This presentation was given at: 1st International Conference "Multiscale Irradiation and Chemistry Driven Processes and Related Technologies" (MultIChem 2022), Boppard am Rhein, Germany, 16-18 May, 2022.

Abstract: Zlatar M. Modeling metal-ligand bonds – from ground to excited states. in Book of abstracts - 1st International Conference "Multiscale Irradiation and Chemistry Driven Processes and Related Technologies" (MultIChem 2022), Boppard am Rhein, Germany, 16-18 May, 2022. 2022; pp.44.

https://hdl.handle.net/21.15107/rcub_cer_5078

Modeling metal-ligand bonds – from ground to excited states

Matija Zlatar

University of Belgrade – Institute of Chemistry, Technology and Metallurgy

National Institute of the Republic of Serbia

matija.zlatar@ihtm.bg.ac.rs

MultIChem 2022

Boppard am Rhein, Germany

18.05.2022

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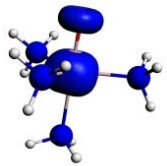
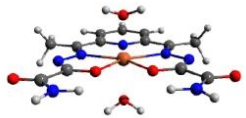
Република Србија
Министарство просвете, науке и технолошког развоја

cost EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY

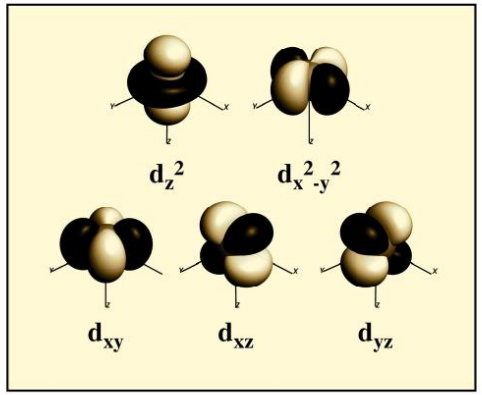
Coordination chemistry

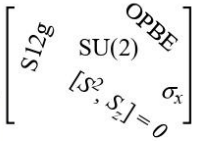


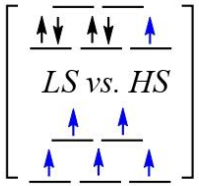
Spin density HS

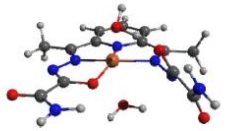


HS

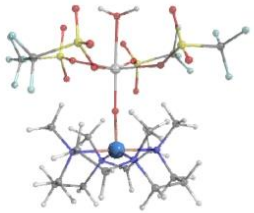


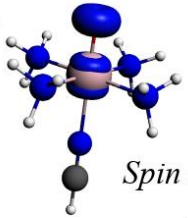




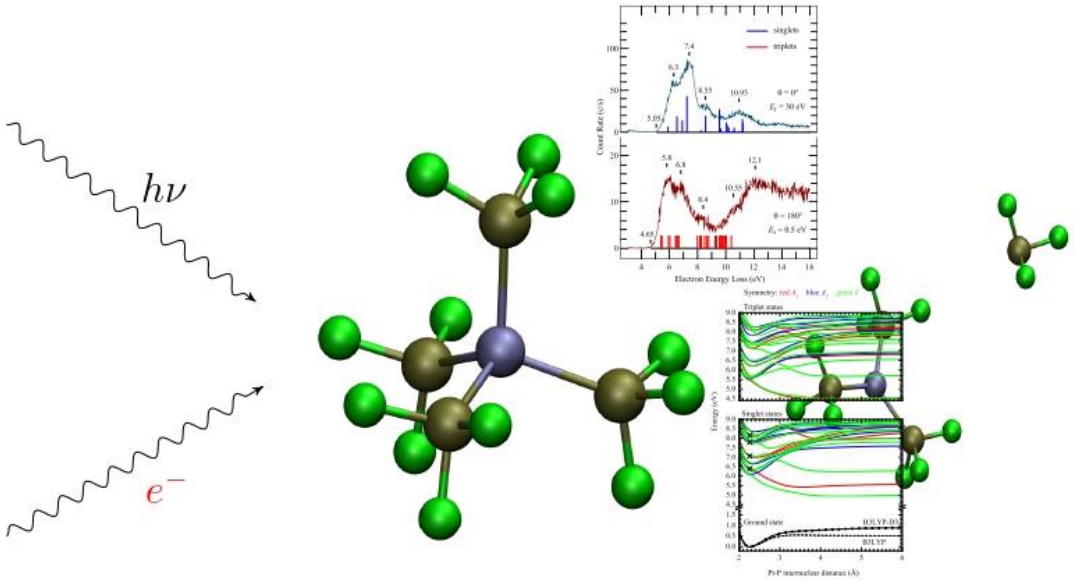


IS

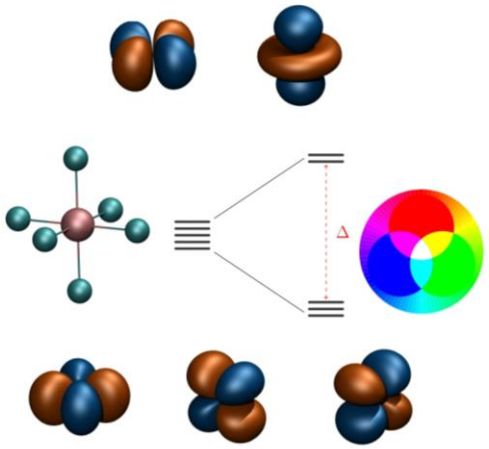


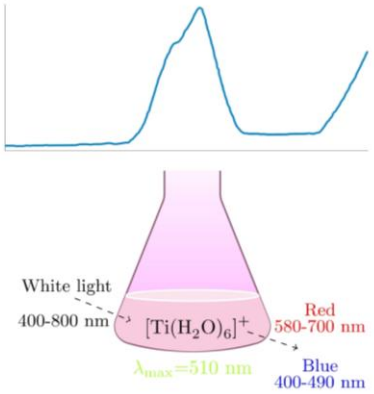


Spin density IS

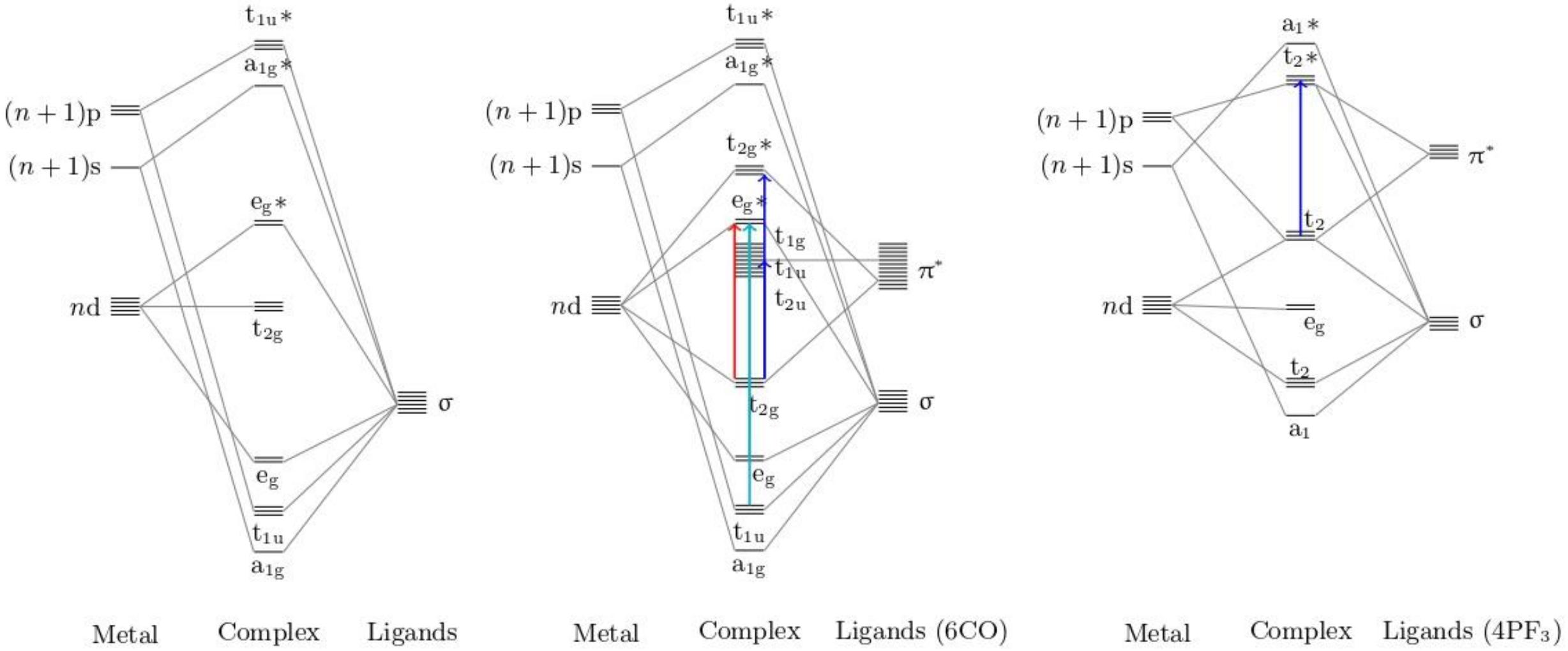


$$\hat{F}^{\mathrm{KS}}|\Phi(t)\rangle = i\frac{\partial}{\partial t}\Phi(t)$$



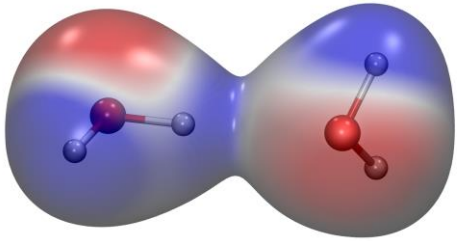


Metal – Ligand bonding

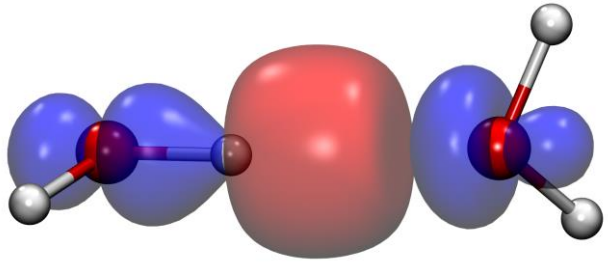


M. Zlatar, M. Gruden, "Introduction to ligand field theory and computational chemistry in Practical Approaches to Biological Inorganic Chemistry, 2nd Edition, 17 (2020)

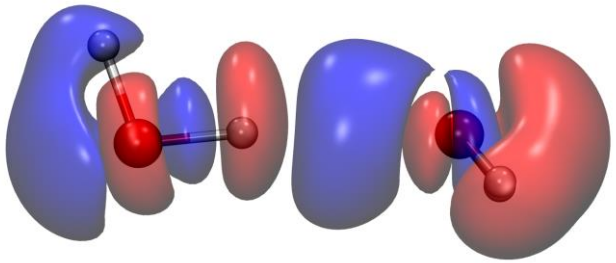
Chemical interactions/bonding – Energy Decomposition analysis



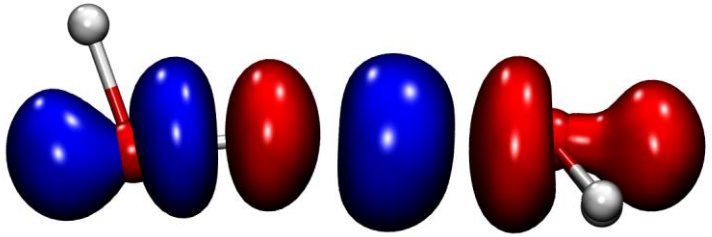
Electrostatics
-6.71 kcal/mol



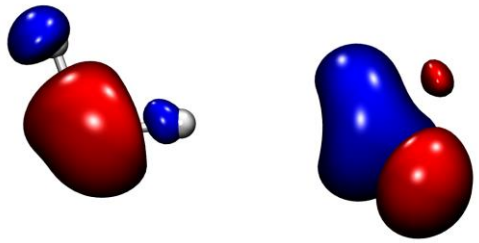
Pauli repulsion
6.14 kcal/mol



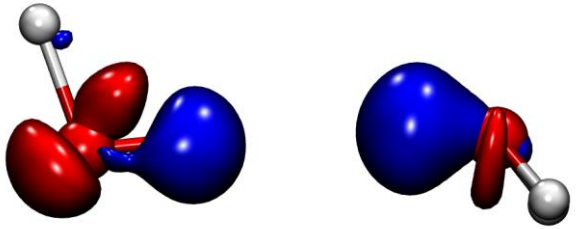
Orbital interactions
-3.19 kcal/mol



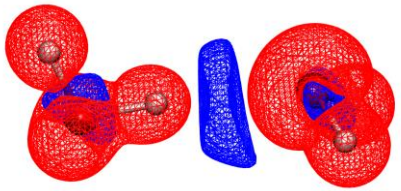
σ covalency
-2.41 kcal/mol



polarization
-0.34 kcal/mol

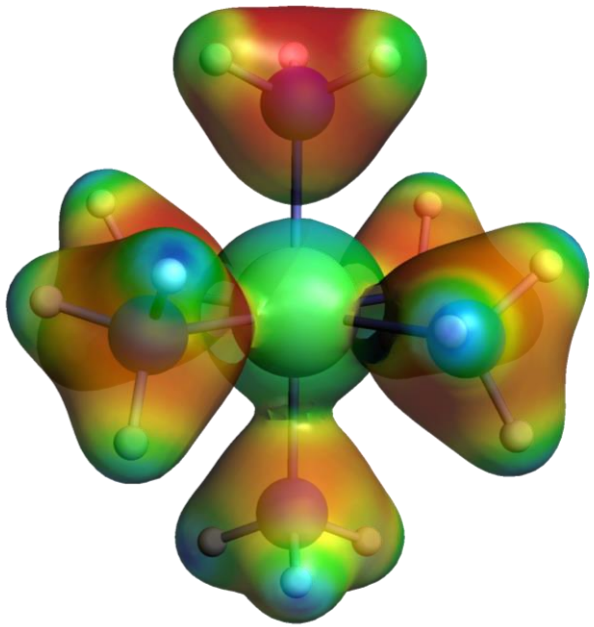


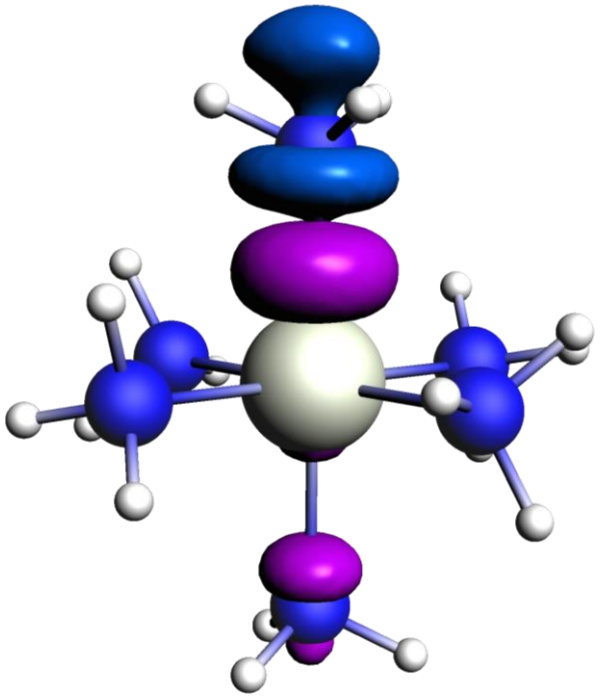
polarization
-0.39 kcal/mol

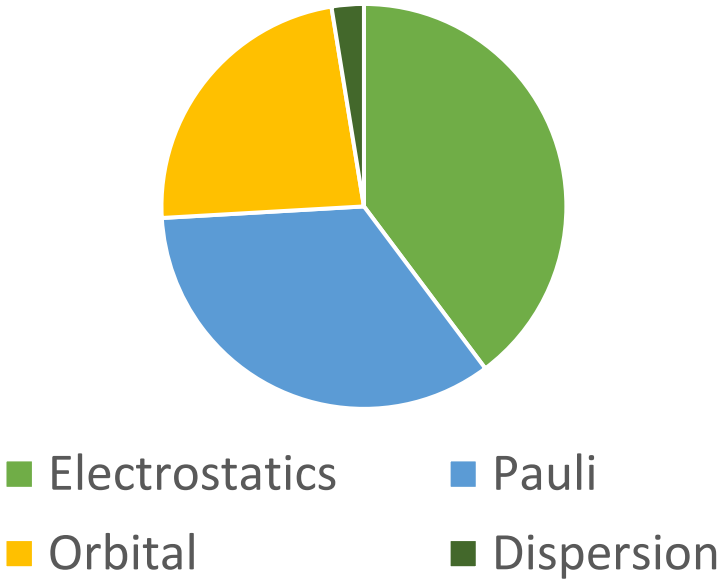


dispersion
-0.91 kcal/mol

Chemical bonding – $[Cr(NH_3)_6]^{3+}$



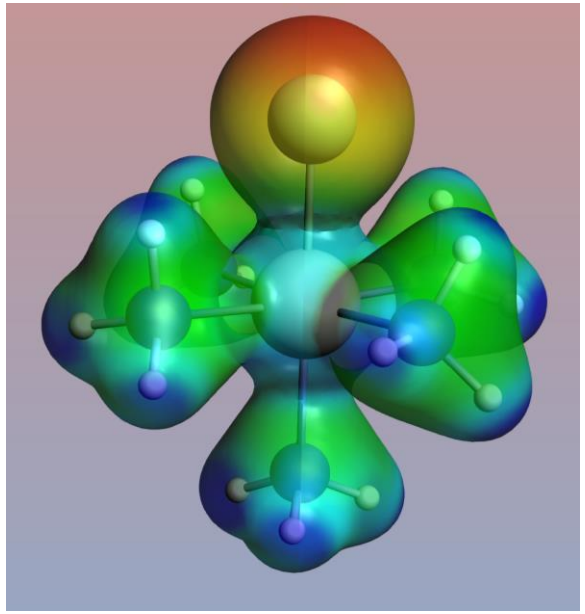




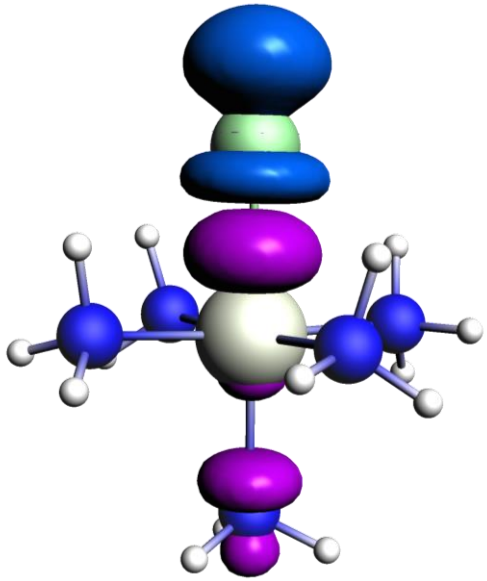
Electrostatics
-79.55

σ covalency
-36.43 kcal/mol

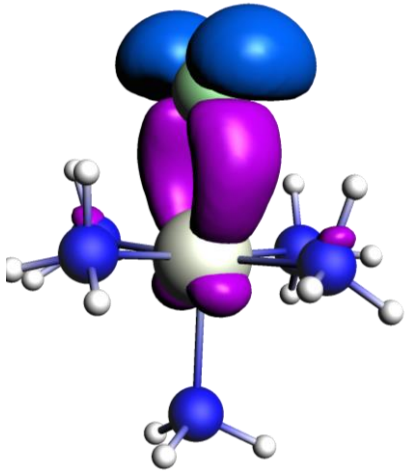
Chemical bonding – $[Cr(NH_3)_5Cl]^{2+}$



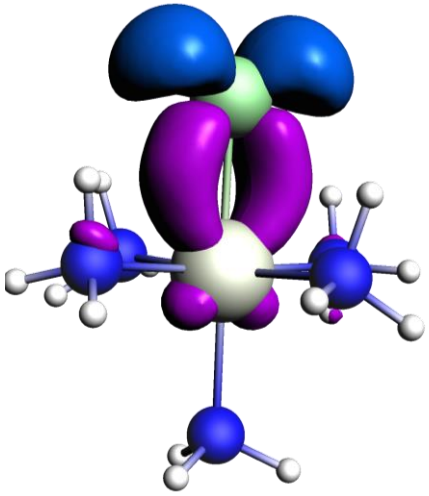
Electrostatics
-381.61 kcal/mol

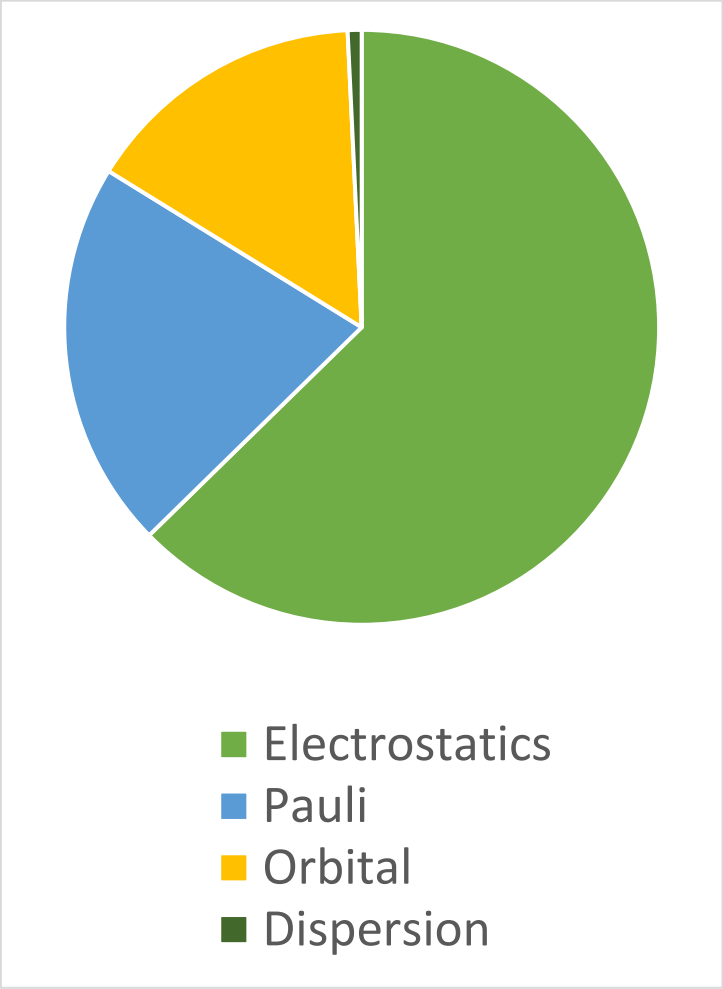


σ covalency
-55.29 kcal/mol

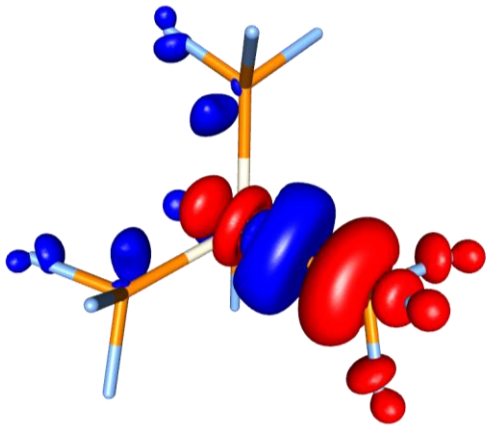


π donation
2*(-9.44) kcal/mol

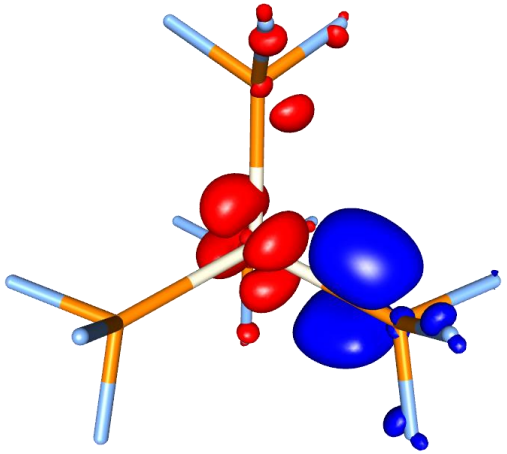




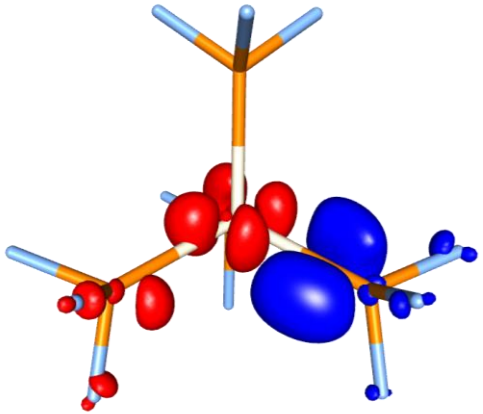
Chemical bonding – covalency in $[Pt(PF_3)_4]$



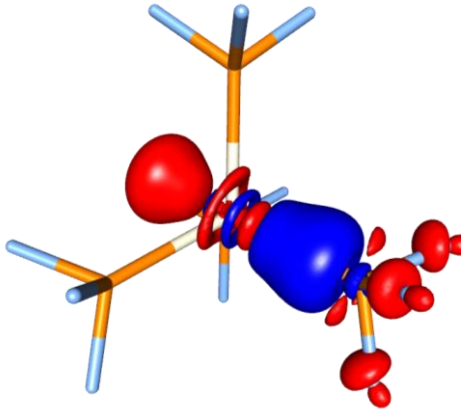
σ donation
-26.52 kcal/mol



π* backdonation
-13.83 kcal/mol



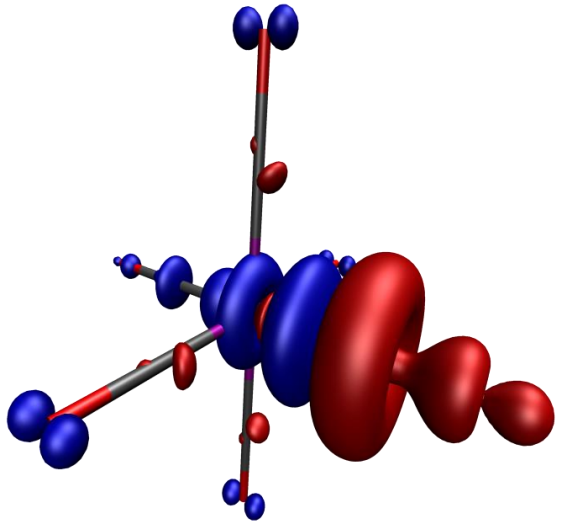
π* backdonation
-13.83 kcal/mol



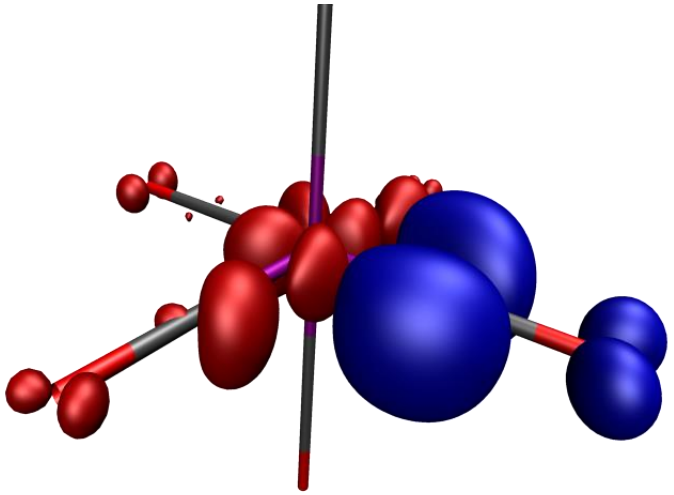
σ back-donation/polarisation
-10.84 kcal/mol

M. Zlatar, M. Allan, J. Fedor, J. Phys. Chem. C, 120 10667 (2016)

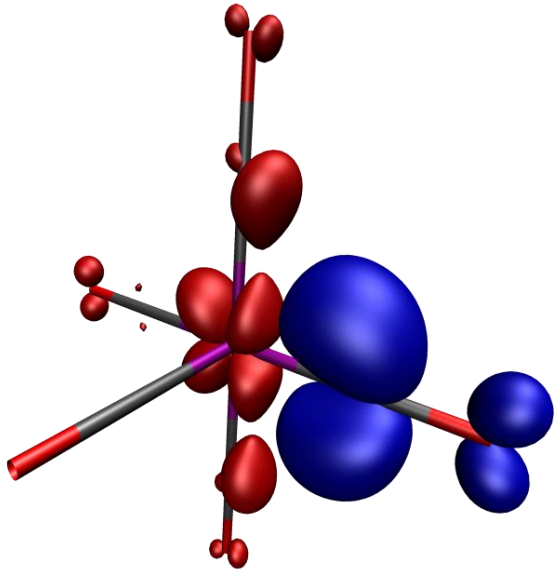
Chemical bonding – covalency in $[Cr(CO)_6]$



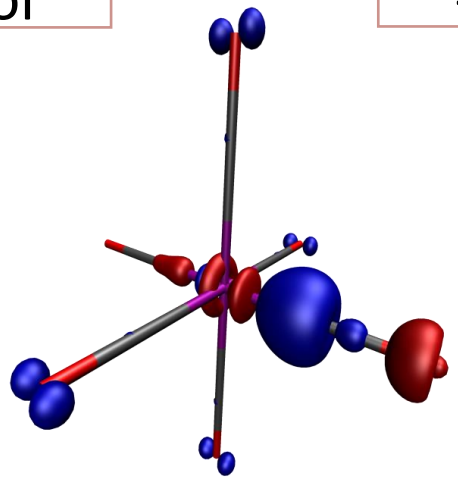
σ donation
-32.98 kcal/mol



π* backdonation
-19.60 kcal/mol

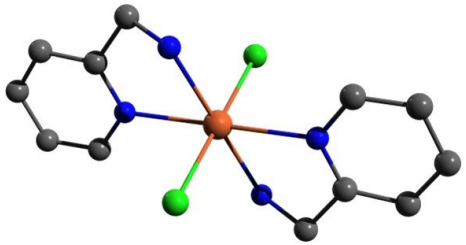


π* backdonation
-19.60 kcal/mol

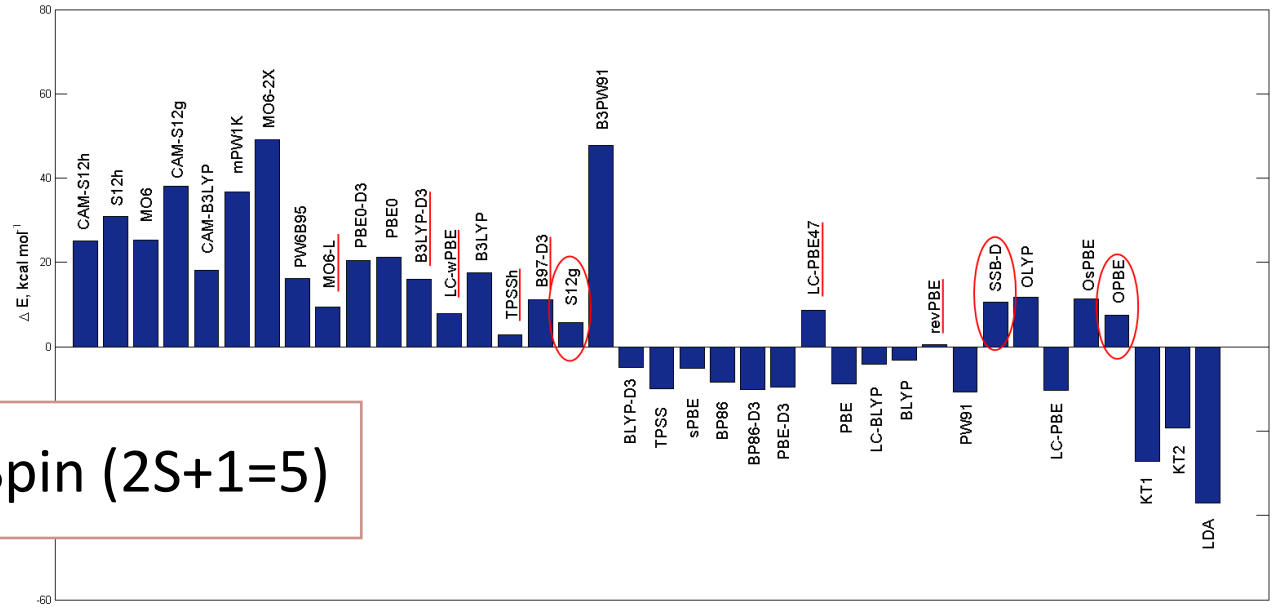


σ polarisation
-1.15 kcal/mol

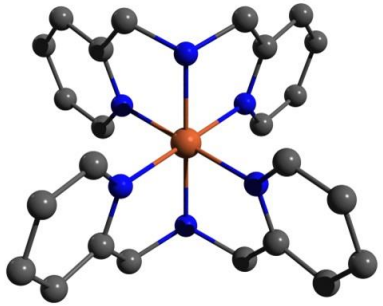
Spin-state splitting – Fe(II)



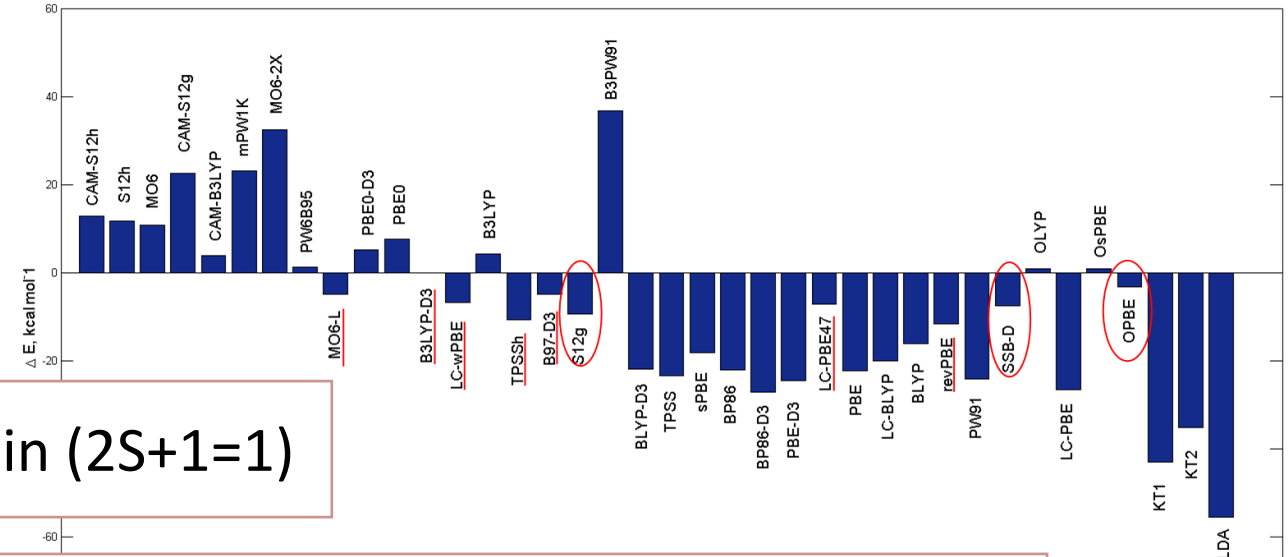
$[Fe(amp)_2Cl_2]$



High-Spin (2S+1=5)



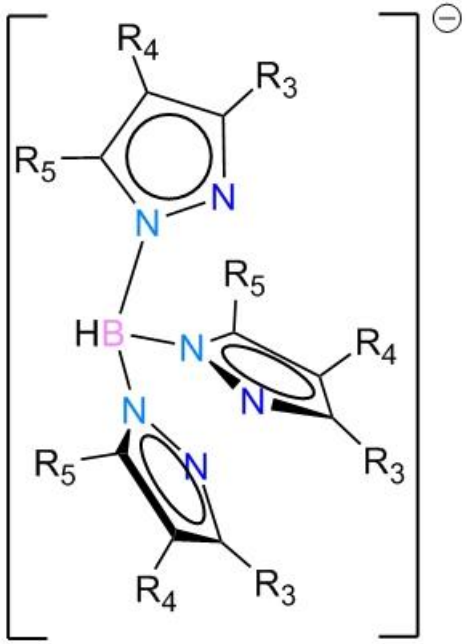
$[Fe(dpa)_2]^{2+}$

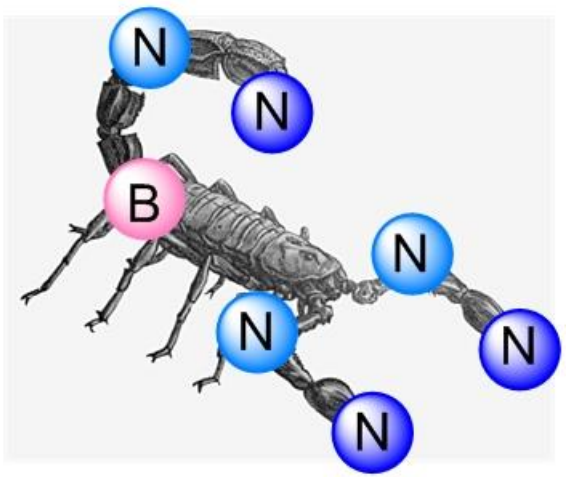


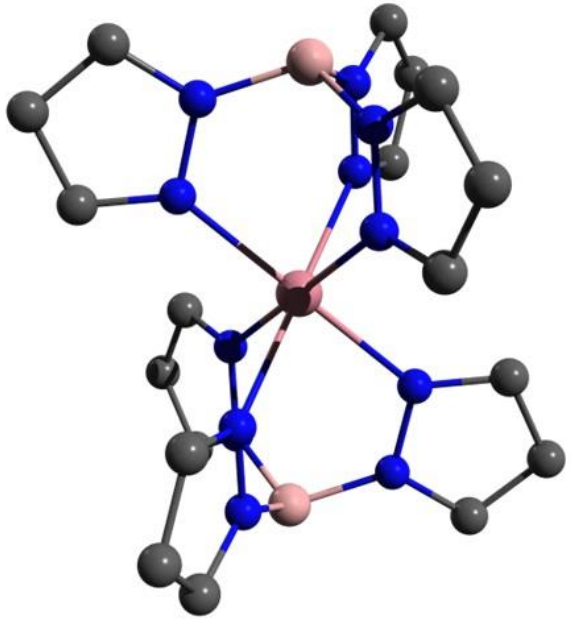
Low-Spin (2S+1=1)

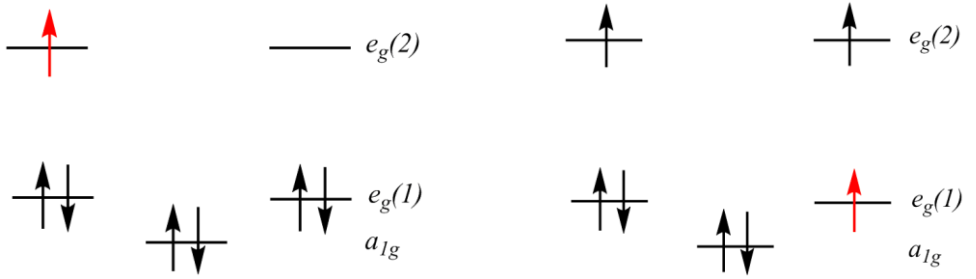
Swart, M. Chem. Phys. Lett. 2013, 580, 166; C. Daul, M. Zlatar, M. Gruden-Pavlović, M. Swart in Spin states in biochemistry and inorganic chemistry: influence on structure and reactivity, 7 (2016)

Spin-state splitting- Co(II) scorpionate









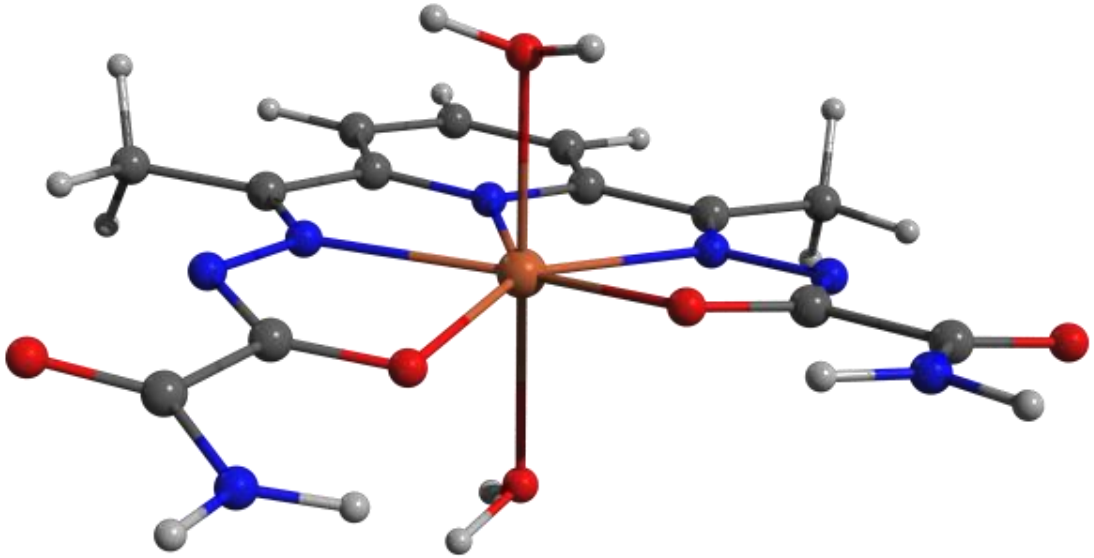
Low-Spin

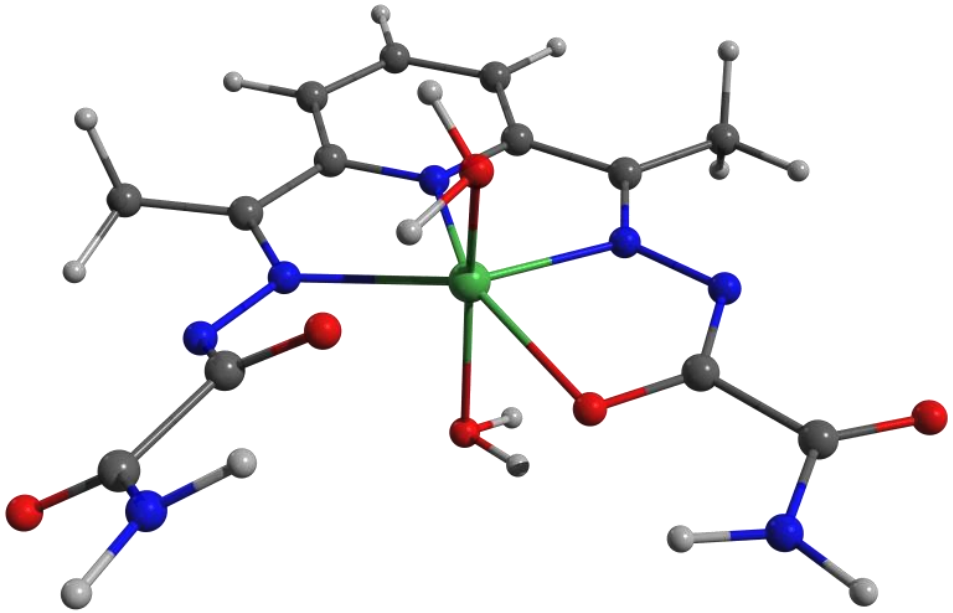
High-Spin

	Spin state	State	Vacuum	Solvation	Gibbs	Exp.
Co (d^7)	HS(D_{3d})	^4E_g	1.11	-	-	
	LS(D_{3d})	^2E_g	7.37	-	-	
	HS(C_{2h})	^4A_g	1.18	0.43	0.35	
	HS(C_{2h})	^4B_g	1.01	0.18	0	HS
	LS(C_{2h})	^2A_g	0	0	1.43	
	LS(C_{2h})	^2B_g	2.50	2.56	4.79	

OPBE, relative to the ground state

Co(II) vs. Ni(II) and HS vs. LS – PBPY-7 complexes

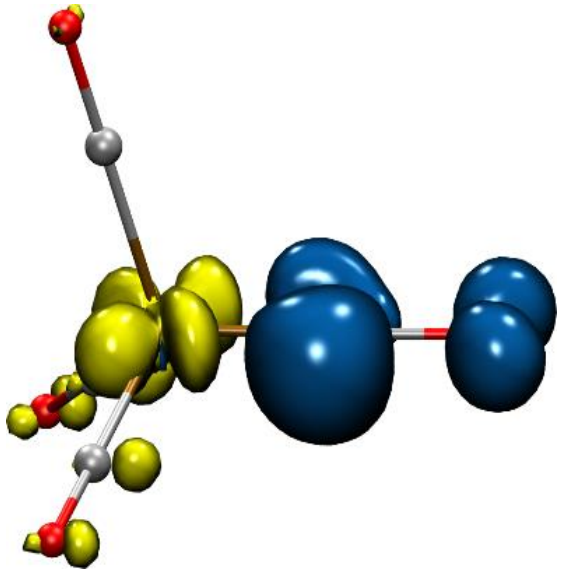




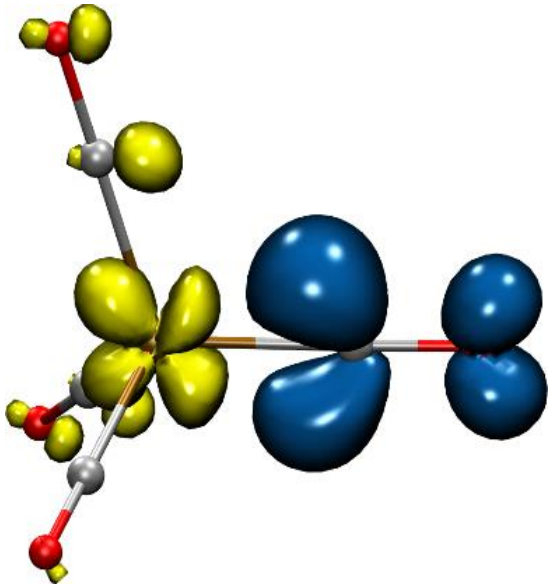
Spin-state changes coordination mode

S. Stepanovic, L. Andjelkovic, M. Zlatar, K. Andjelkovic, M. Gruden-Pavlovic, M. Swart Inorg. Chem. 2013 52 (23), 13415

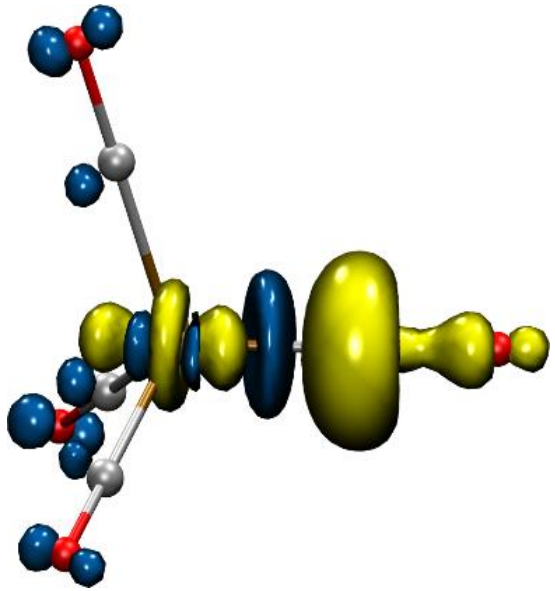
Fe(-II) - Bonding in $[Fe(CO)_4]^{2-}$



E= -38 kcal/mol; Δq=0.29



E= -36 kcal/mol; Δq=0.28

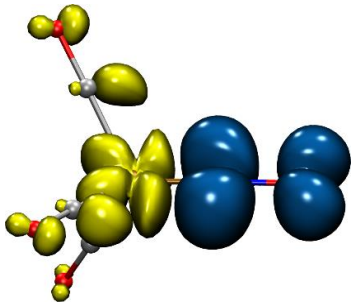


E= -18 kcal/mol; Δq=0.16

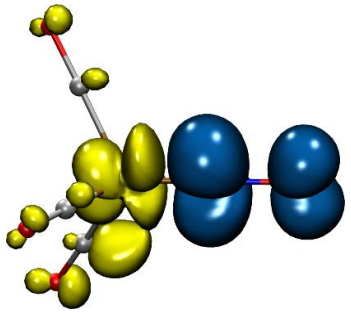
	E_{Pauli}	E_{elst}	E_{orb}	E_{int}	E_{prep}	E	ΔQ
$[Fe(CO)_3]^{2-}$--CO	121.79	-104.05	-102.62	-84.88	14.42	-70.46	0.45 (to CO)

M. Gruden, M. Zlatar, Theoretical Chemistry Accounts, 139, 7, 126 (2020)

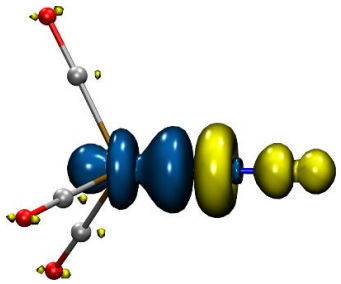
Fe(-II) - Bonding in $[Fe(CO)_3NO]^-$



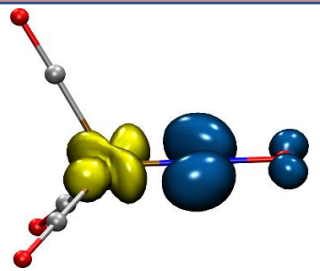
E = -149 kcal/mol;
Δq=0.72



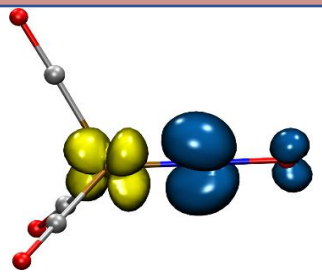
E = -149 kcal/mol;
Δq=0.72



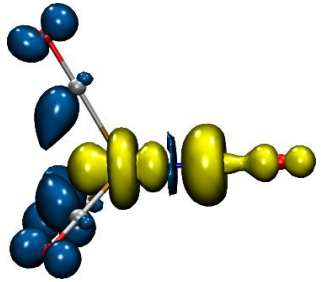
E = -17 kcal/mol;
Δq=0.14



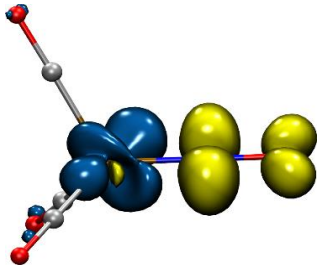
E = -12 kcal/mol;
Δq=0.20



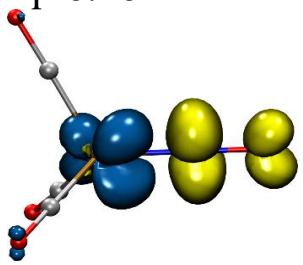
E = -12 kcal/mol;
Δq=0.20



E = -34 kcal/mol;
Δq=0.09



E = -22 kcal/mol;
Δq=0.31

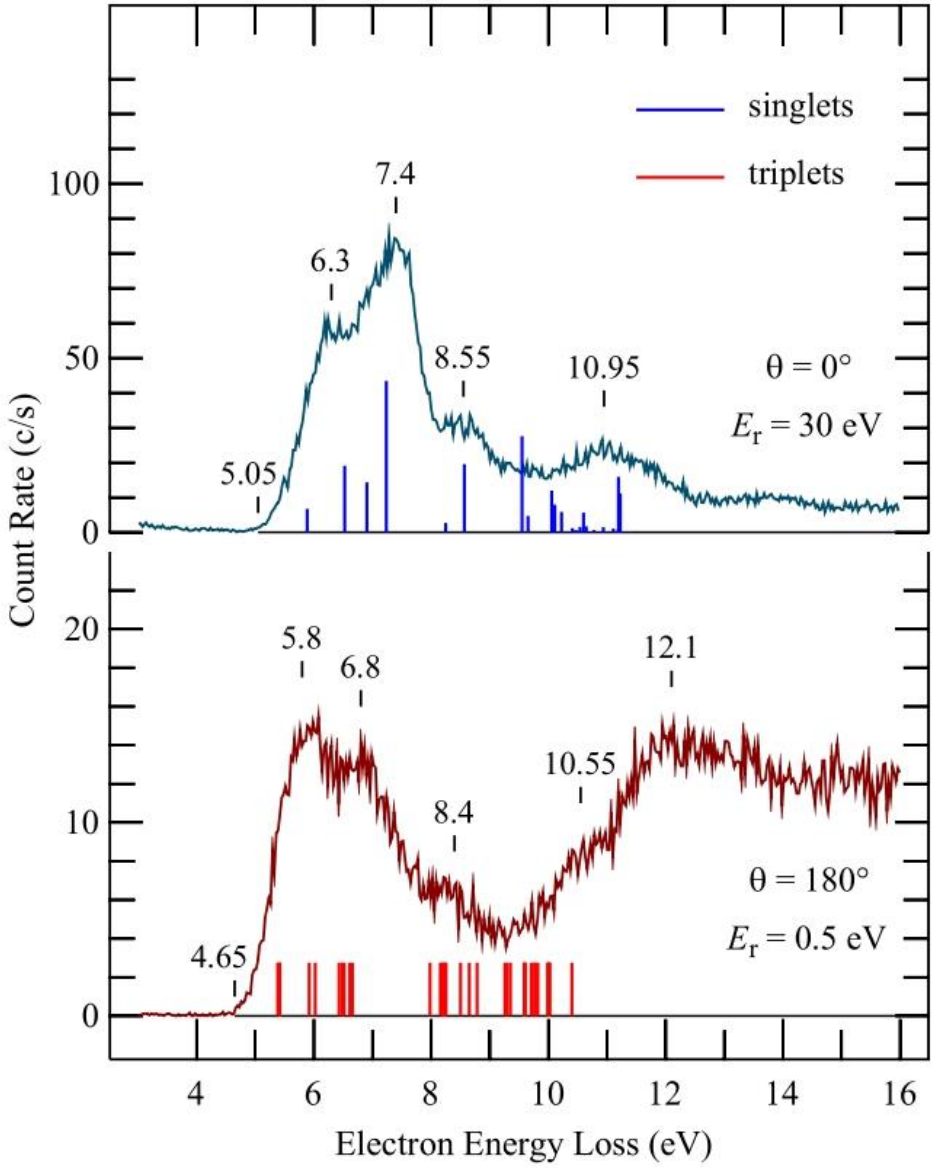


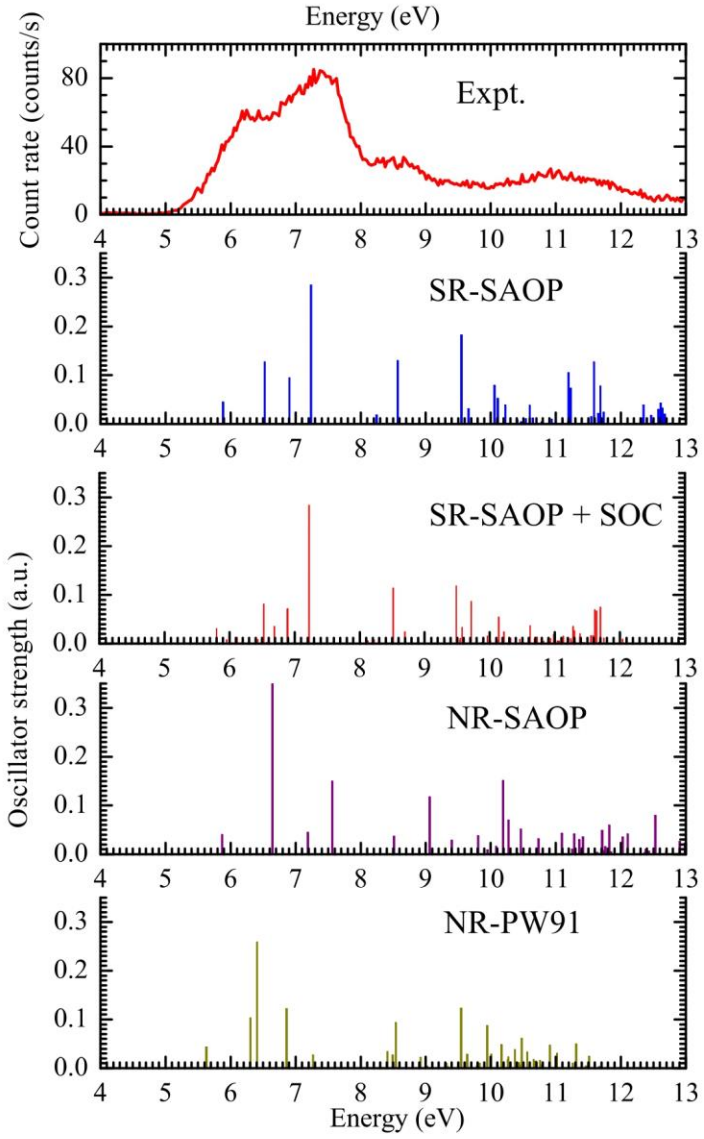
E = -22 kcal/mol;
Δq=0.31

Fe(-II) or Fe(0)?
Closed shell or open shell singlet?

		E_{Pauli}	E_{elst}	E_{orb}	E_{int}	E_{prep}	E_{rel}	ΔQ
i)	$[Fe(CO)_3]^{2-}$-- NO^+	105.95	-210.78	-324.34	-447.17	86.07	-65.17	1.25 (to NO+)
ii)	$^2[Fe(CO)_3]^-$-- ^2NO	160.12	-93.37	-156.68	-89.94	23.95	-65.99	0.46 (to NO)
iii)	$^3[Fe(CO)_3]$ -- $^3NO^-$	195.04	-178.47	**-122.76**	-106.19	4.22	-65.99	0.28 (From No-)

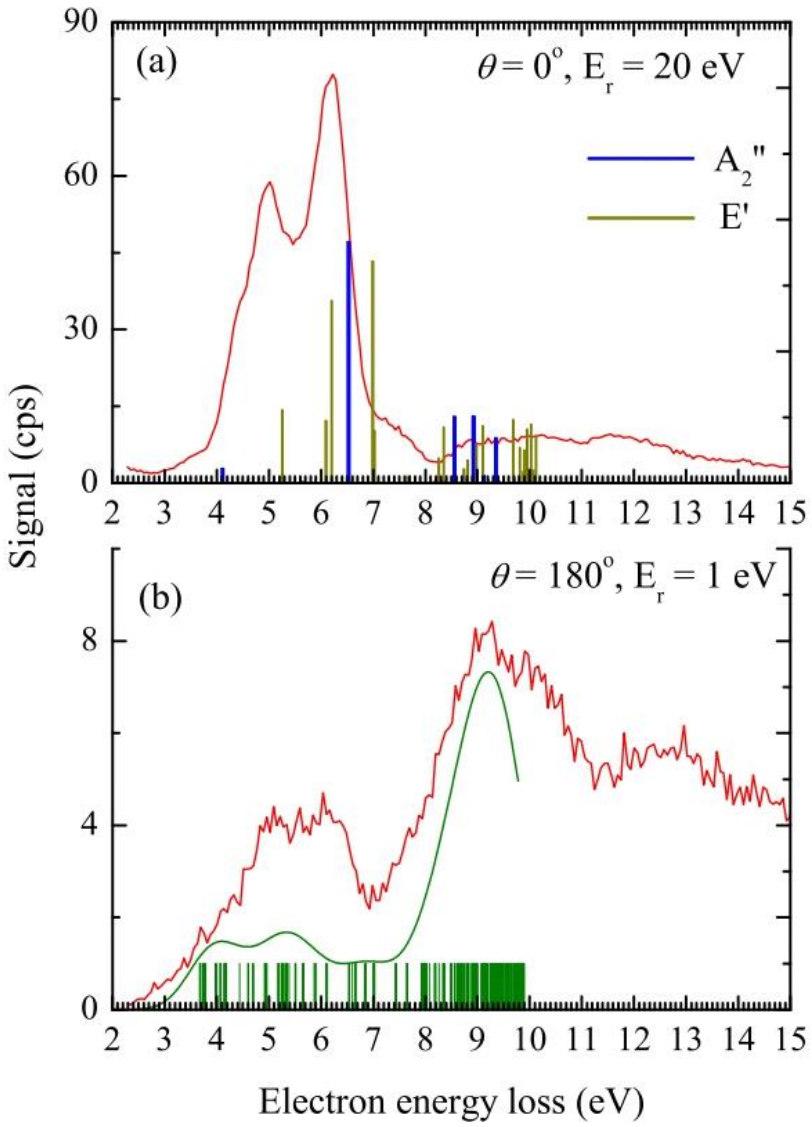
TD-DFT - [Pt(PF3)4]





M. Zlatar, M. Allan, J. Fedor, J. Phys. Chem. C, 120 10667 (2016)

TD-DFT - [Fe(CO)5]

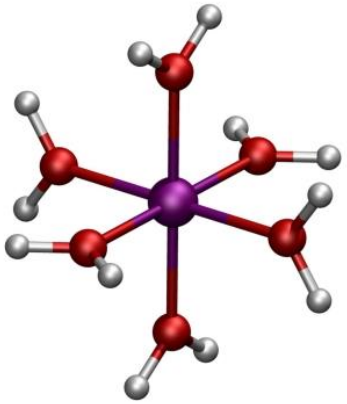


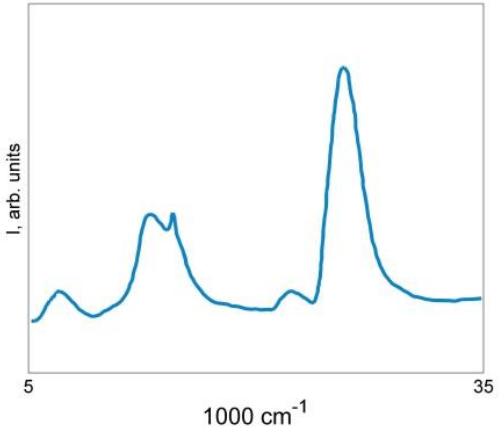
CELINA 2016

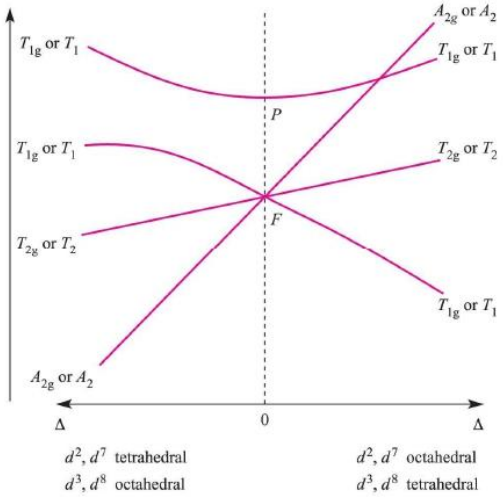
Allan M, Lacko M, Papp P, Matejcik S, Zlatar M, Fabrikant II, Kocisek J, Fedor J. PCCP. 2018; 20(17): 11692-11701.

Failure of TD- DFT $[Ni(H_2O)_6]^{2+}$

	TD-DFT			CASSCF	SORCI	Exp.
	BP86	CAM-B3LYP	SAOP			
^3A_g $(t_g^6 e_g^2)$	0	0	0	0	0	0
^3T_g $(t_g^5 e_g^3)$	16,137	13,926	24,973	6,397	7,760	8,700
^3T_g $(t_g^5 e_g^3)$	19,539	20,480	21,367	11,128	13,160	13,750
^1E_g $(t_g^6 e_g^2)$	14,105	15,226	17,344	18,662	15,740	15,250
^1T_g $(t_g^5 e_g^3)$	20,220	20,244	23,540	24,148	22,710	22,000
^3T_g $(t_g^4 e_g^4)$	-	-	-	27,435	25,320	25,144
MAE $(^3\Gamma \rightarrow ^3\Gamma)$	6,613	5,978	11,945	2,405	570	
MAE $(^3\Gamma \rightarrow ^1\Gamma)$	1,462	890	1,817	2,780	600	
MAE	4,038	3,434	6,881	2,555	580	



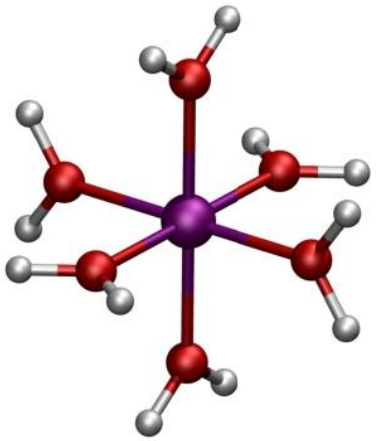


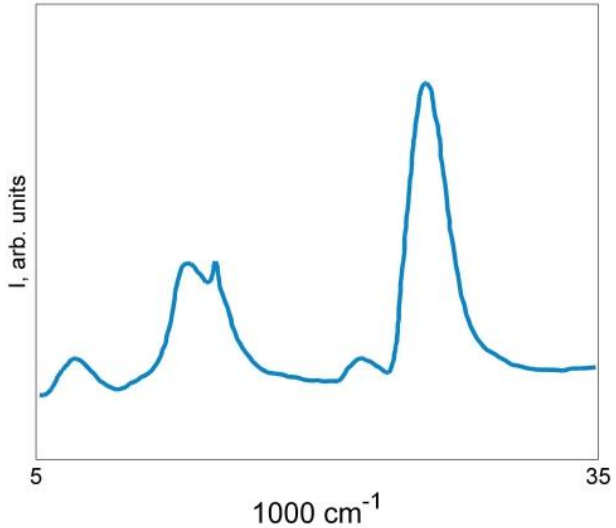


TD-DFT: F. Vlahovic, M. Peric, M. Gruden, MZ, JCP, 142, 214111 (2015); ab-initio: F. Neese, et al. Coord. Chem. Rev. 251, 288 (2007); exp. C. Dobe, E. Gonzalez, P. L. W. Tregenna-Piggott, C. Reber, Dalton Trans. 43, 17864 (2014)

LF-DFT - $[Ni(H_2O)_6]^{2+}$

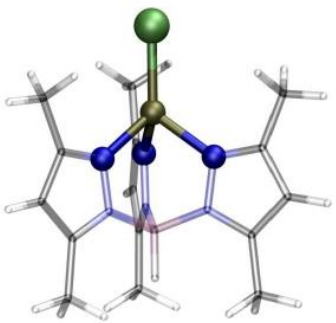
Assignment	BP86	PW91	OPBE	SSB-D	B3LYP	CAM-B3LYP	PBE0	OPBE0	Exp.
^3A_g $(t_g^6 e_g^2)$	0	0	0	0	0	0	0	0	0
^3T_g $(t_g^5 e_g^3)$	9,529	9,521	9,201	8,992	9,316	9,233	9,229	9,114	8,700
^3T_g $(t_g^5 e_g^3)$	15,518	15,506	14,919	14,735	15,273	15,148	15,110	14,870	13,750
^1E_g $(t_g^6 e_g^2)$	12,478	12,410	13,258	13,465	12,232	12,218	12,759	13,321	15,250
^1T_g $(t_g^5 e_g^3)$	21,647	21,569	22,129	22,089	21,162	21,065	21,614	22,081	22,000
^3T_g $(t_g^4 e_g^4)$	26,040	26,026	24,807	25,100	26,059	25,889	25,684	25,061	25,144
MAE $(^3\Gamma \rightarrow {}^3\Gamma)$	1,164	1,153	669	440	1,018	892	810	539	
MAE $(^3\Gamma \rightarrow {}^1\Gamma)$	1,562	1,635	1,060	937	1,928	1,984	1,438	1,005	
MAE	1,324	1,346	825	639	1,382	1,329	1,061	725	

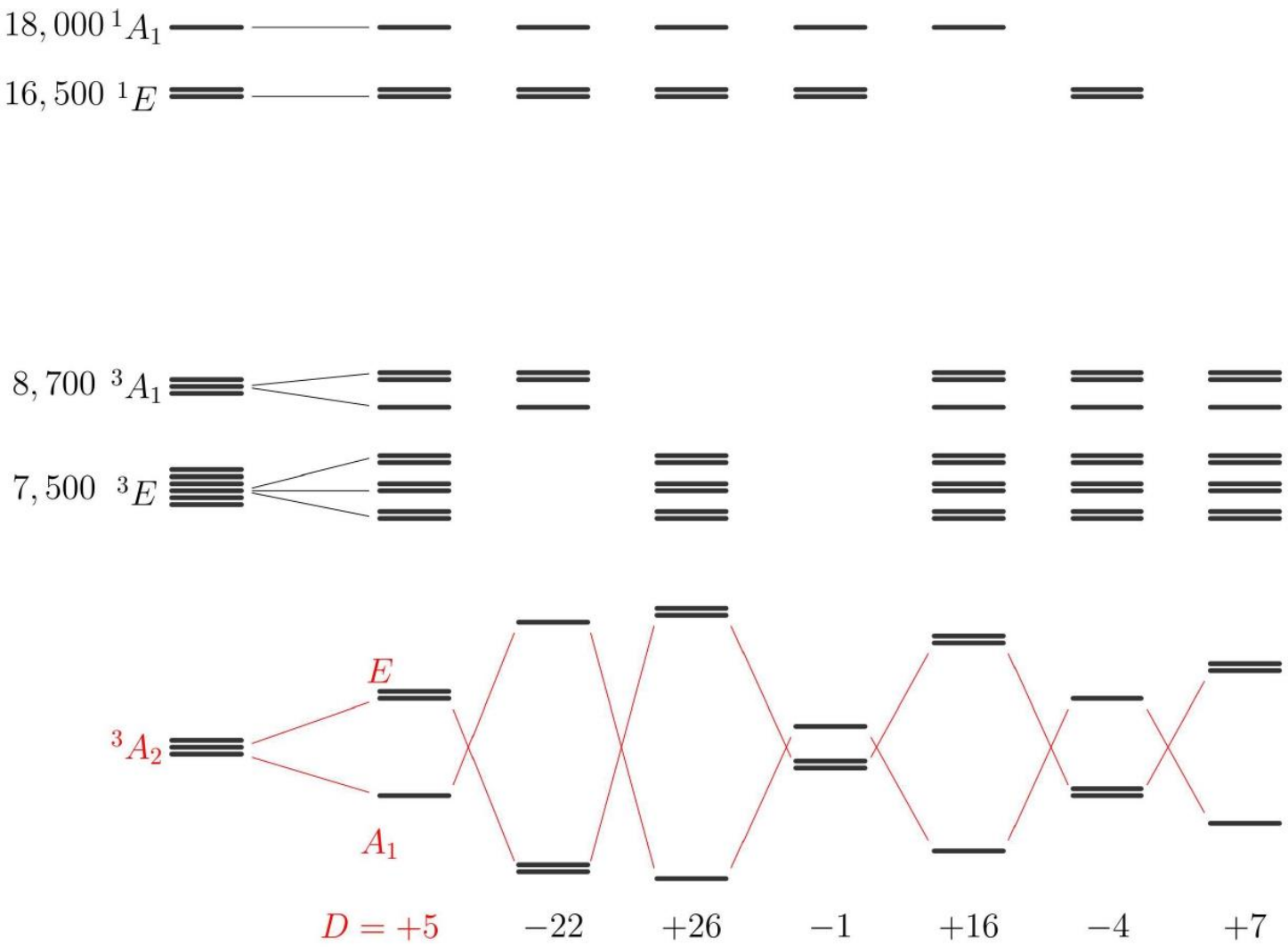




LF-DFT: F. Vlahovic, M. Peric, M. Gruden, MZ, JCP, 142, 214111 (2015); exp. C. Dobe, E. Gonzalez, P. L. W. Tregenna-Piggott, C. Reber, Dalton Trans. 43, 17864 (2014)

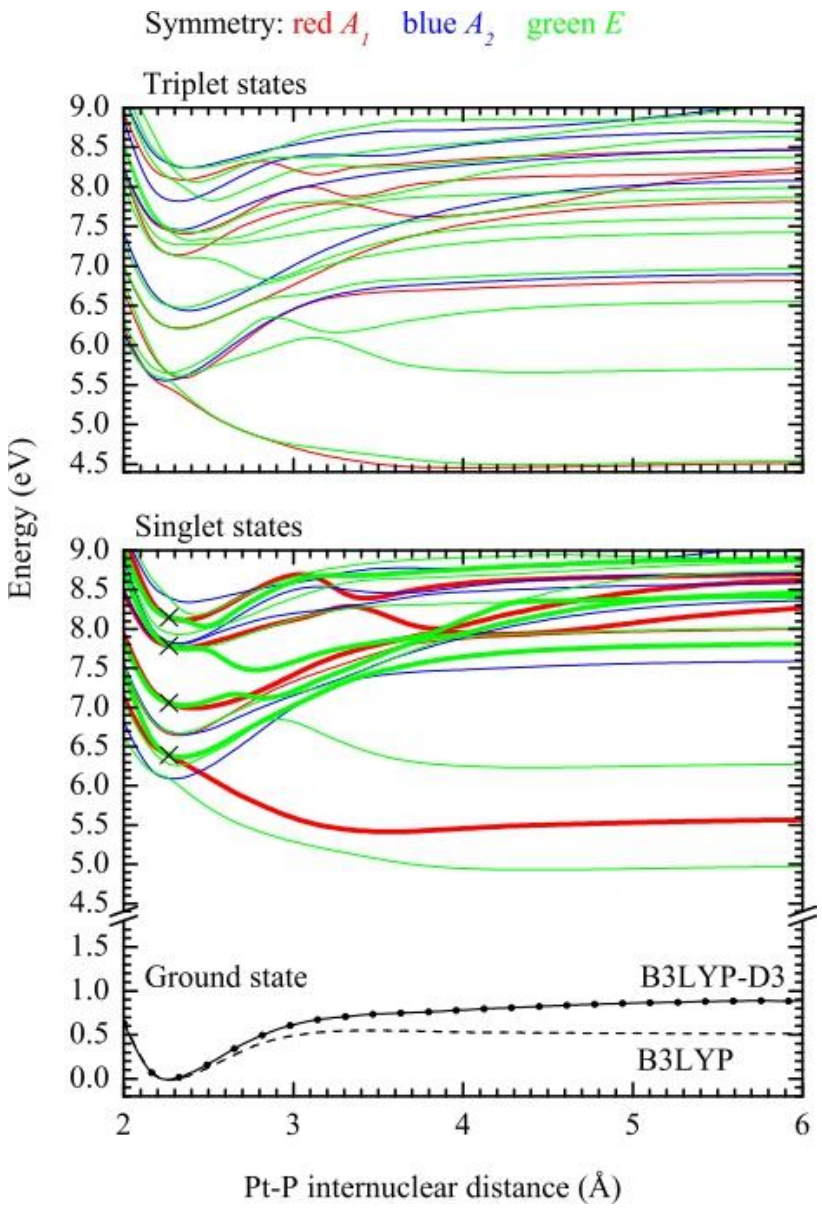
Excited states and magnetic anisotropy - Ni(II) scorpionate

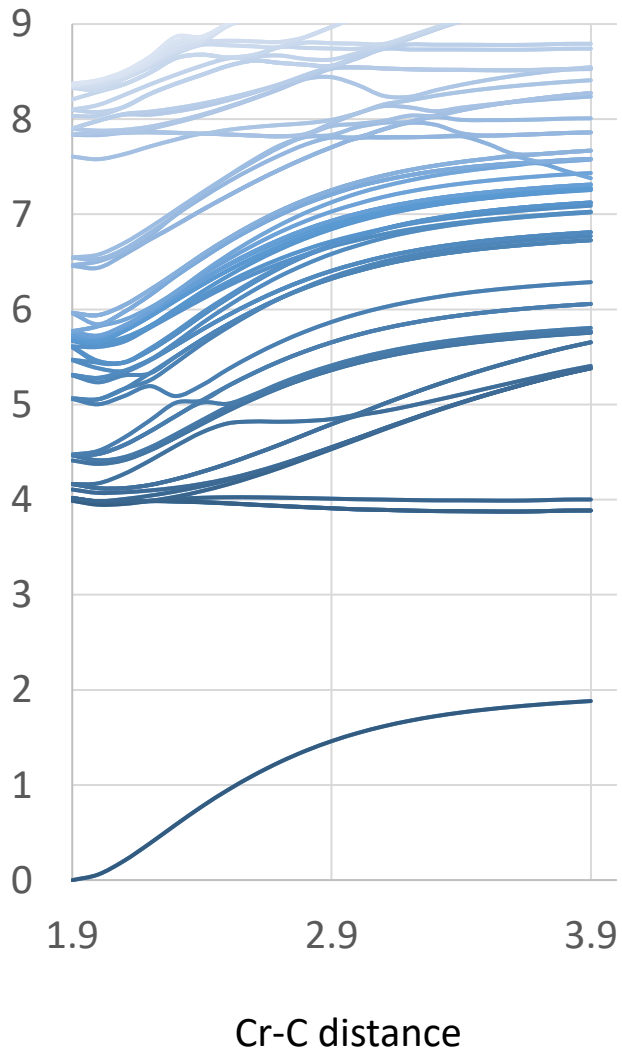


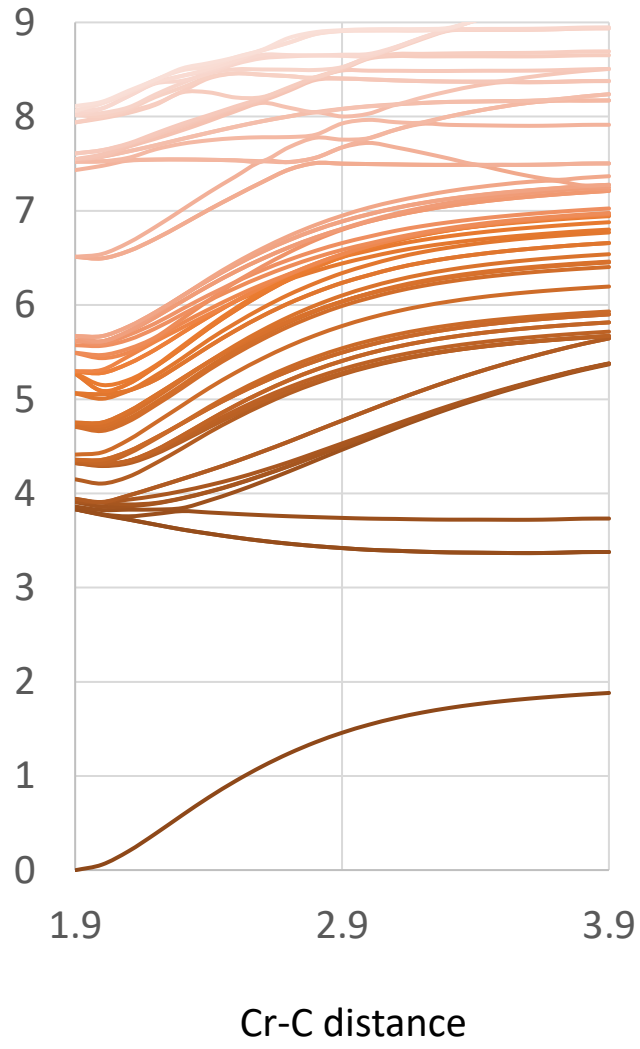


M. Peric, A. Garcia-Fuente, MZ, C. Daul, S. Stepanovic, P. Garcia-Fernandez, and M. Gruden-Pavlovic, Chem. Eur. J. 2015, 21, 3716

Dissociation - [Pt(PF3)4] and [Cr(CO)6]







Perspectives

Fascinating Coordination Chemistry:

- coordination number, molecular symmetry, ligand- field strength, spin-orbit coupling, spin and oxidation states, redox potential, spin, and charge localization, electronic degeneracies
- Ground and excited states
- Interpretation, understanding, predict and design

Neutral dissociation – excited states
Mechanism: role of MOs, spin-states, spin-orbit, vibronic coupling, dynamics
Environment

Thank you for your attention!

TM MagCat

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