From Linnett-Gillespie Model to the Polarization of the Spin Valence Shells of Metals in Complexes.

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Note: Energy and electron density units are atomic units, Hartree and $e/bohr^3$ respectively.

1 Hexa-aquo complexes.

Table 1: Complex energy in high spin, E_{HS}, and low spin, E_{LS}, electron configuration.

Complex	$E_{HS}(E_{LS})$
$[Sc(H_2O)_6]^{3+}$	-1217.9577
$[Sc(H_2O)_6]^{2+}$	-1218.4418
$[Ti(H_2O)_6]^{3+}$	-1306.6278
$[V(H_2O)_6]^{4+}$	-1400.2573
$[Ti(H_2O)_6]^{2+}$	-1307.1601
$[V(H_2O)_6]^{3+}$	-1401.1204
$[V(H_2O)_6]^{2+}$	-1401.6965
$[Cr(H_2O)_6]^{3+}$	-1501.5693
$[Mn(H_2O)_6]^{4+}$	-1607.1576
$[Cr(H_2O)_6]^{2+}$	-1502.1355 (-1502.0829)
$[Mn(H_2O)_6]^{3+}$	-1608.0440 (-1608.0096)
$[Mn(H_2O)_6]^{2+}$	-1608.6897 (-1608.5942)
$[Fe(H_2O)_6]^{3+}$	-1720.7503 (-1720.6871)
$[Fe(H_2O)_6]^{2+}$	-1721.3601 (-1721.2936)
$[Co(H_2O)_6]^{2+}$	-1840.3958 (-1840.3564)
$[Ni(H_2O)_6]^{3+}$	-1965.2355 (-1965.2314)
$[Ni(H_2O)_6]^{2+}$	-1965.9389
$[Cu(H_2O)_6]^{2+}$	-2098.0602
$[Zn(H_2O)_6]^{2+}$	-2236.9818

Table 2: Concentration and depletion of spin density, as a measure of the spin polarization, of the oxygen atom in the $[V(H_2O)_6]^{2+}$ and $[Ni(H_2O)_6]^{2+}$ complexes.

	$\nabla^2\rho_s(r)$	
$M-OH_2$ distance (Å)	$[V(H_2O)_6]^{2+}$	$[Ni(H_2O)_6]^{2+}$
2.90	0.001579	0.033278
2.95	0.002216	0.022762
3.00	0.003508	0.007185
3.05	0.005695	-0.014874
3.10	0.009074	-0.044796
3.15	0.013973	-0.083943
3.20	0.020723	-0.133972
3.25	0.029647	-0.197492
3.30	0.041103	-0.278859
3.35	0.055633	-0.384347
3.40	0.074245	-0.520136
3.45	0.098757	-0.684996
3.50	0.131980	-0.853322
3.55	0.177263	-0.951674
3.60	0.236457	-0.861388
3.65	0.305273	-0.487844
3.70	0.368039	0.260051
3.75	0.402422	1.989656
3.80	0.401889	5.338750
3.85	0.361567	5.766905

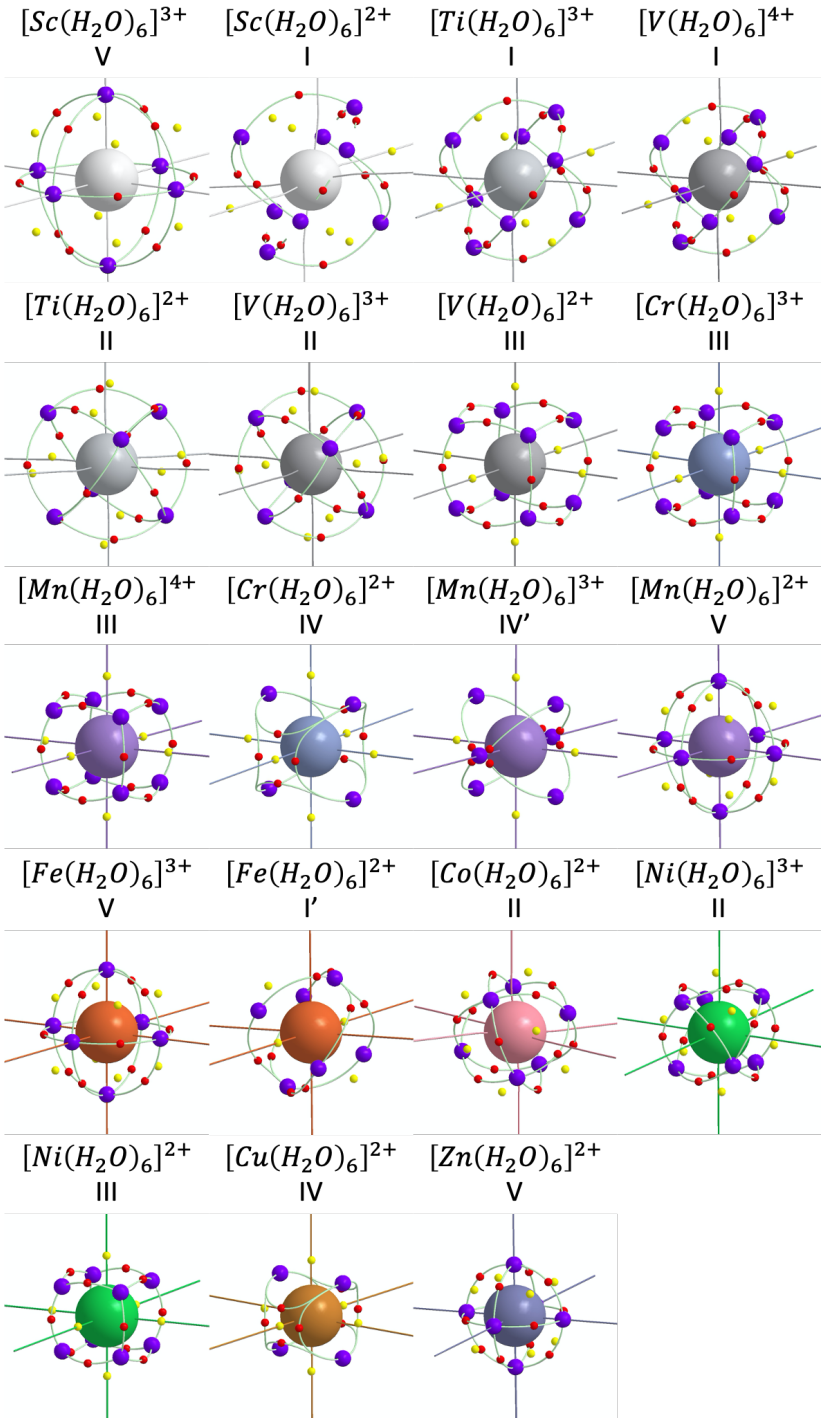

Figure 1: Atomic graphs of metal centers in complexes $[M(H_2O)_6]^{m+}$, where M is first-row d-block metals with oxidation states m. The roman numerals correspond to the type of atomic graph.

2 Evolution of the Metal-Ligand interaction.

The changes associated to different properties in this sections are referenced to isolated species: $\Delta P = P_x - P_{isolated}$, where x is the metal-ligand distance and $P_{isolated}$ corresponds to the values of the isolated metal or six water molecules.

Table 3: Changes in Metal spin population (ΔN_s) with M$-$OH$_2$ distance in complexes [M(H$_2$O)$_6$]$^{2+}$.

Metal	M$-$OH$_2$ distance (Å)							
M	eq.	2.5	3.0	3.5	4.0	4.5	5.0	5.5
Sc	-0.1655	-0.0828	-0.0260	-0.0111	-0.0049	-0.0019	-0.0005	0.0000
Ti	-0.1602	-0.0911	-0.0347	-0.0148	-0.0059	-0.0020	-0.0005	0.0000
V	-0.1822	-0.0877	-0.0313	-0.0119	-0.0040	-0.0011	-0.0002	0.0000
Mn	-0.2120	-0.1157	-0.0400	-0.0125	-0.0031	-0.0006	-0.0001	0.0000
Fe	-0.1602	-0.0762	-0.0240	-0.0065	0.0006	0.0004	0.0001	0.0000
Co	-0.1339	-0.0536	-0.0159	-0.0034	0.0020	0.0007	0.0002	0.0000
Ni	-0.1175	-0.0477	-0.0157	-0.0040	0.0013	0.0005	0.0001	0.0000
Zn	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4: Changes in Ligand spin population (ΔN_s) with M$-$OH$_2$ distance in complexes [M(H$_2$O)$_6$]$^{2+}$.

Ligands	M$-$OH$_2$ distance (Å)							
M	eq.	2.5	3.0	3.5	4.0	4.5	5.0	5.5
Sc	0.1658	0.0830	0.0260	0.0111	0.0049	0.0019	0.0005	0.0000
Ti	0.1603	0.0911	0.0348	0.0148	0.0060	0.0020	0.0005	0.0000
V	0.1822	0.0877	0.0313	0.0119	0.0040	0.0011	0.0002	0.0000
Mn	0.2120	0.1158	0.0400	0.0125	0.0031	0.0006	0.0001	0.0000
Fe	0.1602	0.0762	0.0240	0.0065	-0.0006	-0.0004	-0.0001	0.0000
Co	0.1339	0.0536	0.0159	0.0034	-0.0020	-0.0007	-0.0002	0.0000
Ni	0.1175	0.0476	0.0157	0.0039	-0.0013	-0.0005	-0.0001	0.0000
Zn	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 5: Changes with the metal-ligand distance in the spin intra-atomic energy, $\Delta E_{intra-s}(M)$, and electron-electron repulsive potential energy due to the α and β interactions, $\Delta V_{ee_{\alpha}\beta}(M, M)$, in the metal center for complexes $[V(H_2O)_6]^{2+}$ and $[Ni(H_2O)_6]^{2+}$.

$[V(H_2O)_6]^{2+}$				
Metal-Ligand distance (Å)	$\Delta E_{intra-\alpha}(M)$	$\Delta E_{intra-\beta}(M)$	$\Delta E_{intra-s}(M)$	$\Delta V_{ee-\alpha\beta}(M, M)$
2.18	-0.65	-1.48	0.83	1.87
2.50	-0.49	-0.82	0.33	1.12
3.00	-0.27	-0.34	0.08	0.51
3.50	-0.12	-0.14	0.02	0.21
4.00	-0.05	-0.05	0.00	0.08
4.50	-0.02	-0.02	0.00	0.02
5.00	0.00	0.00	0.00	0.01
5.50	0.00	0.00	0.00	0.00
$[Ni(H_2O)_6]^{2+}$				
Metal-Ligand distance (Å)	$\Delta E_{intra-\alpha}(M)$	$\Delta E_{intra-\beta}(M)$	$\Delta E_{intra-s}(M)$	$\Delta V_{ee-\alpha\beta}(M, M)$
2.08	-1.41	-1.93	0.52	3.04
2.50	-0.91	-1.11	0.20	1.80
3.00	-0.51	-0.57	0.06	0.96
3.50	-0.24	-0.25	0.01	0.44
4.00	-0.09	-0.10	0.01	0.17
4.50	-0.03	-0.03	0.00	0.06
5.00	-0.01	-0.01	0.00	0.02
5.50	0.00	0.00	0.00	0.00

Table 6: Changes with the metal-ligand distance in the spin intra-atomic energy, $\Delta E_{intra-s}(L)$, in ligands for complexes $[V(H_2O)_6]^{2+}$ and $[Ni(H_2O)_6]^{2+}$.

$[V(H_2O)_6]^{2+}$			
Metal-Ligand distance (Å)	$\Delta E_{intra-\alpha}(L)$	$\Delta E_{intra-\beta}(L)$	$\Delta E_{intra-s}(L)$
2.18	-0.43	-0.56	0.13
2.50	-0.36	-0.48	0.12
3.00	-0.31	-0.39	0.08
3.50	-0.29	-0.33	0.04
4.00	-0.27	-0.28	0.02
4.50	-0.24	-0.24	0.00
5.00	-0.20	-0.21	0.00
5.50	-0.18	-0.18	0.00
$[Ni(H_2O)_6]^{2+}$			
Metal-Ligand distance (Å)	$\Delta E_{intra-\alpha}(L)$	$\Delta E_{intra-\beta}(L)$	$\Delta E_{intra-s}(L)$
2.08	-0.58	-0.29	-0.29
2.50	-0.39	-0.28	-0.11
3.00	-0.30	-0.27	-0.02
3.50	-0.27	-0.28	0.00
4.00	-0.25	-0.26	0.01
4.50	-0.23	-0.23	0.00
5.00	-0.20	-0.20	0.00
5.50	-0.17	-0.17	0.00

Table 7: Changes with the metal-ligand distance in the spin components and the spin versions of nucleus-electron attractive potential energy, $\Delta V_{ne}(M,M)$ and electron-electron repulsive potential energy, $\Delta V_{ee}(M,M)$, in the metal center for complexes $[V(H_2O)_6]^{2+}$ and $[Ni(H_2O)_6]^{2+}$.

$[V(H_2O)_6]^{2+}$						
Metal-Ligand distance (Å)	$\Delta V_{ne-\alpha}(M,M)$	$\Delta V_{ne-\beta}(M,M)$	$\Delta V_{ne-s}(M,M)$	$\Delta V_{ee-\alpha\alpha}(M,M)$	$\Delta V_{ee-\beta\beta}(M,M)$	$\Delta V_{ee-s}(M,M)$
2.18	-1.12	-3.06	1.94	0.72	0.98	-0.26
2.50	-0.85	-1.61	0.76	0.54	0.53	0.00
3.00	-0.47	-0.63	0.16	0.29	0.22	0.08
3.50	-0.21	-0.23	0.02	0.13	0.08	0.05
4.00	-0.08	-0.08	0.00	0.05	0.03	0.02
4.50	-0.02	-0.02	0.00	0.02	0.01	0.01
5.00	0.00	0.00	0.00	0.00	0.00	0.00
5.50	0.00	0.00	0.00	0.00	0.00	0.00
$[Ni(H_2O)_6]^{2+}$						
Metal-Ligand distance (Å)	$\Delta V_{ne-\alpha}(M,M)$	$\Delta V_{ne-\beta}(M,M)$	$\Delta V_{ne-s}(M,M)$	$\Delta V_{ee-\alpha\alpha}(M,M)$	$\Delta V_{ee-\beta\beta}(M,M)$	$\Delta V_{ee-s}(M,M)$
2.08	-3.19	-3.56	0.37	1.46	1.52	-0.06
2.50	-1.91	-2.01	0.10	0.92	0.87	0.05
3.00	-1.04	-1.03	-0.01	0.52	0.45	0.06
3.50	-0.50	-0.46	-0.04	0.25	0.20	0.04
4.00	-0.19	-0.18	-0.01	0.10	0.08	0.02
4.50	-0.06	-0.06	0.00	0.03	0.03	0.01
5.00	-0.01	-0.01	0.00	0.01	0.01	0.00
5.50	0.00	0.00	0.00	0.00	0.00	0.00

3 Spin energetic interactions.

Table 8: Atomic electron populations changes associated with the formation of the hexa-aquo complexes and energetic contributions to the $E_{intra}(M)$ of metal center in hexa-aquo complexes. $\Delta P(M) = P_{complex}(M) - P_{isolated}(M)$.

M	$\Delta N(M)$	$\Delta N_\alpha(M)$	$N_\beta(M)$	$\Delta E_{intra}(M)$	$\Delta E_{intra-\alpha}(M)$	$\Delta E_{intra-\beta}(M)$	$\Delta V_{ee-\alpha\beta}(M,M)$
Sc	0.28	0.06	0.21	-0.10	-0.29	-1.26	1.46
Ti	0.33	0.06	0.26	-0.15	-0.50	-1.56	1.92
V	0.38	0.07	0.31	-0.20	-0.64	-1.91	2.35
Cr	0.39	0.07	0.32	-0.22	-0.72	-2.01	2.52
Mn	0.35	0.03	0.32	-0.19	-0.57	-2.02	2.40
Fe	0.41	0.09	0.32	-0.24	-0.85	-2.18	2.79
Co	0.46	0.13	0.33	-0.29	-1.05	-2.52	3.28
Ni	0.51	0.16	0.35	-0.33	-1.24	-2.88	3.79
Cu	0.53	0.19	0.34	-0.36	-1.34	-3.15	4.13
Zn	0.45	0.23	0.23	-0.30	-1.89	0.24	1.36

Table 9: Absolute values of $E_{intra}(M)$ and its energetic components for metal center in complexes $[M(H_2O)_6]^{2+}$.

M	Z	$E_{intra}(M)$	$T(M)$	$V_{ne}(M,M)$	$V_{ee}(M,M)$	$V_{ee-\alpha\beta}(M,M)$
Sc	21	-760	759	-1790	272	155
Ti	22	-849	848	-2000	306	172
V	23	-943	942	-2230	342	191
Cr	24	-1040	1040	-2470	382	211
Mn	25	-1150	1150	-2720	424	232
Fe	26	-1260	1260	-2990	470	258
Co	27	-1380	1380	-3280	520	286
Ni	28	-1510	1510	-3590	573	316
Cu	29	-1640	1640	-3910	630	347
Zn	30	-1780	1780	-4240	689	370

Table 10: Absolute values of $E_{intra-\alpha}(M)$ and its energetic components for metal center in complexes $[M(H_2O)_6]^{2+}$.

M	Z	$E_{intra-\alpha}(M)$	$T_\alpha(M)$	$V_{ne-\alpha}(M,M)$	$V_{ee-\alpha\alpha}(M,M)$
Sc	21	-461	381	-903	62
Ti	22	-519	428	-1020	74
V	23	-582	478	-1150	88
Cr	24	-649	532	-1290	104
Mn	25	-721	591	-1430	122
Fe	26	-787	646	-1560	129
Co	27	-856	703	-1690	136
Ni	28	-927	762	-1830	142
Cu	29	-1000	824	-1970	149
Zn	30	-1070	888	-2120	160

Table 11: Absolute values of $E_{intra-\beta}(M)$ and its energetic components for metal center in complexes $[M(H_2O)_6]^{2+}$.

M	Z	$E_{intra-\beta}(M)$	$T_\beta(M)$	$V_{ne-\beta}(M,M)$	$V_{ee-\beta\beta}(M,M)$
Sc	21	-454	378	-888	56
Ti	22	-502	420	-982	60
V	23	-553	464	-1080	63
Cr	24	-606	510	-1180	66
Mn	25	-661	558	-1290	70
Fe	26	-734	616	-1430	83
Co	27	-812	677	-1590	98
Ni	28	-896	743	-1750	115
Cu	29	-985	814	-1930	134
Zn	30	-1070	888	-2120	160

Table 12: Relationship between spin componentes of $V_{ne}(A,A)$ and $T(A)$ (absolute values) for metal center in complexes $[M(H_2O)_6]^{2+}$.

M	Z	$V_{ne-\alpha}(M,M)/T_\alpha(M)$	$V_{ne-\beta}(M,M)/T_\beta(M)$
Sc	21	-2.37	-2.35
Ti	22	-2.38	-2.34
V	23	-2.41	-2.33
Cr	24	-2.42	-2.31
Mn	25	-2.42	-2.31
Fe	26	-2.41	-2.32
Co	27	-2.40	-2.35
Ni	28	-2.40	-2.36
Cu	29	-2.39	-2.37
Zn	30	-2.39	-2.39

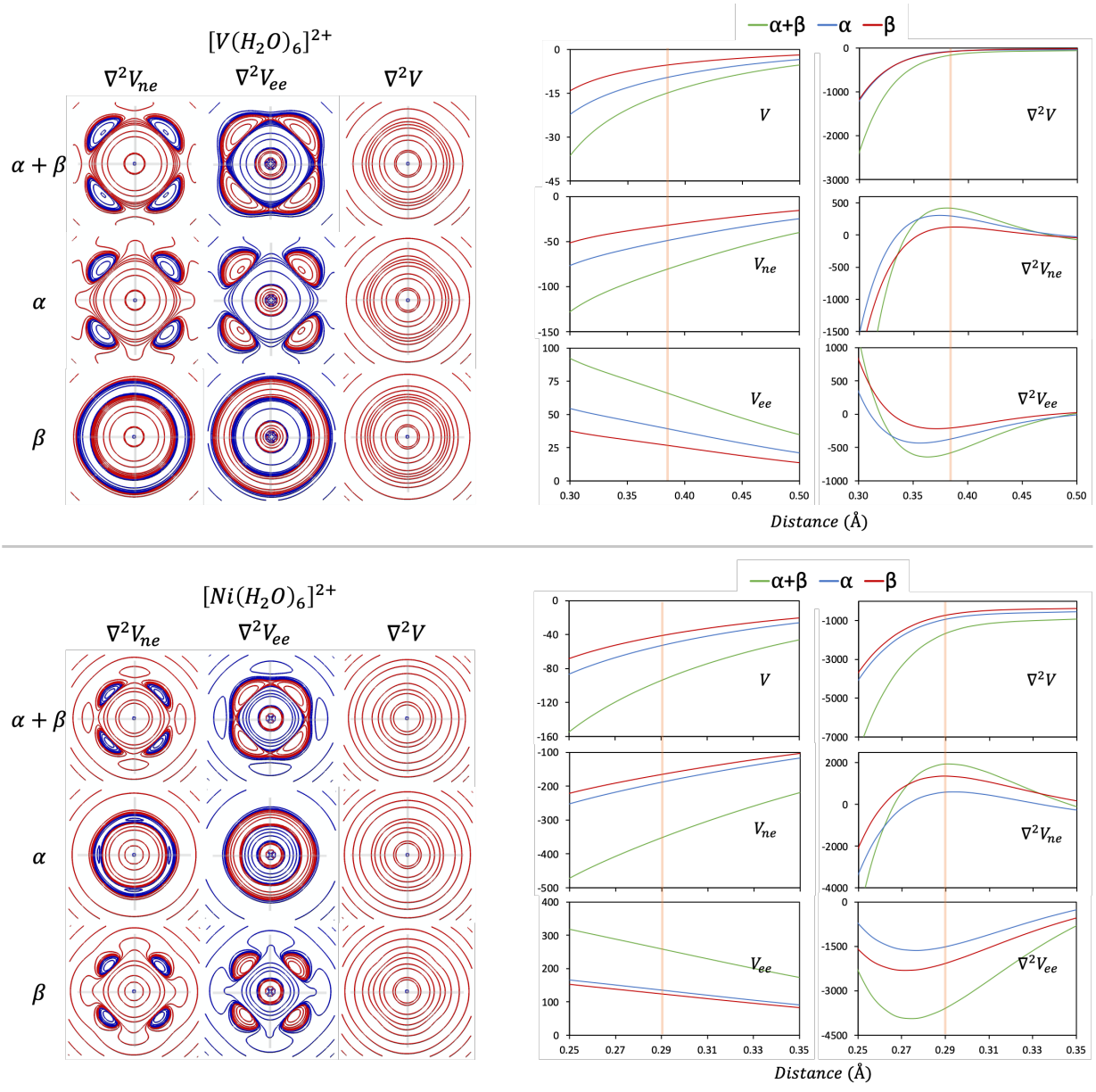

Figure 2: 1D plot in the direction from the metal core to one $CC\ CPs$ and contour maps of $\nabla^2 V_{ne}(\mathbf{r})$, $\nabla^2 V_{ee}(\mathbf{r})$ and $\nabla^2 V(\mathbf{r})$ for total electron density and its spin components in complexes $[V(H_2O)_6]^{2+}$ and $[Ni(H_2O)_6]^{2+}$ at the equatorial plane. Positive values in blue and negative values in red. Lines in gray represent the direction of the ligands.