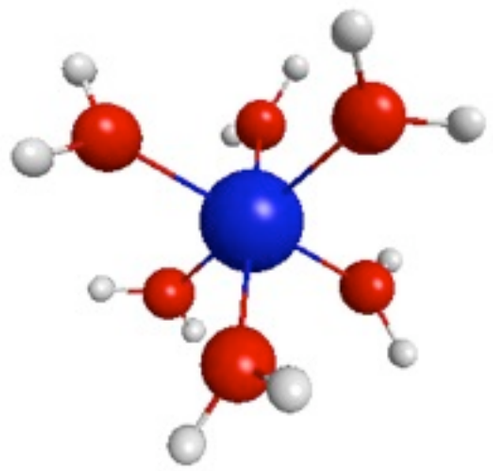
Isoelectronic transition metal molecules have different spin!

Complex	M(μ_B)	Energy
$[CoF_6]^{3-}$	5.3	$E^{HS}-E^{LS} < 0$
$[Co(OH_2)_6]^{3+}$	5.3	$E^{HS}-E^{LS} < 0$
$[Co(NH_3)_6]^{3+}$	0	$E^{HS}-E^{LS} > 0$
$[Co(CN)_6]^{3-}$	0	$E^{HS}-E^{LS} > 0$
$[Co(CO)_6]^{3+}$	0	$E^{HS}-E^{LS} > 0$

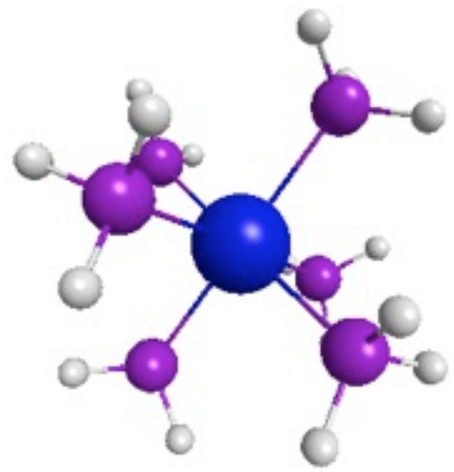
$[Co(H_2O)_6]^{3+}$



S=4/2

High Spin state

$[Co(NH_3)_6]^{3+}$



S=0

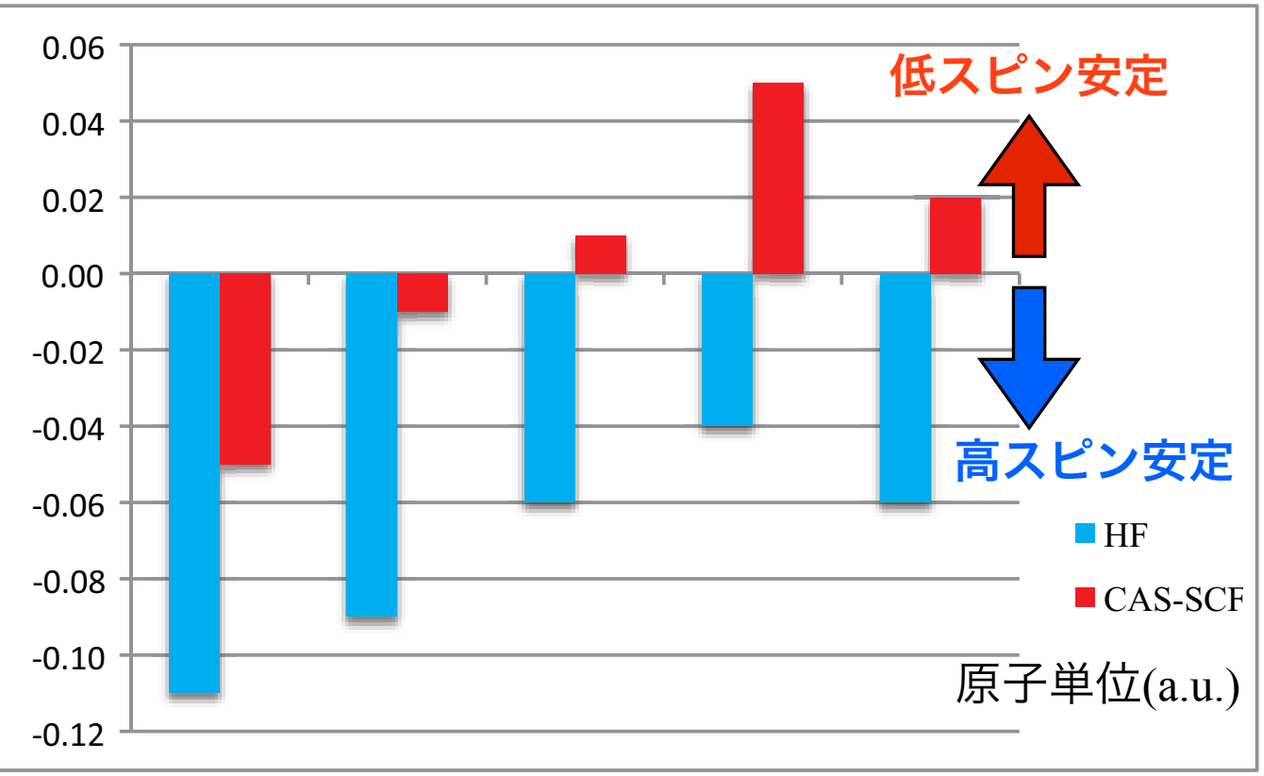
Low Spin state

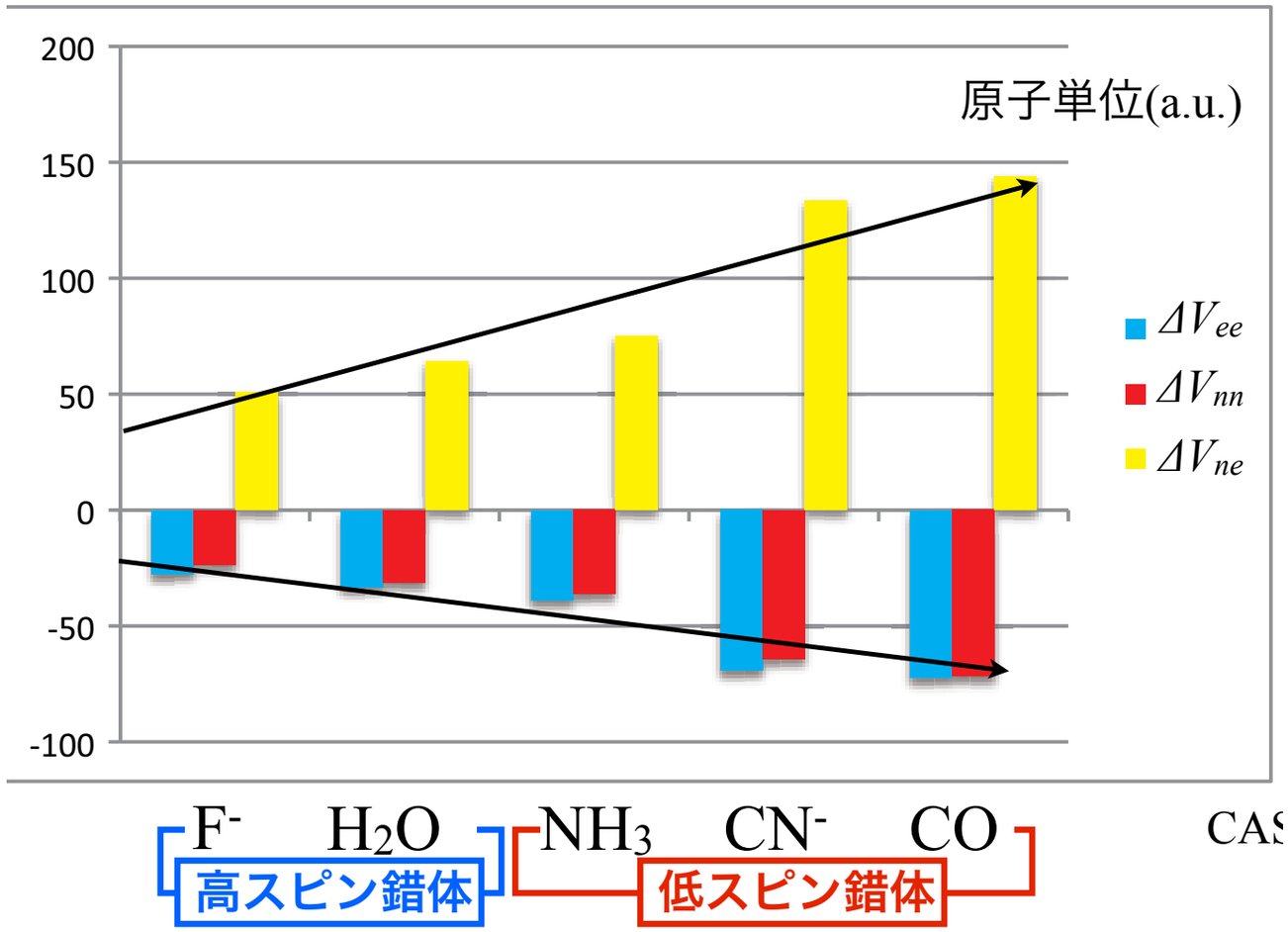
Usually explained using **Ligand field theory** [1–8], which is a 1st order perturbation theory of the electron-electron repulsion from 80 years ago – **is this valid in 2012?**

[1] J. Slater, *Phys. Rev.* **34**, 1293 (1929). [2] J. Van Vleck, *J. Chem. Phys.* **3**, 807 (1935). [3] J. S. Griffith, L. E. Orgel, *Q. Rev. Chem. Soc.* **11**, 381 (1957). [4] Y. Tanabe, S. Sugano, *J. Phys. Soc. Jpn.* **9**, 766 (1954). [5] W. Heitler, F. London, *Z. Phys.* **44**, 455 (1927). [6] W. Heisenberg, *Z. Phys.* **49**, 619 (1928). [7] P. A. M. Dirac, *Proc. R. Soc. London, Ser. A* **123**, 714 (1929). [8] J. Van Vleck, *Phys. Rev.* **45**, 405 (1934).

First principles calculation in 2012 shows complete failure of ligand field theory

[H. Raebiger, S. Fukutomi, and H. Yasuhara, arXiv:1209.6432]





Ligand field theory is a 1st order perturbation theory to evaluate electron-electron repulsion. Our **21st century variational calculation** shows that the leading order contribution spin-crossovers comes from electronuclear attractions, i.e. a *higher order* contribution. Moreover, the correct behavior is **completely impossible** to reproduce using electronic perturbation theories (of any order) that neglect relaxation of nuclear co-ordinates!