970	13.52712253
C	9.08524994	10.31103098	14.93294102
H	10.31257683	14.41308730	7.82929828
C	10.31081771	10.31083362	15.63667718
C	10.31203572	13.96746231	8.83218844
H	10.31128862	10.31082750	16.74089570
C	11.48712670	10.31129969	13.52642786
C	11.53623286	10.31101826	14.93245484
C	10.31168587	14.55840646	10.06727790

H	12.49984028	10.31096625	15.46861396
C	14.55822900	10.31192587	11.64657409
H	10.31151639	15.62197223	10.34271548
C	13.96761872	10.31191188	12.88137855
H	15.62239887	10.31188299	11.37208608
H	14.41366451	10.31247576	13.88421613
N	8.04304869	10.31162139	12.63642894
N	12.57796192	10.31155279	12.63590832
N	10.31182166	8.04265038	9.07610831
N	10.31171281	12.57778431	9.07787354
C	6.78856316	10.31189023	9.22642900
H	7.73252430	10.31146019	8.65248433
H	6.19841781	9.40769316	8.96289871
H	6.19885510	11.21623620	8.96263354
C	13.83308928	10.31177007	9.22667775
H	12.88935467	10.31141940	8.65245600
H	14.42314388	11.21594811	8.96273262
H	14.42348393	9.40764949	8.96305126
C	10.31167843	6.78878908	12.48637033
H	11.21602732	6.19915055	12.75047474
H	10.31131836	7.73292511	13.05993168
H	9.40755133	6.19872337	12.75025604
C	10.31148679	13.83352249	12.48673705
H	9.40745014	14.42407071	12.74994059
H	10.31121823	12.89034646	13.06195374
H	11.21565176	14.42373094	12.75015326
N	10.31150462	13.52816812	11.03995875
N	10.31157051	7.09294061	11.03883143
N	7.09336122	10.31181257	10.67395418
N	13.52815390	10.31181603	10.67379266

Table S10: Cartesian Coordinates of the ground-state by averages from the QM/MM MD trajectories of $[Fe(bmip)_2]^{2+}$.

	QM/MM MD (BP86/TZP(Fe)DZP)		
	GS		
Fe	-0.00075199	0.00336039	0.00133594
N	0.45083486	-0.52766222	1.82090627
N	-0.46286441	0.52744716	-1.81818424
C	1.75503883	-0.88647247	-0.28969277
C	-1.57762008	0.69374398	0.99814183
C	-1.00460446	-1.60221993	-0.61126276
C	0.82531340	1.81035205	-0.09303803
C	-3.42482758	1.51673166	2.08767128
C	-2.19240531	-2.64462920	-2.32693869
C	-2.15818347	-3.48324748	-1.25120909
C	-1.53485894	0.02169273	-3.93753550
C	-2.65259047	0.94107837	3.05390496
C	-1.11314373	1.27190627	-4.42962103
C	-1.18351480	-0.31094087	-2.62507128
C	-0.37100669	2.15338578	-3.62040849
C	-0.07015526	1.73957966	-2.31785166
C	-0.39529105	-0.24925772	2.86015815
C	-0.12028450	-0.62589657	4.17917699
C	1.08190035	-1.31673811	4.42340804
C	1.24190476	3.72160167	-1.36504683
C	1.61339037	-1.19902204	2.08503502
C	1.97092914	-1.61358250	3.37223451
C	1.80126158	3.88987561	-0.13206413
C	3.78077876	-1.89254753	-0.69328847
C	3.57485860	-2.00426853	0.65016996
N	-1.52506866	0.43934362	2.38208845
N	2.33535055	-1.38785920	0.89164712
N	-1.48579031	-1.49693502	-1.92977636
N	0.64614244	2.44912624	-1.33534251
C	-3.31208484	1.86797836	-0.41039623
C	2.55875496	-0.92382921	-2.67952307
C	-1.18443541	-3.46937173	1.07755705
C	2.01079639	2.55797896	2.00353210

N	1.54177797	2.72936525	0.62716355
N	-1.43866451	-2.84184297	-0.22122805
N	-2.76502472	1.36096362	0.85095378
N	2.67505692	-1.21657912	-1.24993095

Table S11: Cartesian Coordinates of the ground- and exited-state optimized structure of $[Cu(phen)_2]^+$.

	Gaussian 16 (B3LYP*/Def2TZVP)					
	GS			ES		
Cu	0.000000	0.000000	-0.000051	0.00000000	0.00000800	0.00035100
N	1.553792	-0.953373	-0.953118	-1.50750600	1.26458800	-0.44046700
N	1.553827	0.953389	0.953092	-1.50758500	-1.26442000	0.44102500
C	3.928602	-1.997928	-1.997297	-3.90057800	2.64544200	-1.07584200
C	3.928674	1.997917	1.997212	-3.90076300	-2.64525700	1.07602800
C	2.756414	-0.508257	-0.508125	-2.74461100	0.66719700	-0.25184800
C	2.756431	0.508259	0.508070	-2.74465700	-0.66702900	0.25218800
C	1.536662	-1.892549	-1.891980	-1.47406900	2.50925400	-0.97509000
C	1.536730	1.892562	1.891954	-1.47423600	-2.50907400	0.97569700
C	3.984205	-1.002960	-1.002661	-3.97552700	1.33725800	-0.54006200
C	3.984242	1.002948	1.002575	-3.97562000	-1.33708500	0.54020600
C	2.702727	-2.441829	-2.441057	-2.63808500	3.22405500	-1.30476500
C	2.702815	2.441830	2.441004	-2.63830700	-3.22386300	1.30518800
C	5.210405	-0.480369	-0.480250	-5.21432300	0.63477500	-0.26299900
C	5.210422	0.480344	0.480133	-5.21436800	-0.63460100	0.26292600
N	-1.553793	-0.953302	0.953202	1.50765200	1.26442700	0.44081400
N	-1.553826	0.953332	-0.953135	1.50743900	-1.26458200	-0.44067600
C	-3.928602	-1.997794	1.997444	3.90092500	2.64525100	1.07549000
C	-3.928675	1.997780	-1.997335	3.90041600	-2.64545100	-1.07637500
C	-2.756413	-0.508220	0.508176	2.74469500	0.66702800	0.25181100
C	-2.756432	0.508228	-0.508087	2.74457300	-0.66719900	-0.25222300
C	-1.536662	-1.892411	1.892129	1.47438300	2.50908400	0.97548500
C	-1.536731	1.892445	-1.892060	1.47392200	-2.50924700	-0.97529600
C	-3.984205	-1.002893	1.002741	3.97570100	1.33707600	0.53966200
C	-3.984242	1.002879	-1.002630	3.97544600	-1.33726800	-0.54060300
C	-2.702726	-2.441659	2.441241	2.63850300	3.22386600	1.30481700
C	-2.702815	2.441670	-2.441151	2.63788900	-3.22405500	-1.30512900
C	-5.210405	-0.480342	0.480290	5.21440700	0.63458500	0.26221700
C	-5.210422	0.480305	-0.480157	5.21428300	-0.63479200	-0.26370800
H	-6.145496	-0.869036	0.868902	6.16194100	-1.14566600	-0.47789300
H	-6.145528	0.868982	-0.868753	6.16216600	1.14544500	0.47598700
H	-4.848792	2.404141	-2.403608	4.82051000	3.19530900	1.31184300
H	-2.624367	3.205620	-3.204952	2.54567100	4.22914700	1.73044100

H	-0.560304	2.226413	-2.225988	0.48188400	2.94363600	1.14471200
H	-0.560223	-2.226354	2.226045	0.48134500	-2.94379600	-1.14407200
H	-2.624250	-3.205606	3.205041	2.54485400	-4.22934600	-1.73068400
H	-4.848704	-2.404174	2.403731	4.81989100	-3.19552600	-1.31312000
H	0.560304	2.226544	2.225867	-6.16209400	-1.14546700	0.47682500
H	2.624366	3.205830	3.204755	-6.16201200	1.14564200	-0.47705700
H	4.848791	2.404310	2.403452	-4.82008800	3.19551100	-1.31246300
H	6.145528	0.869050	0.868698	-2.54511400	4.22934700	-1.73033100
H	6.145496	-0.869086	-0.868839	-0.48151800	2.94381000	-1.14399800
H	4.848705	-2.404330	-2.403561	-0.48171200	-2.94361900	1.14479300
H	2.624251	-3.205829	-3.204805	-2.54541100	-4.22914100	1.73080400
H	0.560224	-2.226523	-2.225866	-4.82031300	-3.19532000	1.31250600

Table S12: Cartesian Coordinates of the ground- and exited-state optimized structure of $[Cu(phen)_2]^+$.

	GPAW (BP86/TZP(Cu)DZP)					
	GS			ES		
Cu	11.21622187	8.24806539	8.24620522	11.16154685	9.21436584	6.78460000
N	12.76538820	7.29038344	7.29022936	9.66529216	7.95698276	7.23359987
N	12.76567801	9.20000942	9.19578964	9.66369469	10.46989509	6.33095641
C	15.18239554	6.21619695	6.21753171	7.26351115	6.57756372	7.90608185
C	15.18287621	10.27060888	10.26574413	7.26178205	11.84936483	5.66085278
C	14.00127396	7.73184515	7.73087513	8.41621619	8.54917152	7.04114055
C	14.00108408	8.75679613	8.75365913	8.41542933	9.87695232	6.52396287
C	12.75350729	6.32998908	6.33116460	9.69923499	6.71366539	7.79337958
C	12.75363876	10.15918561	10.15410349	9.69742432	11.71374920	5.77287798
C	15.24421723	7.22512605	7.22522352	7.18318451	7.87938424	7.34434593
C	15.24418003	9.26232057	9.25843378	7.18208018	10.54640895	6.22071396
C	13.93239365	5.77075103	5.77293842	8.53245264	6.00274701	8.14095952
C	13.93379875	10.71657300	10.71093210	8.53025016	12.42485137	5.42609226
C	16.48380707	7.75462788	7.75379982	5.94373783	8.57823535	7.05603921
C	16.48386066	8.73201173	8.72952565	5.94340846	9.84659475	6.50944785
N	9.66436426	7.29116246	9.19780353	12.65879003	7.95530422	6.33771457
N	9.66459680	9.20037006	7.29031272	12.65851359	10.47233963	7.23171702
C	7.24652341	6.21515804	10.26427579	15.06325221	6.57863181	5.66507126
C	7.24649380	10.26751313	6.21525757	15.06143934	11.85210736	7.90417447
C	8.42882107	7.73281965	8.75487988	13.90689826	8.55009135	6.52786755
C	8.42890843	8.75705848	7.73167661	13.90672174	9.87913082	7.04130710
C	9.67578987	6.33031253	10.15516324	12.62702120	6.70993180	5.78045198
C	9.67584281	10.15826606	6.33011981	12.62536820	11.71800952	7.78981566
C	7.18585628	7.22513351	9.25851834	15.14069625	7.88096627	6.22462703
C	7.18587358	9.26112704	7.22462279	15.14022631	10.55033792	7.34385388
C	8.49597610	5.77003017	10.71009908	13.79508985	6.00095334	5.43162565
C	8.49595940	10.71372028	5.77046613	13.79192749	12.42831852	8.13854288
C	5.94603025	7.75381595	8.72814300	16.37910209	8.58273111	6.51077588
C	5.94602082	8.73010319	7.75275955	16.37936578	9.85137400	7.05605126
H	4.99134434	7.35828191	9.12142431	17.33567432	10.36100540	7.27729208
H	4.99128697	9.12355578	7.35750098	17.33498644	8.07355547	6.28805757
H	6.31210933	10.68478399	5.79529108	15.98776450	6.02775853	5.41269689
H	8.58036722	11.49132212	4.99095096	13.70049759	4.99602698	4.98489152

H	10.67230577	10.49866400	5.99149585	11.62676628	6.26987159	5.61310758
H	10.67227329	5.99184826	10.49567273	11.62466911	12.15675684	7.95622286
H	8.58037706	4.99049765	11.48772283	13.69723628	13.43310431	8.58485803
H	6.31213925	5.79513320	10.68151757	15.98523829	12.40451425	8.15607570
H	11.75701551	10.49770700	10.49318098	4.98732820	10.35574718	6.28915059
H	13.84823844	11.49479345	11.48936064	4.98799062	8.06949657	7.27922523
H	16.11669786	10.68932929	10.68462838	6.34093018	6.02341428	8.15789572
H	17.43811373	9.12656399	9.12395398	8.62877292	4.99773754	8.58641253
H	17.43784249	7.35949448	7.35918603	10.70024775	6.27633195	7.96126200
H	16.11596111	5.79673018	5.79798705	10.69826353	12.15036311	5.60347167
H	13.84577247	4.99238805	4.99462543	8.62623694	13.42985776	4.98091868
H	11.75707996	5.99083616	5.99213675	6.33886638	12.40321099	5.41051127

Table S13: Cartesian Coordinates of the ground-state by averages from the QM/MM MD trajectories of $[Cu(phen)_2]^+$.

	QM/MM MD (BP86/TZP(Cu)DZP)		
	GS		
Cu	0.01425117	0.02876706	0.05211784
N	1.26474955	-0.91492158	-1.26681364
N	1.69111680	1.12220811	0.43661525
C	3.28112013	-1.87389685	-2.97362754
C	4.20317665	2.35053370	0.67082963
C	2.51488816	-0.36593796	-1.25126819
C	2.74617167	0.71349924	-0.33265695
C	1.03854189	-1.91512353	-2.12457760
C	1.90360519	2.11642025	1.30531345
C	3.56417129	-0.81798952	-2.08771194
C	4.02665098	1.30663788	-0.25703721
C	2.01595570	-2.41775610	-2.98899130
C	3.13831071	2.74923218	1.45176639
C	4.84149331	-0.18974298	-1.99497886
C	5.06472587	0.82527874	-1.11432542
N	-1.10033727	-0.83164964	1.52676049
N	-1.82080048	0.69729073	-0.56593092
C	-2.98747078	-1.83067621	3.34427390
C	-4.51120641	1.31784951	-1.09882668
C	-2.43356279	-0.56797460	1.36939108
C	-2.81956402	0.23857638	0.24541787
C	-0.73059707	-1.57027809	2.57796581
C	-2.17313824	1.44448090	-1.61834116
C	-3.42177679	-1.05388078	2.25475200
C	-4.18731331	0.52907000	0.02203271
C	-1.64029533	-2.08236651	3.50334277
C	-3.50010906	1.77177408	-1.91685447
C	-4.79321670	-0.73882452	2.00360518
C	-5.16092804	0.01703068	0.93132331

Table S14: Cartesian Coordinates of the excited-state (right and left)[a] by averages from the QM/MM MD trajectories of $[Cu(phen)_2]^+$.

	QM/MM MD (BP86/TZP(Cu)DZP)					
	ES (left; t>4ps)			ES (right; t>4ps)		
Cu	-0.00052034	-0.00073083	-0.01414819	-0.00189366	0.01232863	0.01054504
N	1.66649634	-0.91664331	-0.69641264	1.48314449	0.09610419	-1.35220357
N	1.31585810	1.37292604	0.65171156	1.49312945	0.40526944	1.30845338
C	4.20407783	-1.76134089	-1.60770143	3.85262910	0.14406505	-2.88723887
C	3.48391647	2.95442919	1.52222737	3.82579465	1.12343955	2.73098077
C	2.80127722	-0.18270044	-0.40198490	2.70652803	0.34604367	-0.75470921
C	2.61809942	1.01588883	0.34412830	2.70627247	0.54725565	0.65364151
C	1.80896201	-2.01992232	-1.46740576	1.46763767	-0.16779673	-2.67954613
C	1.12157079	2.47168087	1.41846242	1.45629194	0.66545025	2.63604095
C	4.10116612	-0.58954457	-0.82335295	3.92078011	0.40242440	-1.49980377
C	3.73677160	1.79903385	0.74804969	3.90873418	0.88474610	1.34076018
C	3.05111754	-2.46875121	-1.94187547	2.62270787	-0.15663512	-3.47403473
C	2.17186707	3.28092037	1.87086070	2.59091887	1.02700613	3.37529519
C	5.21613567	0.22269912	-0.42115341	5.12743563	0.71903930	-0.78573185
C	5.04347557	1.35729315	0.33874802	5.12019497	0.96097986	0.56868044
N	-1.28602434	-1.54552570	0.15023500	-1.36036921	-0.89658211	1.19617704
N	-1.69633921	1.08404080	-0.15554270	-1.62162445	0.42284304	-1.12237638
C	-3.40857058	-3.37055238	0.54160435	-3.53496475	-2.19159615	2.44563659
C	-4.28015524	2.18230958	-0.44163719	-4.14000384	0.91315065	-2.29962338
C	-2.60136906	-1.11507984	0.12445210	-2.63416879	-0.81468290	0.65933644
C	-2.81916149	0.27630309	-0.07757131	-2.77851945	-0.07993952	-0.55091509
C	-1.05382115	-2.85327317	0.41256118	-1.18791267	-1.64711231	2.30839000
C	-1.87731352	2.40029970	-0.41650271	-1.74327522	1.18680264	-2.23289583
C	-3.69890960	-2.00985186	0.29422638	-3.76038660	-1.43457063	1.27388562
C	-4.13961429	0.79800577	-0.19116435	-4.06439634	0.12450610	-1.12977710
C	-2.07984147	-3.78875060	0.61403686	-2.24117106	-2.30796957	2.95511700
C	-3.14273688	2.98226417	-0.56975379	-2.97517631	1.45664280	-2.84346181
C	-5.02350778	-1.46161399	0.20286611	-5.04577600	-1.24459717	0.65742761
C	-5.23408062	-0.12333631	-0.04127651	-5.19272409	-0.48825785	-0.48210072

[a] The two structures are stereoisomers corresponding to a right- and left-handed twist of the ligands, respectively.