Abstract Submitted
for the MAR13 Meeting of
The American Physical Society

Stability of high and low spin states[1] HANNES RAEBIGER, SHUHEI FUKUTOMI, Yokohama Nat'l Univ, HIROSHI YASUHARA, IMR, Tohoku Univ., Sendai — Octahedral CoL_6 complexes exhibit high or low spin states, depending on ligand L. We present an explicitly correlated first principles calculation of CoL_6 with five different ligands, and show that the total energy difference ΔE between the high and low spin states is variationally determined in an intricate interplay of the interelectron repulsion V_{ee}, internuclear repulsion V_{nn}, and electronuclear attraction V_{ne}. This is in stark contrast to "ligand field theory" [1,2], where ΔE is approximated as $\Delta E \approx \Delta V_{ee}$ in a first order perturbation theory. Moreover, we show that ΔV_{ee} exhibits the opposite trend to ΔE and is three or four orders of magnitude greater than ΔE, which demonstrates the failure of ligand field theory both quantitatively and qualitatively. Correctly, the crossover of high and low spin states is a consequence of different Co–L bondings, ionic or covalent, which is found by an accurate treatment of Coulomb correlation between ligand p and cobalt d electrons in the present calculation. [1] J. H. Van Vleck, J. Chem Phys **3**, 807 (1935). [2] Y. Tanabe and S. Sugano, J. Phys. Soc. Jpn. **9**, 766 (1954).

[1]Funded by JSPS Grant-in-Aid for Young Scientists (A) No. 21686003.

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Date submitted: 09 Nov 2012 Electronic form version 1.4